

COMISION NACIONAL DE ENERGIA ATOMICA
DEPENDIENTE DE LA PRESIDENCIA DE LA NACION

PROGRAMA MULTINACIONAL DE METALURGIA
(Programa Regional de Desarrollo Científico y Tecnológico-OEA)

ESTUDIO DE SUPERFICIES, PROPIEDADES Y TECNICAS DE ANALISIS

PARTE II

Jesse R. Lumsden

Tercer Seminario Latinoamericano en el Nivel de Postdoctorado
Tema: CORROSION

Buenos Aires-Argentina
1977

**COMISION NACIONAL DE ENERGIA ATOMICA
DEPENDIENTE DE LA PRESIDENCIA DE LA NACION**

**PROGRAMA MULTINACIONAL DE METALURGIA
(Programa Regional de Desarrollo Científico y Tecnológico-OEA)**

ESTUDIO DE SUPERFICIES, PROPIEDADES Y TECNICAS DE ANALISIS

PARTE II

Jesse R. Lumsden

**Tercer Seminario Latinoamericano en el Nivel de Postdoctorado
Tema: CORROSION**

**Buenos Aires-Argentina
1977**

AUGER ELECTRON SPECTROSCOPY

A. JOSHI, L.E. DAVIS and P.W. PALMBERG

I. Introduction

During the last few years, the technique of Auger electron spectroscopy (AES) has emerged as one of the most widely used analytical techniques for obtaining the chemical composition of solid surfaces. A high sensitivity for chemical analysis in the 5–20 Å region near the surface, a rapid data acquisition speed, and the ability to detect all elements above He mark the basic advantages of this technique. The Auger spectrum provides reliable quantitative information and in many cases the status of chemical bonding.

While AES was initially used purely as a research technique, it is now a routine analytical tool. Its range of applications comprises numerous fields, such as semiconductor technology, metallurgy, catalysis, mineral processing, and crystal growth. The range of these applications is growing rapidly and the fundamental mechanisms in AES are becoming better characterized. Several reviews describing the technique and some of its applications have appeared recently [1]. This chapter, while dealing briefly with the principles involved in the Auger process, is primarily aimed at reviewing recent developments in experimental techniques and applications.

The Auger effect was discovered by Auger [2] in 1925 while working with X-rays. The technique of using electron-excited Auger electrons to identify surface impurities was suggested by Lander [3] in 1953. The high sensitivity of the technique was not realized, however, until 1968 when Harris [4] demonstrated the use of differentiation of the energy distribution, $N(E)$ vs. E , curves to obtain the Auger spectra in the present familiar form. The technique became highly popular when Weber and Peria [5] in 1967 demonstrated that the readily available LEED optics were suitable Auger electron spectrometers. Most present day Auger spectrometers employ the cylindrical mirror analyzer [6] which was shown by Palmberg et al. [7] to increase greatly the speed and sensitivity of AES. Quite often, AES is used in conjunction with inert gas ion sputtering to obtain compositional variations as a function of depth [8]. In more recent developments [9], finely focused electron beams with conventional deflection and rastering capability are utilized to obtain two-dimensional compositional analysis of surfaces. In

combination with inert gas ion sputtering the scanning system makes three-dimensional elemental imaging possible. While other sources of excitation, such as X-rays [10] and ions [11], can also be used to excite Auger electrons, electron sources are the most widely used. The applications discussed in Section V are limited to electron-excited AES.

II. Fundamentals

The fundamental mechanisms involved in AES are ionization of atomic core levels by the incident electron beam, the radiationless Auger transition, and the escape of the Auger electron into the vacuum where it is detected with an electron spectrometer. The Auger electrons are manifest as small peaks in the total energy distribution function $N(E)$, such as that in Fig. 1, which is produced from a silver target by a 1 kV incident electron beam. The Auger peaks are evident in the $N(E)$ function, but become more pronounced by electronic differentiation which removes the large background consisting mainly of backscattered primary electrons and inelastically scattered Auger electrons. The $N(E)$ function also includes a low energy peak, corresponding to ejected lattice electrons, a pronounced peak at 1 kV consisting of elastically reflected primary electrons, and several small peaks corresponding to characteristic energy losses of reflected primary electrons.

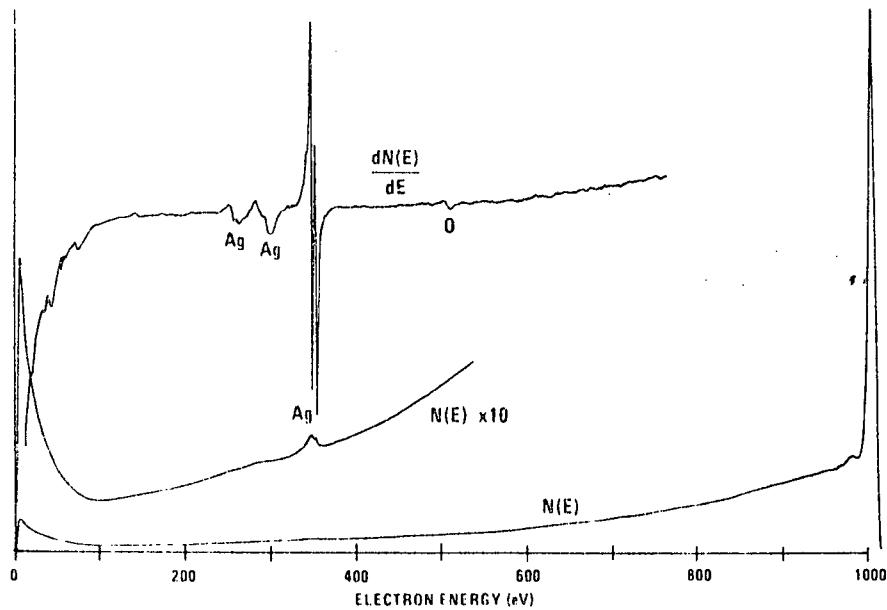


Fig. 1. Energy distribution $N(E)$ and dN/dE for a silver target with primary beam of electrons at 1000 eV.

A. THE AUGER PROCESS

The Auger process can be understood by considering the ionization process of an isolated atom under electron bombardment. When an incident electron with sufficient primary energy, E_p , ionizes a core level, the vacancy is immediately filled by another electron, as depicted by an $L_1 \rightarrow K$ transition in Fig. 2. The energy ($E_K - E_{L_1}$) from this transition can be released in the form of characteristic X-rays (the basis for X-ray fluorescence spectroscopy) or be transferred to another electron, e.g. in the L_2 level, which is ejected from the atom as an Auger electron. The measured energy of the electron is approximately equal to $E_K - E_{L_1} - E_{L_2} - \phi_A$, where ϕ_A is the work function of the analyzer material. This ejection process is termed the KL_1L_2 Auger transition. Several such transitions (KL_1L_1 , KL_1L_2 , $M_2M_4M_4$...) can occur with various transition probabilities. The Auger electron energies are characteristic of the target material and independent of the incident beam energy.

It is obvious from the above discussion that at least two energy states and three electrons take part in an Auger process. Hence, H and He atoms cannot give rise to Auger electrons. Similarly, isolated Li atoms having a single electron in the outermost level cannot give rise to Auger electrons. In a solid, however, the valence electrons are shared and the Auger transitions of the type KVV occur involving the valence electrons of the solid. Thus, the Auger electrons from Li have been observed in various compounds containing Li.

The kinetic energy of Auger electrons originating from a WXY transition can be estimated from the empirical relation

$$E_{WXY} = E_W(Z) - E_X(Z) - E_Y(Z + \Delta) - \phi_A$$

The work function of the analyzer material is represented by ϕ_A and Z is the atomic number of the atom involved [1(d)]. The binding energy values may be obtained from the X-ray emission energy tables. The term Δ is introduced because the energy of the final doubly ionized state is somewhat larger than the sum of the energies for individual ionization of the same levels. Experi-

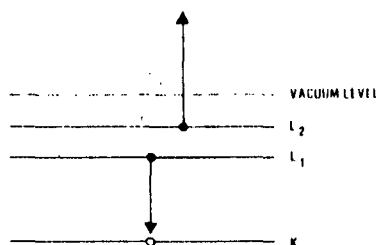


Fig. 2. Energy level diagram depicting relaxation by an L_1 level electron dropping into the K level and emission of an L_2 electron as an Auger electron.

mental values for Δ lie between $1/2$ and $3/4$. Another expression [12] for estimating Auger transition energies is

$$E_{WXY} = E_W(Z) - 1/2 \{E_X(Z) + E_X(Z+1)\} - 1/2 \{E_Y(Z) + E_Y(Z+1)\} - \phi_A$$

Very few calculations have been attempted [13,14] to determine the Auger energies from first principles. Difficulties involved in these calculations relate to the coupling schemes governing the transition from a singly ionized to a doubly ionized state of the atom. The calculations generally involve [15] the magnetic interaction fields produced by the spins and the orbital angular momenta of the partially filled shells in addition to the other electronic interactions (coulomb and exchange). The magnetic interactions are dominant for core electrons of heavy elements, and the electronic configuration follows the jj coupling scheme. LS coupling dominates for light

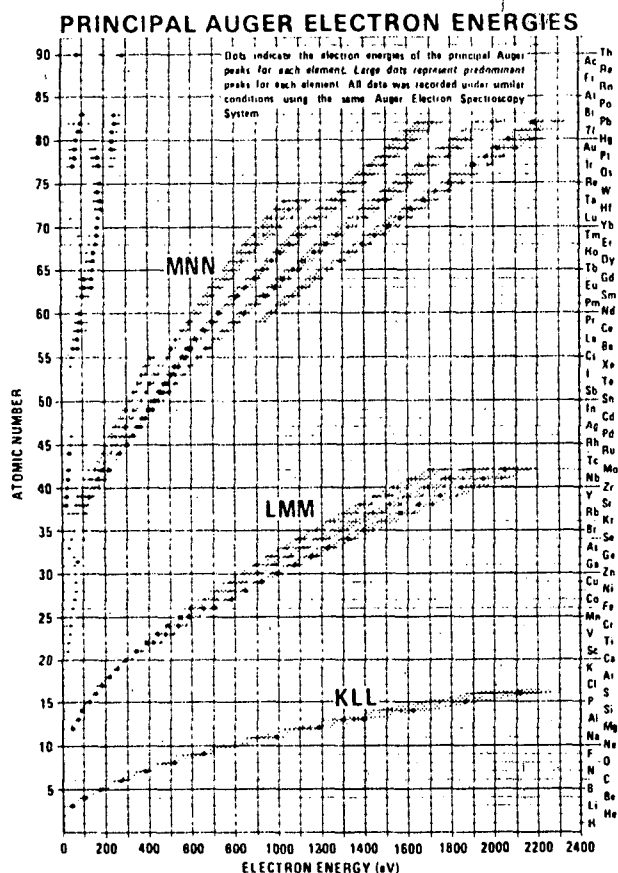


Fig. 3. Most prominent Auger transitions observed in AES.

elements and for the transitions involving low energies. It is necessary to add a spectroscopic term (e.g. 1P_1) to the WXY notation to characterize the transitions fully. These coupling schemes govern the energies as well as the transition probabilities. While the energies obtained by such calculations are normally not very accurate, recent calculations by Shirley [16] obtained by the introduction of relaxation energy into the intermediate coupling scheme led to very accurate KLL Auger energies.

The most pronounced Auger transitions observed in AES are given in Fig. 3. These involve electrons of neighboring orbitals, e.g. KLL, LMM, MNN, NOO, MMM, and OOO families. The Auger electron emission and X-ray emission are competing processes in bringing the initially excited atom to a low energy state, but under the conditions normally employed in AES (observed Auger peaks generally involve electron binding energies less than 2.5 keV), the probability of X-ray emission is negligible [1(f),10]. As indicated in Fig. 3, the most prominent Auger peaks result from KLL transitions for elements with $Z = 3-14$, LMM transitions for elements with $Z = 14-40$, MNN transitions for elements with $Z = 40-79$, and NOO transitions for heavier elements. For convenience, the Auger peak energy is commonly identified by the maximum negative excursion in the $dN(E)/dE$ peak. Complete Auger spectra for most elements and some compounds are available in the literature [17].

B. AUGER ELECTRON ESCAPE DEPTH

The high surface sensitivity of AES is due to the limited mean free path of electrons in the kinetic energy range 20–2500 eV. Auger electrons, which lose energy through plasma losses, core excitations, or interband transitions, are removed from the observed Auger peaks and contribute to the nearly uniform background upon which the Auger peaks are superimposed. Since phonon losses are small compared with the natural width of Auger peaks, they do not affect the Auger escape depth. Hence the Auger yield is not dependent on sample temperature.

The Auger electron escape depth is generally determined empirically by depositing atomically uniform overlayers on metallic substrates, while monitoring the diminution of Auger peaks from the substrate. The Auger peaks decay exponentially with overlayer coverage which is consistent with an exponential dependence of escape probability on the depth of the parent atom. A compilation of data from a variety of experimenters has been used to generate the "universal" escape curve shown in Fig. 4, which indicates that the escape depth is not strongly dependent on the matrix. This behavior is expected because the prominent loss mechanisms involve valence band excitations and the valence electron density is not a widely varying function of material. As discussed in Section IV, the small variation of escape depth with material greatly simplifies quantitative analysis.

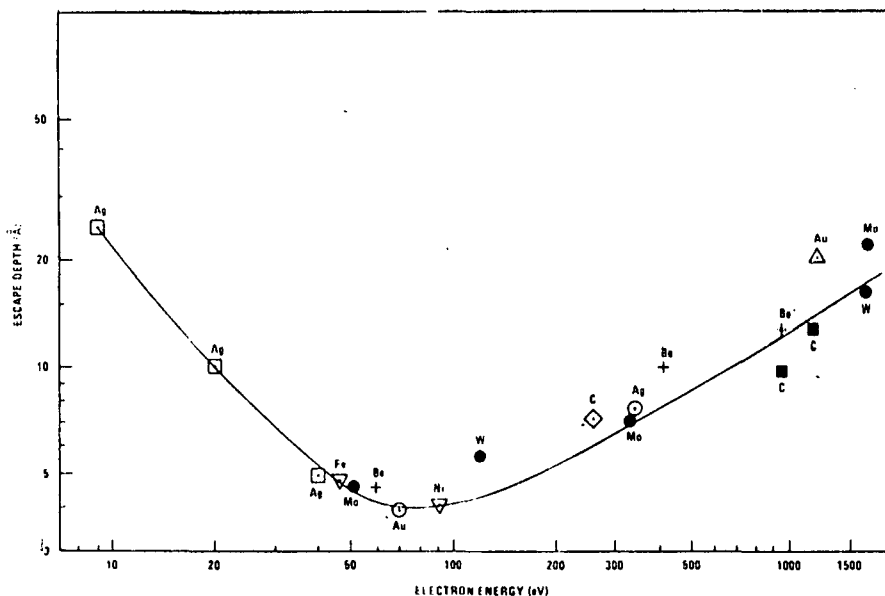


Fig. 4. Auger electron escape depths vs. energy for various materials. ●, M.L. Tarrg and G.K. Wehner, Phys. Elect. Conf., 1972; ○, D.E. Eastman, P.E.C. Albuquerque, 1972; △, J.W.T. Ridgeway and D. Haneman, Surface Sci., 24 (1971) 451, 26 (1971) 683; ◊, P.W. Palmberg and T.N. Rhodin, J. Appl. Phys., 39 (1968) 2425; ◊, K. Jacobi and J. Hölz, Surface Sci., 26 (1971); △, Y. Baer et al., Solid State Commun., 8 (1970) 1479; ■, R.G. Steinhardt et al., Proc. Int. Conf. Electron Spectrosc., Asilomar, 1971, p. 557; +, M.P. Seah, Surface Sci., 32 (1972) 703. (Modified version of figure compiled by J.C. Tracy, General Motors Corporation.) After Palmberg [44].

C. CORE LEVEL IONIZATION PROBABILITIES BY ELECTRON IMPACT

Since the Auger transition probability and Auger electron escape depth are independent of the incident electron beam energy, E_p , the dependence of the Auger peak amplitude on E_p is governed completely by the ionization cross-section of the initial core level. Ionization occurs primarily by the incident electrons during their initial passage through the escape depth region (~ 5 – 20 Å thick), but backscattered primary electrons can also contribute to the Auger yield when the incident beam energy is substantially greater than the binding energy of the core level involved. In gaseous specimens, where the contribution of scattered primary electrons is negligible, the ionization cross-section vs. E_p characteristics may be determined directly by measuring the Auger electron intensity as a function of primary energy. Hence the contribution of backscattered primary electrons to the Auger yield may be assessed by comparison of characteristic curves from gaseous and solid samples. Vrakking and Meyer [18] have measured the L-shell ionization cross-sections, σ , for gaseous S, P, and Cl, and compared these

results with Auger yield vs. E_p curves on solids to evaluate the backscattering factor for silicon.

DuCharme and Gerlach [19] have measured the cross-section behavior as a function of E_p by measuring the KLL Auger current emitted by a monatomic layer of C, N, O, and Na atoms covering a W(100) surface. As E_p/E_K (E_K is the binding energy of the core level) increases from unity, σ rises rapidly from zero to a maximum at $E_p/E_K \approx 3$. A further increase in primary energy over a large range does not cause a substantial variation in σ . The measurements were compared with theoretical calculations adopted from a first-Born approximation theory [20] of Burhop and the Coulomb-Born theory formulated by Rudge and Schwartz [21]. While the latter theory generally gave a better fit with the data, the measured values were generally higher for $E_p > 2.5 E_K$. Similar results were obtained for L-shell cross-sections estimated [19] by studying the LMM Auger transitions of S, Cl, Ti, and Cu.

The contribution to σ from backscattered electron excitation is required in these experiments to evaluate single event cross-sections. The calculated energy distribution of the backscattered primaries within the escape depth region is theoretically very complex. Gerlach and DuCharme [22] have used simplifying assumptions to estimate that the backscattering contributions for C on a W(100) substrate from secondary events is about 25% for 1200 eV ($E_p/E_K = 4.23$), normally incident primary electrons. Calculations made by Bishop [23] predict an increasing contribution to ionization with both increasing atomic number and primary energy. The backscattering contribution to ionization is expected to show relatively small variation with the angle of incidence of the primary beam [10]. Experimental backscattering contributions of 10% for Be [24] at $E_K = 1.0$ keV, 20% for Si [25] at $E_p/E_K = 10$, and 25% for Ag [25] at $E_p/E_C = 4$ have been reported.

An estimate of the possible Auger current, I_A , can be made for C on W from the formula, $I_A = \sigma I_p N$, where $\sigma = 3.2 \times 10^{-19} \text{ cm}^2$ for $E_p \approx 1136$ eV [22], $I_p = 10 \text{ } \mu\text{A}$, and $N = 10^{15}$ carbon atoms/cm². The result is an Auger current of $3.2 \times 10^{-9} \text{ A}$ or an Auger yield of 3.2×10^{-4} .

The acceptance angle and the transmission of the analyzer further reduces this quantity. For a 90% reduction, the magnitude of the detected current is 3.2×10^{-10} or 2×10^9 electrons/sec.

D. MATRIX EFFECTS

Since Auger electron emission frequently involves valence electrons and always involves the binding energy of core levels, the line shape as well as the most probable energy is strongly influenced by chemical environment. If strong (e.g. ionic) chemical bonding of two or more atoms occurs, the core electron levels may shift several electron volts. In ionic bonding, electron levels of electronegative elements are shifted to lower binding energies, and

those of electropositive elements are shifted to higher binding energies due to the net charge transfer. A corresponding chemical shift in Auger electron kinetic energy is observed. When the electron density of states in the valence band is altered with chemical environment, a change in shape of Auger peaks from transitions involving valence electrons is observed.

In practice, measurable and frequently large shifts in Auger energies corresponding to changes in chemical environment are observed. Szalkowski and Somorjai [26] have found a linear energy shift of ~ 0.6 eV for the $L_3M_{23}M_{23}$ Auger peaks from vanadium oxides as a function of oxidation number. Conversely, energy shifts of valence electrons from the $L_3M_{23}V$ transition could not be related to the oxidation states. This result suggests that energy shifts of Auger peaks involving valence electrons reflect more the redistribution of the density of states in the valence band than core level energy shifts.

Wagner and Biloen [27,28], using ESCA, have found large energy shifts in peaks from core level (i.e. excluding the valence band) Auger transitions in metal oxides and nonconducting salts. A shift of 7.0 eV was reported [28] for the $KL_{23}L_{23}$ transition for silicon compared with oxidized silicon and 5.4 eV for sodium in NaF, respectively. The corresponding photoelectron binding energy shifts for the above levels ($2P_{3/2}$) were 3.9 eV for oxidized silicon and, essentially, no shift for sodium. The large differences between Auger peak shifts and photoelectron binding energy shifts appear to be due to extra atomic relaxation (polarization) energies arising primarily from polarization of the electron clouds of adjacent atoms toward the core level vacancies. Calculations made by Kowalczyk et al. [29] predict that the extra atomic relaxation energy can cause an energy shift of approximately 10 eV for $LM_{45}M_{45}$ copper and zinc Auger electrons in metallic copper and zinc. Calculations have not been made for relaxation energies in different chemical environments, but it is likely that relaxation is the dominant factor in explaining large Auger peak shifts for core level transitions. Wagner [28] has made use of the difference in Auger and photoelectron energies to characterize the chemical state of oxides and compounds since, in most cases, this is more easily measured than a shift in photoelectron binding energy.

For some time, spectra of valence Auger electrons [1(h), 30–33] have been used to characterize the chemical state of solid surfaces empirically. Figure 5 (top) is an Auger spectrum of a silicon wafer after oxidation. The low energy (60–100 eV) Auger distribution is composed of LVV transition electrons and is characteristic of SiO_2 (75 eV). In this case, the Si peak associated with SiO_2 has undergone both a change in shape as well as a shift in energy. After sputtering, Fig. 5 (bottom), the spectrum is characteristic of elemental silicon with a peak energy of 91 eV.

An interesting example [30] of characterizing surface chemical states using AES is shown in Fig. 6 for the KLL carbon Auger spectra of CO on W(112), W_2C , graphite, and diamond. Hybridization of L shell electrons and,

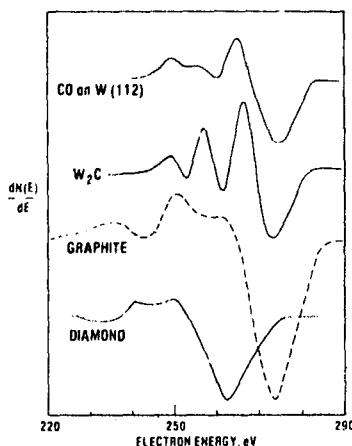
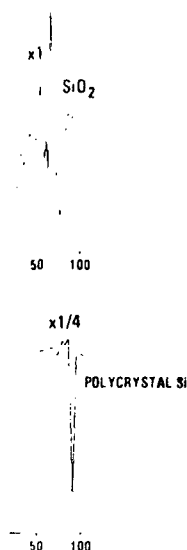


Fig. 5. LVV Auger spectra of SiO_2 and pure polycrystalline silicon.

Fig. 6. Spectra of the carbon KLL Auger transitions for CO on W(112), W_2C , graphite, and diamond. After Haas et al. [30].

thus, changes in the transition probability density is suggested as the cause for the differences in peak shapes.

The shape of the Auger electron line is not a direct measure of the density of states, but rather is a reflection of the transition probability density. Thus, first principle calculations to determine density of states from Auger spectra, or vice versa, is a complex problem. Amelio [34] compared deconvoluted valence spectra of silicon with the theoretical density of states. The comparison of reduced experimental data and theoretical calculations showed considerable agreement in the major maxima and minima features of the density distribution.

Hagstrum [35] and Becker and Hagstrum [36] by deconvoluting Auger line shapes have determined Auger transition probability density functions for the chalcogenides of nickel from ion neutralization spectroscopic studies. They have shown that features in the probability functions correspond to molecular orbital structure characteristic of surface chemical bonds. Sickafus [37] has shown that it is possible to apply similar treatments to electron-stimulated Auger electron line shapes. Specifically, good agreement with ion neutralization spectroscopic results was found for clean nickel and $\text{Ni}(110)\text{-C}(2 \times 2)\text{S}$.

The fine structure apparent in the Auger spectrum is not always entirely

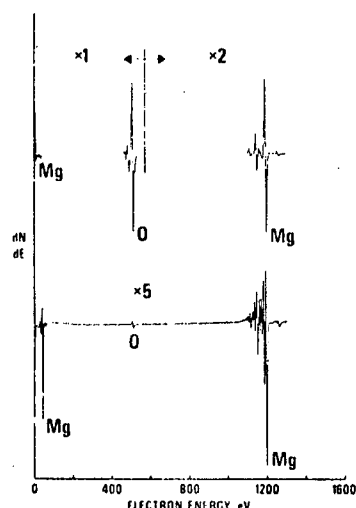


Fig. 7. AES and characteristic loss structure of vacuum-cleaved MgO (top) and evaporated Mg film on cleaved MgO (bottom).

due to the valence band electron density distribution. Auger electrons escaping the surface may lose discrete amounts of energy through plasmon excitations, core level ionization, and interband excitations and appear as distinguishable peaks. In the Auger spectrum these peaks will be apparent at characteristic energies less than the Auger electron energy. Because plasmon losses dominate in Auger fine structure, only these excitations will be discussed.

Plasmons are created by energetic electrons losing discrete amounts of energy to excite collective oscillations of valence electrons under the influence of positive atomic cores [38]. The characteristic frequency ω_p corresponding to the loss energy can be expressed classically as $(4\pi ne^2/m)^{1/2}$ where n is the electron density, e is the electronic charge, and m is the mass. From this expression, it can be seen that the plasmon loss energy is characteristic of a specific solid and will change according to chemical environment. The large differences in the Auger fine structure from Mg and MgO is shown in Fig. 7.

Mularie and Peria [39] showed that some of the fine structure below the LVV Si Auger transition energy at 91 eV matched energy loss peaks due to plasmon excitations. The 91 eV silicon peak and fine structure were compared to plasmon loss peaks produced by elastically scattered electrons. The fine structure from pure silicon apparent at 73 eV in Fig. 5 (bottom) is attributed to a bulk plasmon loss.

III. Experimental methods

AES instrumentation in its simplest form involves a vacuum system, an electron gun for target excitation, and an electron spectrometer for energy analysis of the emitted secondary electrons. Because the AES technique is surface sensitive, an essential requirement is a UHV system capable of an ultimate vacuum in the 10^{-10} torr range. If every incident gas particle sticks to a surface, a monolayer is adsorbed in about one second at 10^{-6} torr. Even at a vacuum of 10^{-10} torr, an appreciable fraction of a monolayer of C and O can adsorb on active surfaces in a period of 30 min. Contamination from the vacuum system environment is obviously most critical for highly reactive metal surfaces where the sticking coefficient for most residual gases is near unity.

Surfaces which are passivated through exposure to air have a very low sticking coefficient, and hence the vacuum requirements are much less stringent. A vacuum in the low 10^{-8} torr range is usually sufficient for analysis on passivated surfaces. As discussed in Section III.C, the vacuum requirements are also relaxed for profile measurements in which the surface is continuously eroded by an argon ion beam during Auger analysis.

In addition to the basic requirements of an electron gun and an electron spectrometer, most AES systems presently in use employ an ion gun for in-depth profiling measurements, a manipulator for positioning the sample, a means for precisely locating the area of analysis, and frequently an attachment for performing in situ fracture or cleavage of specimens. In this section no attempt will be made to review the numerous variations of AES apparatus; only apparatus which has found widespread use will be considered.

A. ELECTRON ENERGY ANALYSIS

In the development of AES as a practical tool for surface analysis, several types of electron energy analyzers have been employed. These include the 127° cylindrical analyzer used by Harris [4] in his pioneering work in AES, the LEED—Auger apparatus first employed by Weber and Peria [5], and the cylindrical mirror analyzer [6,7]. Because of its superior signal-to-noise capability, the cylindrical mirror analyzer (CMA) is used almost exclusively for modern AES apparatus.

The two parameters which characterize electron velocity analyzers are the transmission, T , and the luminosity, L , where $L = \iint T(x,y) dx dy$. T is the probability that an electron of proper energy originating from a point (x,y) on the sample will be transmitted through the analyzer. The output signal, I , is then given by

$$I = \iint j(x,y) T(x,y) dx dy \quad (1)$$

where $j(x,y)$ is the spatial distribution of Auger electrons emitted from the target surface. When the target is excited uniformly over the region where T has appreciable value, eqn. (1) reduces to $I = jL$, where j is the Auger current density emitted over the acceptance area of the analyzer. In this case, it is the luminosity rather than transmission which is the proper figure of merit for the instrument.

When the diameter of the electron beam used to excite the target is very small (typically $<100\ \mu\text{m}$) compared with the region over which T has appreciable value, eqn. (1) reduces to $I = TJ$, where J is the total Auger current emitted from the sample. Therefore, the highest signal levels will be obtained from an instrument with the highest possible transmission rather than the highest luminosity which is a primary consideration in ESCA apparatus. It is for this reason that the CMA, which is characterized by an unusually large transmission factor, is used almost exclusively in Auger apparatus.

A schematic diagram which illustrates the operation of a CMA for obtaining Auger spectra is shown in Fig. 8. The cylindrical mirror analyzer includes an internal electron gun mounted with its optical axis coincident with the CMA symmetry axis. The electron beam is focused to a fine point on the surface of the specimen which is positioned at the source point of the CMA. Electrons ejected from the point of excitation move radially outwards until they pass through a grid-covered aperture on the inner cylinder. A negative potential applied to the outer cylinder directs electrons with specific energy

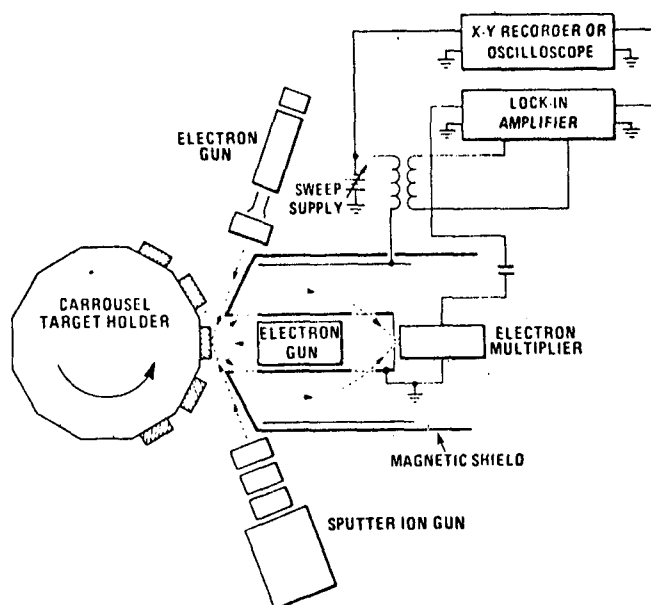


Fig. 8. Operation of the cylindrical mirror analyzer as an Auger spectrometer.

back through a second aperture on the inner cylinder and finally through a small exit aperture on the CMA symmetry axis. The pass energy, E , of the CMA is proportional to the potential applied to the outer cylinder. The range of electron energies, ΔE , which are transmitted is determined by the resolution R given by $R = \Delta E/E$. For commercial Auger spectrometers, R is typically 0.5%.

The secondary electron energy distribution, $N(E)$, is generated by plotting the output of the electron multiplier vs. the negative voltage applied to the outer cylinder. The $dN(E)/dE$ function is generated by superimposing a small a.c. voltage on the outer cylinder voltage and synchronously detecting the in-phase signal from the electron multiplier with a lock-in amplifier. The Y-axis of the X-Y recorder is then proportional to $dN(E)/dE$, and the X-axis is proportional to the kinetic energy of electrons emitted from the specimen.

B. SIGNAL-TO-NOISE CONSIDERATIONS

The sensitivity of AES is determined by the signal-to-noise ratio that can be obtained with the instrumentation. The detectable limit of concentration is limited by shot noise associated with the background current upon which the Auger peaks are superimposed. The background current consists predominantly of primary electrons which are backscattered through the surface a second time after loss of various amounts of energy through electronic excitation in the bulk. The total backscattered current with energy greater than 50 eV is typically 30% of the primary beam current. Assuming a uniform distribution of the backscattered current throughout the energy range from zero to E_P , the background current in the transmitted signal from a CMA is given by

$$I_B = 0.3 T I_P \Delta E/E_P \quad (2)$$

where I_P is the incident beam current and ΔE is the energy window of the analyzer. The transmitted Auger current is given by

$$I_A = \beta I_P T \Delta E/\gamma \quad (\Delta E \ll \gamma) \quad \text{or} \quad \beta I_P T \quad (\Delta E \gg \gamma) \quad (3)$$

where β is the Auger yield for the Auger transition of interest and γ is the inherent width of the Auger peak. In the shot noise limit, the equivalent noise current is given by [40]

$$I_N = (2 I_B e B)^{1/2} \quad (4)$$

where e is the electronic charge, B is the measurement bandwidth, and I is the current exiting from the analyzer. In the shot noise limit, the Auger signal-to-noise ratio is derived from eqns. (2)–(4).

$$I_A/I_N = (\beta/\gamma) (I_P T \Delta E E_P / 0.6 e B)^{1/2} \quad \Delta E \ll \gamma \quad (5)$$

$$I_A/I_N = \beta (I_P T E_P / 0.6 \Delta E e B)^{1/2} \quad \Delta E \gg \gamma$$

In eqn. (5) it is evident that the maximum signal-to-noise ratio is achieved when the energy window of the analyzer is approximately equal to the natural width of the Auger peak. Typical parameters are $I_p = 10 \mu\text{A}$, $E_p = 5 \text{ kV}$, $T = 0.1$, $\beta = 10^{-4}$, $\gamma = 3 \text{ eV}$, and $B = 1 \text{ Hz}$. Under these conditions, the maximum signal-to-noise ratio is 1.3×10^4 , which means that the limit of detectability is approximately 77 ppm. The optimum signal-to-noise ratio is normally not achieved, however, because ΔE and γ are not matched. A typical detection limit is 1000 ppm.

From the above considerations it is apparent that the energy window of the analyzer should match the natural width of Auger peaks as closely as possible over the energy range 0–2000 eV. Since Auger peaks are typically 3–10 eV wide, an energy resolution of about 0.5% is about optimum for the best signal-to-noise performance averaged over the entire range. Higher energy resolution can yield fine structure in Auger peaks which is not evident with a resolution of 0.5%, but will result in a significant reduction in signal-to-noise performance for many Auger peaks, especially in the low energy range.

C. THIN FILM ANALYSIS

In combination with ion etching, the inherent surface sensitivity of AES may be utilized to profile the elemental concentration with depth in thin films. As illustrated in Fig. 9, the ion beam forms a crater which is large

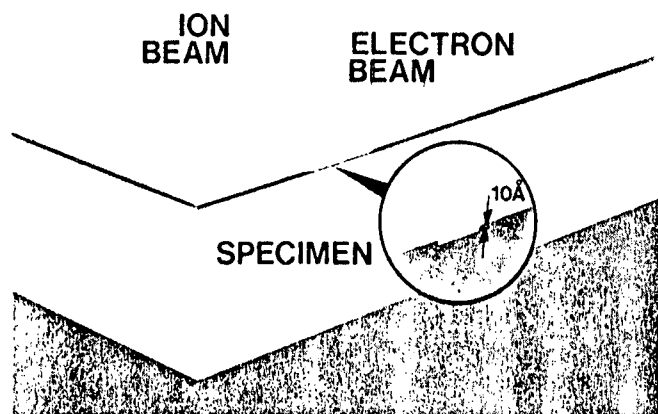


Fig. 9. Illustration of simultaneous ion beam milling and Auger analysis for thin film profiling.

compared with the diameter of the electron beam probe. In-depth profiling is accomplished by continuously sensing the elemental composition of the crater bottom during sputter erosion. Simultaneous ion bombardment has little effect on the Auger measurement, since the number of secondary electrons created by the ion beam is small compared with the secondary electron current created by the electron beam. The static pressure of 5×10^{-5} torr Ar required to operate the sputter ion gun also has a negligible effect on the Auger spectrometer operation.

A major advantage of the simultaneous ion etching and AES detection method over a sequential process in which the ion etching is stopped during the Auger measurement is that surface contamination is greatly reduced. In typical profile measurements, the surface is sputter eroded at a rate of several atomic layers per second. If the partial pressure of active gases can be maintained at 10^{-7} torr or below, the maximum arrival rate for surface contaminants is 0.1 monolayers/sec. Under these conditions, the concentration of surface contaminants cannot exceed a few percent of an atomic layer. When active gases are removed from the static pressure of Ar by a liquid nitrogen cooled Ti sublimation pump, the surface concentration of residual gas impurities can be maintained at a considerably lower level.

In early depth profile measurements [8], the data were acquired by repetitively scanning the pass energy of the CMA over a range sufficiently large to encompass all Auger peaks of interest. The variation in amplitude of the Auger peaks of interest was ascertained from a time base recorder output. The technique is generally quite inefficient, because only a small portion of the scanned energy range contains Auger peaks. In addition, the amplitude vs. sputtering time curves were plotted manually. When the in-depth concentration profiles of only a few elements are of interest, a multiplexing system greatly reduces data acquisition time and provides a more convenient display of the data. An illustration of a multiplexing technique is given in Fig. 10. Energy windows are adjusted to encompass only the peaks of interest, namely Si, O, Cr, and Ni. These energy windows are repetitively scanned in the sequence 1, 2, 3, 4, 1, 2, 3, 4, etc. As each energy window is scanned, the peak-to-peak amplitude of the corresponding Auger peak is electronically measured and plotted automatically on the Y-axis of an X-Y recorder, when the upper limit of the energy range is reached. The displacement of the X-axis is proportional to the elapsed sputter etching time. In multiplexing schemes, it is also useful to vary the measurement sensitivity independently for each channel. A direct recording of the O, Cr, Ni, and Si Auger peak amplitudes vs. etching time for a nichrome film is given in Fig. 11.

Several factors affect the depth resolution of the AES/ion etching profiling technique. These include ion beam uniformity across the sampled area, the Auger electron escape depth, and sample inhomogeneity. Loss of depth resolution from ion beam non-uniformity is negligible if the ion beam is large compared with the electron beam. The contribution from the Auger escape

NICHROME FILM AFTER 450° C IN AIR FOR 30 SECONDS

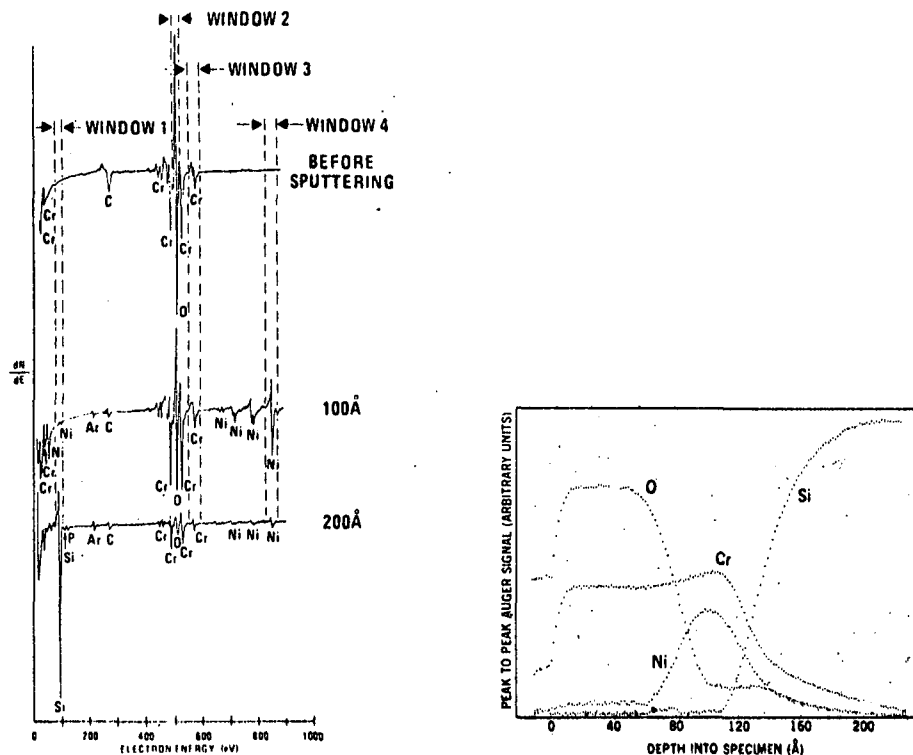


Fig. 10. Auger spectra from nichrome thin film before sputtering and after etching to depths of 100 and 200 Å. Energy windows indicate regions scanned in the multiplexing technique.

Fig. 11. In-depth profile of nichrome thin film on silicon.

depth is only 5–20 Å and remains constant with sputter depth. Sample inhomogeneity is the most important factor limiting depth resolution and can occur as a non-uniform thickness of thin films over the sampled area, as polycrystalline grains which are comparable in dimension with the thickness of the film, and as precipitation of constituent elements into particles. A non-uniform film thickness obviously limits the depth resolution to a value less than the percent uniformity of the film thickness over the sampled area. The depth resolution is determined by the relative sputtering rates of the precipitates and the matrix in films containing precipitates, and by a variation in sputtering yield with grain orientation in polycrystalline films. In general, the depth resolution of the AES/ion etching technique is limited to about 10% of the sputtered depth, but can approach 3% in optimum cases.

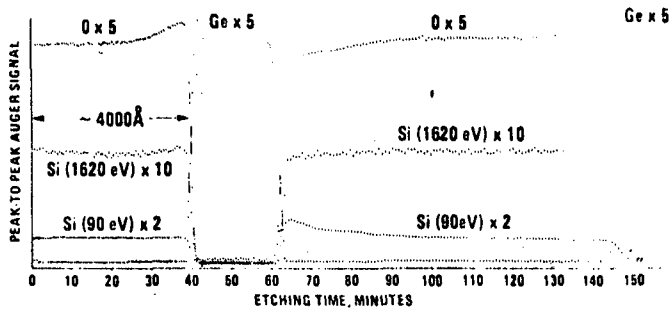


Fig. 12. In-depth profile of optical coating.

The best in-depth resolution that has been achieved occurs in amorphous films. As an example of the type of resolution which has been achieved, Fig. 12 illustrates the sputter profile from an optical film in which the in-depth resolution is about 3% of the sputtered depth.

D. SCANNING AUGER MICROSCOPY

When combined with a finely focused electron beam for target excitation, AES can be used to perform two-dimensional surface elemental analysis. The first attempt of this type was made by MacDonald [9] who combined a CMA with a commercial SEM and demonstrated point analysis [9] as well as elemental maps [41] with sub-micron spatial resolution. The second approach to scanning Auger microscopy was made by Pocker and Haas [42] who installed a field emission electron microscope gun on a standard UHV AES system. A severe limitation in their system was a poor signal-to-noise performance because of unstable beam current from field emission sources. A third approach to scanning Auger microscopy [43] involves optimization of an electrostatic gun inside of the CMA. The primary advantage of this approach is greatly simplified sample alignment.

A schematic diagram of a scanning Auger system [43] which utilizes an internal electrostatic gun is shown in Fig. 13. The electrostatic gun contains four electron optical components: a triode source with a tungsten filament, a condenser lens, an objective lens, and deflection plates. The electron gun control provides the necessary focusing voltages for the lenses and the power for the filament. The scanning system control provides the necessary voltages for deflecting the focused electron beam on the specimen, the deflection voltages for the record display and storage monitor, and the TV interface electronics. Electronics required to monitor and display the target current, secondary electron current, and the Auger signal are included in the scanning system control.

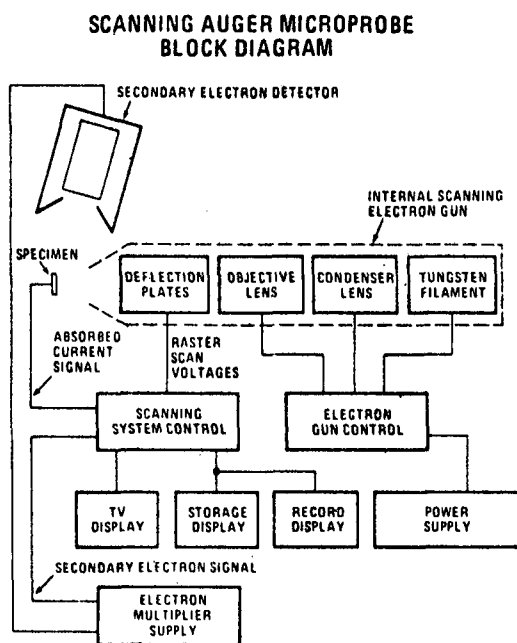
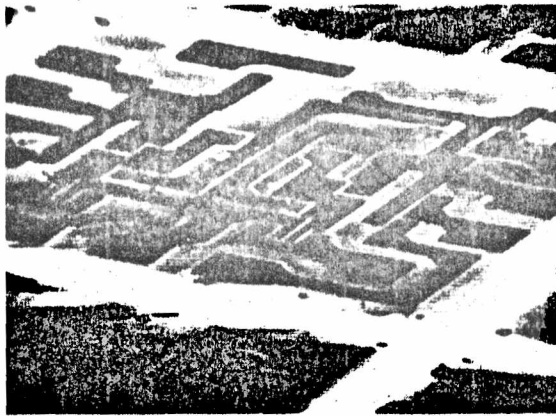


Fig. 13. Block diagram of electron gun and controls used for scanning Auger microscopy.

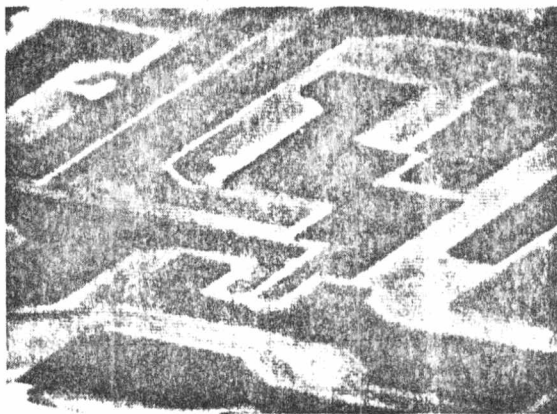
The electron gun operation is similar to that in a conventional SEM. Two lenses demagnify the crossover formed by the triode source, and the deflection plates raster the beam on the sample. At a minimum beam size of about three microns, the beam current is in the range of $0.1 \mu\text{A}$. By relaxing the condenser lens voltage, the beam current can be increased up to about $10 \mu\text{A}$ with a corresponding increase in beam size. The magnification of the scanning system is controlled by the voltage amplitude applied to the deflection plates.

This scanning Auger system [43] can be used to perform point Auger analysis with a spatial resolution less than three microns or to obtain a two-dimensional mapping of the concentration of a selected surface element. The usual low energy secondary electron or absorbed current displays are used to monitor the surface topography and locate the areas of interest on the sample. To obtain an elemental map (Auger image), the intensity of the display is controlled by the magnitude of the selected Auger peak. The most negative excursion in the differentiated Auger spectrum is taken as a measure of the Auger current.

To demonstrate the operational modes of a scanning Auger system, MacDonald [43] has performed three-dimensional analysis of a microelectronic circuit. The TV display is first used to locate the areas of interest on the circuit chip. Absorbed current micrographs (Fig. 14) are then recorded on



← 250 μm →



← 125 μm →

Fig. 14. Absorbed current micrographs of an integrated circuit (top) and an area on the integrated circuit that includes a transistor (bottom). $I_p = 0.4 \mu\text{A}$, $E_p = 5\text{kV}$.

the record display. The dark areas on these micrographs are metal interconnections consisting of a Au/Mo thin film composite; lighter areas are P/Si. Point analysis is accomplished by slowly reducing the scan voltage on the electron gun deflection plates to zero, while maintaining the area of interest at the center of the TV display. The surface composition of the SiO_2 layer is determined by recording an Auger spectrum as shown in Fig. 15.

A two-dimensional elemental map of the surface is obtained by setting the pass energy of the electron spectrometer at the negative excursion of the Auger peak of interest, and using the output of the lock-in amplifier to

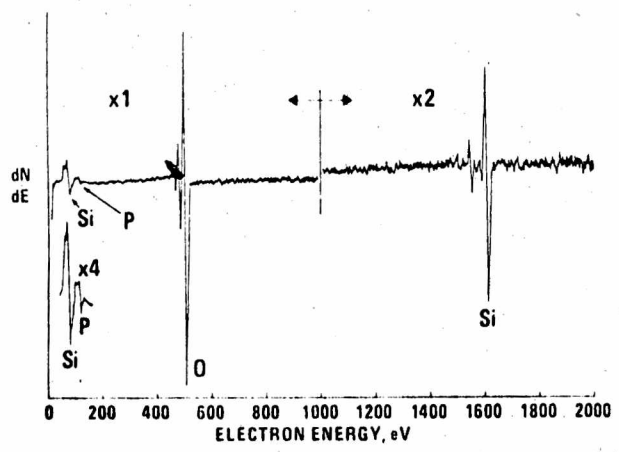


Fig. 15. Auger spectrum for a point analysis of phosphorus-doped SiO_2 on an integrated circuit.

intensity modulate the record display as the electron beam is rastered across the sample. Auger images for the elements Si, O, P, and Au are given in Fig. 16. Bright areas on these Auger images correspond to a high concentration of the element analyzed. The recording time for these Auger images was one minute using a beam current of $0.4 \mu\text{A}$ and a beam voltage of 5 kV.

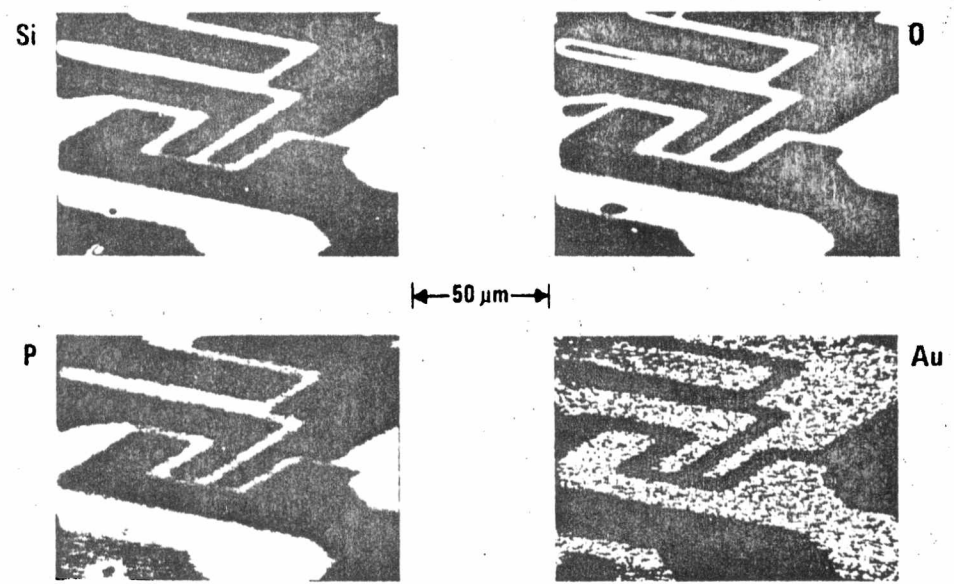


Fig. 16. Auger images of Si, O, P, and Au on an integrated circuit transistor.

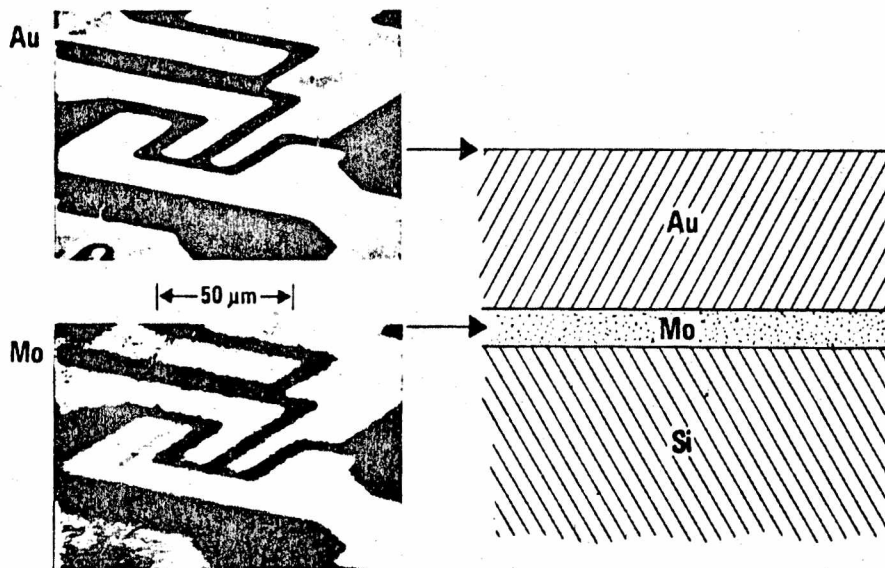


Fig. 17. Three-dimensional analysis of a Si-Mo-Au thin film showing the Au Auger image, the Mo Auger image, after sputter etching into the Mo layer, and a schematic of the composite structure.

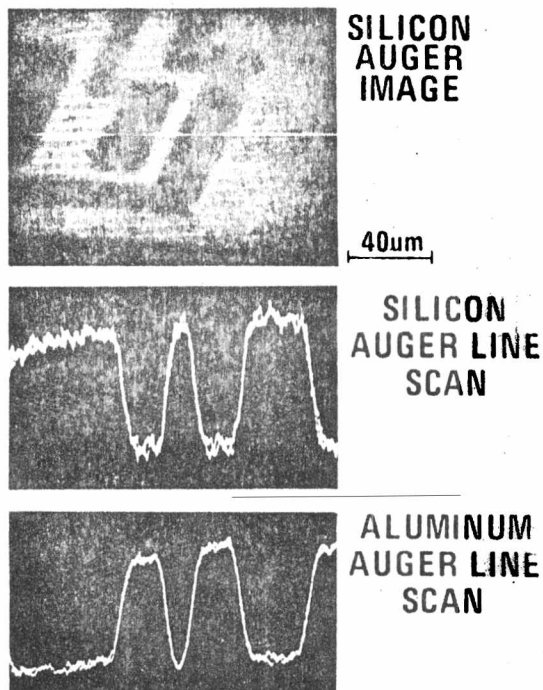


Fig. 18. Absorbed current micrograph of a transistor with a line scan. Auger line scan, and an Al Auger line scan (bottom).

Three-dimensional analysis using a combination of scanning Auger microscopy and sputter etching is illustrated in Fig. 17. The scanning Auger image for Au was obtained before sputtering to delineate the Au electrode pattern. Ion sputter etching was then performed while monitoring the Mo Auger peak. After sputtering one micron of Au from the sample, the Mo peak appeared, the sputter etching was terminated, and the Mo Auger image shown in Fig. 17 was recorded. These data demonstrate that the Mo layer, which serves to enhance adhesion between the Au electrode and the Si substrate, is uniformly distributed.

A more quantitative measure of the distribution of a particular element on a surface can be obtained by performing a line scan as illustrated in Fig. 18. In this approach, the electron beam is scanned across the integrated circuits as shown in the upper micrograph of Fig. 18, while the amplitude of the Al or Si Auger peak is used to Y-modulate the record display. In the lower portion of Fig. 18, the Y deflection is a direct measure of the concentration of Al.

IV. Quantitative analysis

In practical applications of AES, semiquantitative determination of the elemental composition is often sufficient. AES has been extremely successful in failure analysis, for example by simply using comparative analysis, i.e. demonstrating a difference in the surface composition between good and bad devices. In the evaluation of new processes and chemical characterization of new materials, however, it is frequently important to obtain accurate quantitative information. In this section the fundamental aspects and ultimate capability of AES for quantitative analysis are examined.

A. BASIC MECHANISMS AND ABSOLUTE MEASUREMENTS

To achieve absolute quantitative analysis in AES, it is necessary to relate the Auger current from a specific element to the population density of that

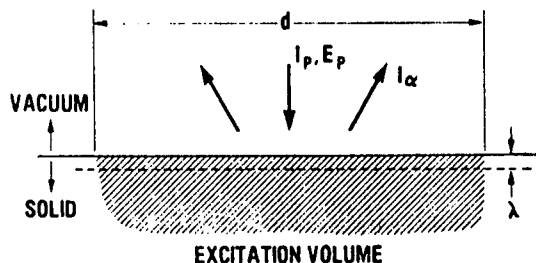


Fig. 19. Schematic representation of source volume of Auger electrons and the primary excitation volume.

element in the surface region. The Auger electron source volume generated by an incident electron beam of diameter d and energy E_p is depicted schematically in Fig. 19. The emitted Auger current produced by a WXY Auger transition in element α can be expressed as [44]

$$I_{\alpha}(WXY) = \int_{\Omega} \int_{E_W}^{E_p} \int_0^{\infty} I_p(E, Z) \sigma_{\alpha}(E, E_W) N_{\alpha}(Z) \gamma_{\alpha}(WXY) \exp[(-Z/\lambda)] d\Omega dE dZ \quad (6)$$

where $I_p(E, Z)$ is the excitation flux density, $\sigma_{\alpha}(E, E_W)$ is the ionization cross-section of the core level W, $N_{\alpha}(Z)$ is the atomic density of element α at a depth Z from the surface, $\exp(-Z/\lambda)$ is the Auger electron probability for escape, and $\gamma_{\alpha}(WXY)$ is the WXY Auger transition probability factor. For simplicity, two-dimensional homogeneity of the elemental composition parallel to the surface has been assumed.

To simplify eqn. (6), three-dimensional homogeneity of the chemical composition will be assumed for the region in which the escape probability has significant value. It is also useful to separate the excitation flux density into two components, $I_p(E, Z) = I_p + I_B(E, Z)$, where $I_B(E, Z)$ is the excitation flux due to backscattered primary electrons. With these assumptions, the detected Auger current can be expressed as [44]

$$I_{\alpha}(WXY) = I_p T N_{\alpha} \gamma_{\alpha}(WXY) \sigma_{\alpha}(E_p, E_W) \lambda (1 + R_B) \quad (7)$$

where R_B is defined as the backscattering factor, and T is the transmission of the analyzer.

To carry out accurate quantitative analysis from first principles utilizing eqn. (7), the ionization cross-section, the Auger yield, and the backscattering factor must be known to the desired degree of accuracy. In addition, the absolute Auger current must be accurately measured. A further complication is surface roughness which generally reduces the Auger yield relative to a flat surface [45]. Since these requirements are generally not met for routine Auger analysis, quantitative analysis using first principles is not considered practical at the present time. In the following sections, two methods which offer considerable possibilities for quantitative AES are discussed.

B. MEASUREMENTS WITH EXTERNAL STANDARDS

In this method, Auger spectra from the specimen of interest are compared with that of a standard with a known concentration of the element of interest. The concentration of element α in the test specimen (N_{α}^T) can be related to that in the standard (N_{α}^S) using eqn. (7).

$$N_{\alpha}^T/N_{\alpha}^S = (I_{\alpha}^T/I_{\alpha}^S) (\lambda^S/\lambda^T) [(1 + R_B^S)/(1 + R_B^T)] \quad (8)$$

An important advantage of this method is that ionization cross-section and Auger yield data are not required, and the Auger current is reduced to a relative measurement. When the test sample composition is similar to that of the standard, the escape depth and backscattering factor are also removed from eqn. (8) and quantitative analysis reduces to a relative Auger current measurement. It is, of course, essential that the two measurements be made under identical experimental conditions.

When the composition of the standard is not similar to that of the test specimen, careful consideration must be given to the influence of matrix on both the backscattering factor and the escape depth. Also, a variation in matrix which alters the shape of the Auger peak invalidates the use of the Auger peak-to-peak height in the differentiated Auger spectrum as an accurate, relative measure of Auger current [46].

As discussed in Section II.C, estimates of the backscattering factor can be obtained by comparing Auger yield vs. E_p curves with theoretical ionization cross-section vs. E_p curves or with Auger yield vs. E_p data from gaseous specimens where the backscattering factor has negligible value. As expected, experiments of this type [18] demonstrate that the backscattering factor increases with the weight density of the matrix and the primary beam energy, relative to the binding energy of the atomic core level involved. An obvious method of reducing the backscattering factor is to operate E_p near the ionization threshold, but this procedure also reduces the sensitivity through a reduction in ionization cross-section. A more practical solution is the development of formulas based on empirical data derived from the type of experiments mentioned above. It seems probable that an empirical backscattering factor of the form $R_B(E_p, E_w, D)$, where D is the weight density of the matrix, could be sufficiently accurate for quantitative analysis.

An elegant experiment which clearly illustrates the influence of backscattering on the Auger yield has been reported by Tarng and Wehner [47]. They deposited Mo uniformly on W while monitoring various Auger peaks from each element. As indicated in Fig. 20, the 120 eV Mo Auger signal rises to a value about 20% greater than that from pure Mo at an overlayer thickness of about eight monolayers. This overlayer thickness is slightly larger than the escape depth, but small compared with the penetration depth of the incident electron beam. Under these conditions, the backscattering factor is predominately determined by the heavier W substrate; the backscattering factor for the 120 eV Mo peak is 20% greater for a W matrix than for a Mo matrix.

The influence of the matrix on escape depth is not well established. As discussed in Section II.B, available Auger data appear to lie close to a "universal" escape depth curve, but the accuracy of the data is not sufficient to rule out matrix effects of sufficient magnitude to preclude quantitative analysis. More precise measurements on the matrix dependence of the escape depth are required for improving the quantitative capability of AES.

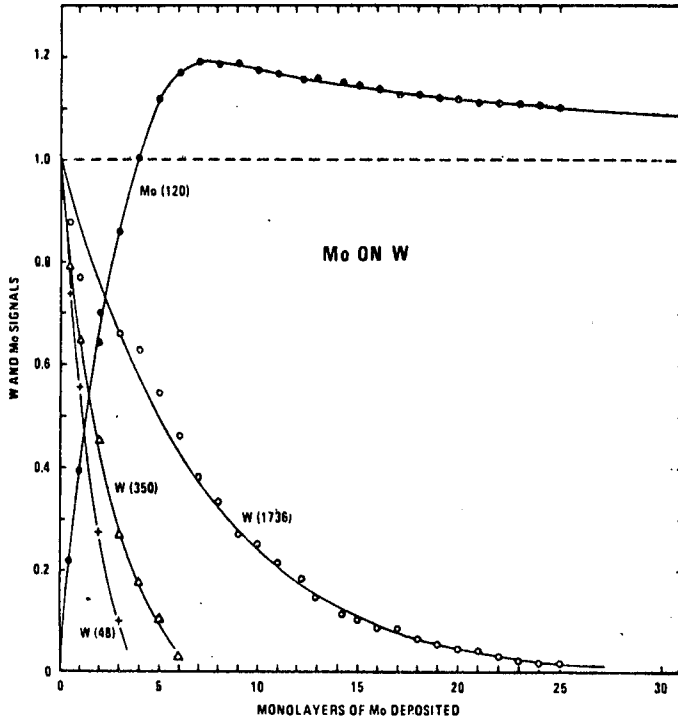


Fig. 20. Mo and W Auger signals as a function Mo overlayer coverage on W substrate. After Tarnag and Wehner [47].

C. MEASUREMENTS WITH ELEMENTAL SENSITIVITY FACTORS

A less accurate but highly useful method for quantitative analysis involves the use of elemental sensitivity factors. Assuming that meaningful sensitivity factors can be assigned to all elements, the atomic concentration of element X can be expressed as [17,44]

$$C_X = (I_X/S_X) / \sum_{\alpha} (I_{\alpha}/S_{\alpha}) \quad (9)$$

where S_{α} is the relative sensitivity of element α . The use of matrix-independent sensitivity factors obviously neglects variations in the backscattering factor and escape depth with material, and hence the method is normally only semiquantitative. Two important advantages of this method are the elimination of standards and insensitivity to surface roughness. The latter advantage is realized because all Auger peaks are uniformly affected by surface topography.

A first approximation to sensitivity factors can be obtained from Palm-

berg et al. [17] in which Auger spectra of pure elemental standards were obtained under identical experimental conditions. Specifically, the instrumental sensitivity is given for each spectrum and was calibrated using a silver specimen just prior to obtaining each spectrum. This means that the spectra given can be conveniently used to obtain elemental sensitivity factors relative to Ag for use in eqn. (9). Since the data were taken in the conventional $dN(E)/dE$ mode, it is necessary to base the sensitivity factors on the peak-to-peak height which is only valid when the peak shape is invariant with matrix [46].

D. EXPERIMENTAL RESULTS

To test the validity of the elemental sensitivity factor approach, an Inconel alloy was prepared for a ductile fracture inside a UHV system [48]. The Auger measurement included examination with a scanning Auger system to locate the incident beam on a region which was free from intergranular fracture surfaces. The Auger spectrum in Fig. 21 demonstrates that the only surface impurity in detectable quantity was carbon. Sensitivity factors based on available data [17] were applied to the MNN peak-to-peak heights of Ti, Fe, Cr, and Ni and the atomic concentrations determined from eqn. (9). In Table 1, the calculated atomic concentration levels from ductile fracture measurements of stainless steels and Inconel are compared with spectroscopically determined bulk concentrations. The experimental values derived from AES are in good agreement with the spectroscopically determined bulk values and are not affected appreciably by sputtering with argon ions. The agreement is expected since the Auger peak shapes remain nearly constant in

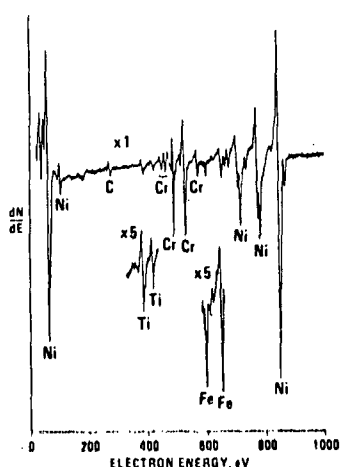


Fig. 21. Auger spectrum from ductile fracture surface of Inconel.

TABLE 1

Comparison of bulk atomic concentrations and values calculated from peak-to-peak height measurements obtained from ductile fracture surfaces [48]

Alloy	Element	S_x^a	Atomic concentration		
			Bulk atomic absorption	Surface AES	After sputtering AES
304 Stainless	Cr	0.31	0.205	0.24	0.23
	Fe	0.21	0.702	0.68	0.67
	Ni	0.26	0.093	0.09	0.10
316 Stainless	Cr	0.31	0.200	0.18	0.22
	Fe	0.21	0.656	0.71	0.67
	Ni	0.26	0.127	0.10	0.10
	Mo	0.25	0.018	0.01	0.02
600T Inconel	Cr	0.31	0.177	0.20	0.21
	Fe	0.21	0.084	0.07	0.07
	Ni	0.26	0.736	0.72	0.71
	Ti	0.44	0.003	0.01	0.01

^aRelative elemental sensitivity factors S_x obtained directly from Palmberg et al. [17].

metal alloy matrices, and the similarity of the alloy constituents ensures a minimal variation in the backscattering factor and escape depth. Also, surface roughness to first-order approximation will have an equivalent effect on all signals.

In the case of ionic compounds such as oxides, however, the peak shape of the metallic component is often significantly altered relative to the pure metal. Also, the variation in matrix is expected to produce significant changes in the escape depth and backscattering factor. In Fig. 7, the Auger spectra of vacuum cleaved MgO and evaporated Mg on cleaved MgO were compared to demonstrate characteristic differences in Auger fine structure [44]. If the Auger yield is independent of matrix and the peak-to-peak technique is a valid measure of the Auger current, the density of Mg in the pure metal must be only half that in MgO. The actual atomic density of magnesium in MgO is 1.24 times as large as elemental magnesium. Since backscattering factors for Mg and MgO should be small and not significantly different, the difference must be attributed to either a longer escape depth in MgO or errors in the Auger current measurement caused by a change in peak shape.

Care must be used to eliminate electron beam artifacts when making standardized measurements on oxides, fluorides, chlorides, etc. with intense

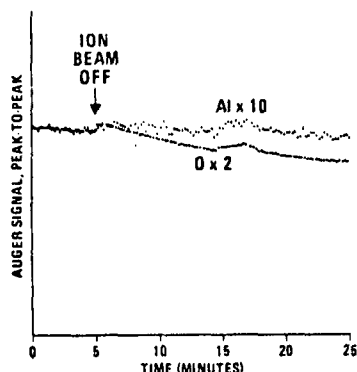


Fig. 22. Electron beam fragmentation of sapphire. $E_p = 5$ kV.

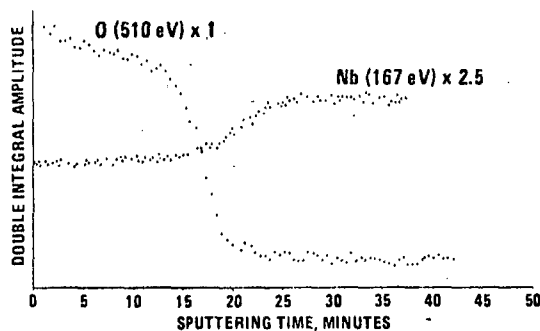


Fig. 23. Double integral amplitude profile of anodized niobium.

electron beam sources [49]. As an example, aluminum and oxygen peak-to-peak amplitudes from Al_2O_3 were measured as a function of time with and without ion beam sputtering. As indicated in Fig. 22, the oxygen signal decreased relative to the aluminum when the ion beam was turned off. The data is interpreted as dissociation and release of the oxygen from the sapphire surface. Subsequent studies showed that beam damage is negligible for electron beam current densities of 10^{-4} A cm^{-2} or less.

It has been pointed out [50] that in those cases where the shape of the peak is altered by the chemical matrix, measuring the total Auger current could be an improved method of measurement. In a recent study [51], the differentiated Auger signals of metal oxides were doubly integrated electronically and compared with pure metals. The electronic scheme accounted for a linear slope in the background through the Auger peak in the $N(E)$ curve. In Fig. 23, the double integral amplitudes were monitored as a function of time while sputtering a 1000 Å anodized niobium film. Assuming that the anodized region is predominantly Nb_2O_5 , the ratio of the niobium atomic density in pure niobium to that in Nb_2O_5 is 2.8. In Fig. 23, the ratio of the Nb signals in pure Nb to those from Nb_2O_5 is 1.5. Since the weight densities of the two matrices are similar, the backscattering factors should be nearly equal and, therefore, cannot account for this large discrepancy. The discrepancy must be related to differences in the electron mean escape depths between the metal and metal oxide. These results suggest that absolute mean escape depth measurements may be required for quantitative analysis.

The results presented here demonstrate that quantitative analysis with an accuracy of a few percent is possible with elemental sensitivity factors when the matrix of the test specimen is similar to that of the specimens used to

derive the sensitivity factors. In more routine analysis where matrix variations are large, the accuracy is reduced to 30–50%. Future developments in quantitative analysis will require precise measurement of backscattering factors and escape depths. In these experiments, techniques such as in situ fracture or cleaving provide a convenient means to prepare surfaces with known homogeneous concentration. Ion sputtering or scribing can also be used, but with some caution due to preferential sputtering. The validity of any of these techniques can be easily tested by examining several compositions of the alloy system of interest [52,53].

V. Applications

Numerous applications of AES have appeared in the literature during the past few years. While the initial applications were mostly fundamental in nature, recent trends and developments in high sensitivity and versatile instrumentation have led to many practical applications. In the following sections, numerous examples of typical AES applications in several fields are presented.

A. FUNDAMENTAL SURFACE SCIENCE

Initial applications of AES were primarily related to fundamental surface studies because of the simplicity of converting the LEED systems to AES instruments. In most of these studies, LEED was used to determine the atomic structure and AES for chemical analysis. In more general applications, AES is used to monitor the elemental composition of surfaces during physical property measurements. Several phenomena such as adsorption, desorption, surface segregation from the bulk, measurement of diffusion coefficients, and catalytic activity of surfaces have been investigated. AES has also been used to study the surface compositional changes in alloys during ion sputtering which is covered in greater detail elsewhere [53].

1. Identification of anomalous structures

LEED provides direct information of the two-dimensional translational symmetry of surface atomic arrangements, but does not identify the chemical species giving rise to the structure. In combination with LEED, AES has often been utilized to provide chemical identification of surface species. An example of this application is the identification of "ring" structures on the Pt(100) surface [1(a)]. The structure forms irreversibly when the specimens are heated in the 600–800°C range. The Auger spectrum [Fig. 24(a)] obtained from a Pt(100) surface before any heating shows primarily carbon. Little or no Pt is detected indicating that the carbon layer is sufficiently

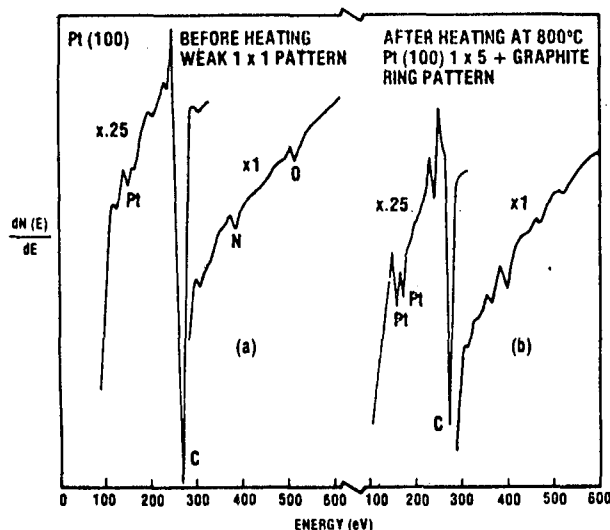


Fig. 24. Auger spectra from Pt(100): (a) Immediately after insertion into vacuum, and (b) after heating at 800°C. After Palmberg [1(a)].

thick to prevent the escape of Pt Auger electrons. A very weak 1×1 LEED pattern indicated a highly disordered structure. After briefly heating the specimen at 800°C, the LEED pattern showed a ring structure superimposed on the LEED pattern corresponding to the substrate. The Auger spectrum obtained is shown in Fig. 24(b). Auger peaks from the substrate as well as a change in the fine structure of the C Auger peak are observed. These results coupled with observations of the ring pattern suggests that heating causes the carbon to aggregate into graphite islands. Several other super structures on the single crystal surfaces have been related to the presence of impurities [1(a)].

2. Adsorption—desorption studies

In many adsorption and desorption studies, AES has been used to monitor surface coverage. The coverage is usually calibrated from supplementary techniques such as LEED, interferometry, quartz microbalance measurements, or ellipsometry. Palmberg [54] used the peak-to-peak amplitude in the dN/dE curve as a measure of surface coverage in a study of Xe adsorption on a Pd(100) surface. The variation of Xe peak height as a function of surface coverage at 77°K (Fig. 25) indicates that the sticking coefficient of Xe on Pd(100) remains near unity up to approximately a full monolayer coverage and then drops abruptly to zero. Also shown in the same plot is the variation of work function, $\Delta\phi$, with surface coverage. Many other studies of

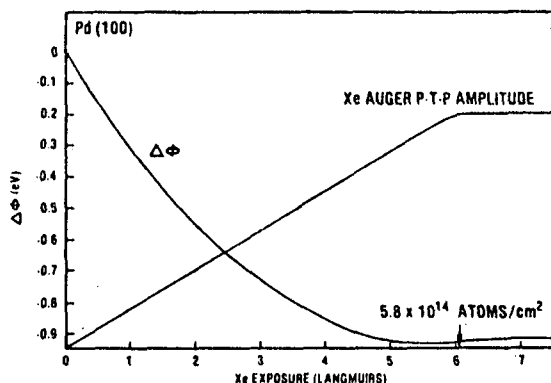


Fig. 25. Change in work function ($\Delta\phi$) and Xe Auger peak-to-peak amplitudes as a function of Xe exposure on a Pd(100) surface. After Palmberg [54].

adsorption and desorption of gases [55–60], as well as other elements [61–63] on solid surfaces, have appeared in the literature.

Adsorption–desorption studies are sometimes complicated by dissociation or desorption caused by electron beam irradiation. For example, the decomposition of CO into C and O makes the adsorption kinetics of CO impossible to study by using electron beams [64]. In most cases, however, the electron beam effects can easily be recognized in the experiment. Utilization of low primary beam energies and current densities and pulsed current techniques [65] often reduces electron beam effects sufficiently to allow examination by AES.

3. Surface segregation

Harris [4,66] was the first to report observations of surface segregation using AES. The specimen was positioned in front of the analyzer and heated from the back by electron bombardment. Harris observed that S segregates at the surface when Ni containing small amounts of S is heated between 600°C and 900°C. Since the S was readily removed by a brief exposure to air at room temperature and because its presence did not obscure the spectral lines of Ni, it was concluded that the extent of surface segregation was only one or two atomic layers. Harris has also observed that S segregates at the free surfaces of Ti, V, Fe, Cu, Nb, Mo, Ta, and W and that Cr and Sb segregate at the free surfaces of steel. Jenkins and Chung [67] observed C and S segregation to Cu(111) surfaces at 750°C. In the latter study it was also shown that segregated S occupies preferred sites on the surface, thereby giving a $\sqrt{7} \times \sqrt{7}$ surface structure. Taylor [68] reported S and P segregation at the surface of 304 stainless steel.

Results of a recent scanning Auger study of S and P segregation in 304 stainless steel are shown in Figs. 26 and 27. It is clear from Fig. 26 that S

190

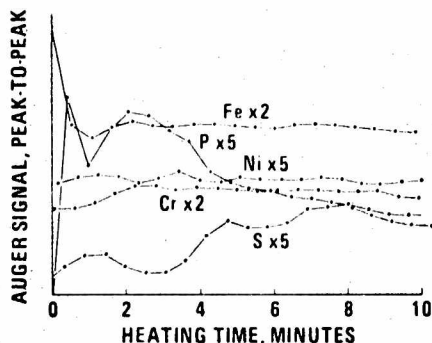


Fig. 26. Variation of surface composition during heating a 304 stainless steel foil specimen at 750°C.

diffuses to the surface more slowly than P (the bulk concentrations are known to be approximately 0.07 atomic percent each).

After 10 min at 650°C, the specimen was cooled to room temperature. The surface distribution of S and P (Fig. 27) indicates a nearly uniform distribution of P on the surface, while S is highly localized.

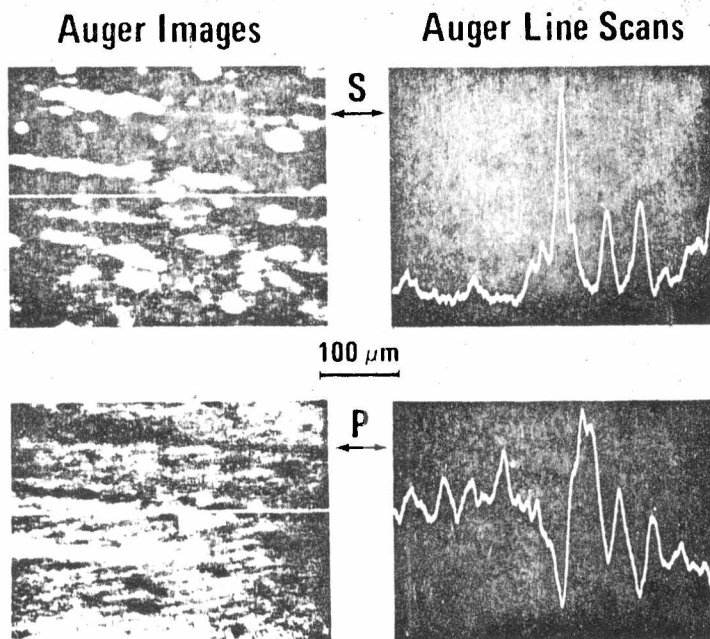


Fig. 27. Surface distribution of S and P after heating: Auger images and line scans.

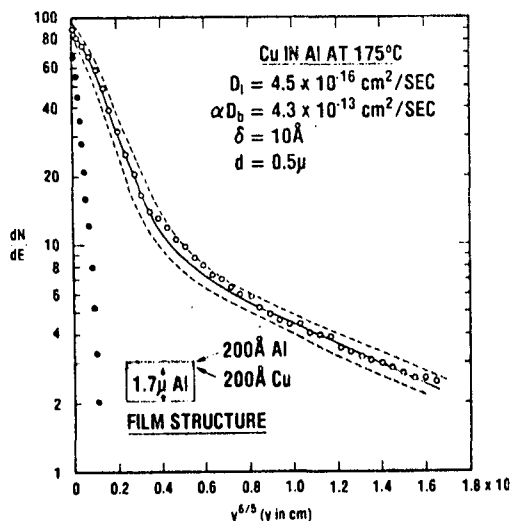


Fig. 28. Diffusion profile for Cu in Al thin film obtained after annealing for 85 min at 175°C. The solid circles show the unannealed profile. After Wildman et al. [73].

experiments in conjunction with AES have clearly demonstrated that the extent of segregation from the surface for both S and P is very small.

Diffusion parameters have been determined in some systems by studying the desorption and dissolution [69] or the segregation [70] kinetics of solute at the external surfaces. AES measurements of diffusion and surface segregation of deposited species from one side of a thin film to the other have been reported by several workers [71,72]. From such measurements the diffusion of Si through W [71] and of Cr through Pt [72] in the temperature ranges examined were determined to occur primarily via grain boundaries. Concentration variation of the diffusing species within the thin film has been measured by utilizing ion sputtering and AES [72,73]. Results of a diffusion profile for Cu in Al at 175°C after 85 min of annealing are shown in Fig. 28, where Y is the penetration distance measured from the center of the oxygen signal obtained at the Al/Cu interface. Based on the Whipple [74] analysis for grain boundary diffusion, these measurements enabled Wildman et al. [73] to separate the grain boundary contribution from lattice diffusion of Cu in Al.

Equilibrium segregation, which refers to the increase in surface concentration of one or more components as thermal equilibrium is established under conditions that correspond to a one-phase field in the phase diagram, has been studied in many systems [57,58,75–81] by monitoring the surface composition as a function of time at different temperatures. The thermodynamics of such segregation can be expressed [82] as

$$O_2/(1 - O_2) = [X_2/(1 - X_2)] \exp(Q/RT)$$

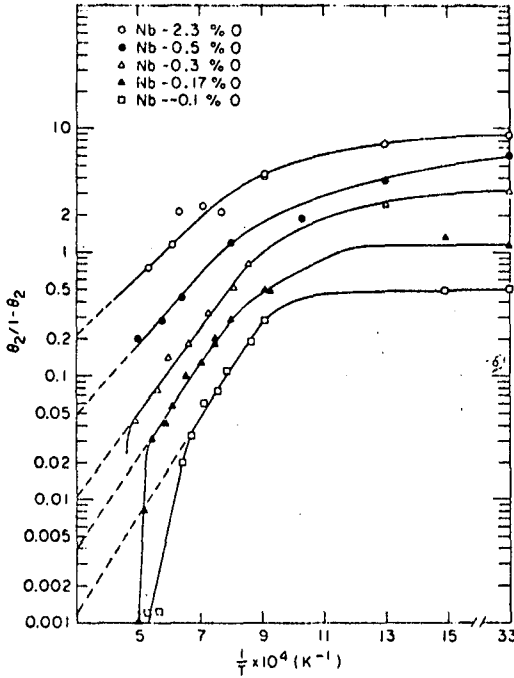


Fig. 29. Variation of oxygen surface coverage as a function of temperature in Nb—O alloys. θ_2 is the fraction of occupied sites to those actually available. After Joshi and Strongin [58].

where θ_2 is the ratio of the number of surface sites occupied by component 2 to the total number of available surface sites, X_2 is the ratio of the number of lattice sites, and Q is the energy change involved in transferring one mole of solute from the interior to the free surface of the sample.

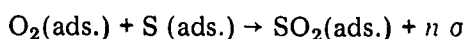
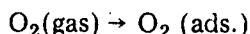
Equilibrium surface segregation of O in Nb—O and Ta—O alloys has been observed in the 800–1700°C temperature range. The temperature dependence of oxygen segregation to surfaces in a series of alloys is shown in Fig. 29. In the low temperature region, surface saturation and kinetically limited diffusion occur, while in the high temperature region, loss of solute due to evaporation of Nb oxides is evident. In the intermediate temperature range, the surface reaches a steady equilibrium state from which the distribution coefficient, $K = K_0 \exp(\Delta H/RT)$, could be obtained. In this temperature range (825–1200°C), ΔH for oxygen segregation varied from 17 to 11 kcal/(g atom) in Nb and from 19 to 6.6 kcal/(g atom) in Ta as the bulk oxygen varied from 0.1 to 2.2 at.%, an actual decrease with increasing bulk concentration of O. The AES studies performed in conjunction with ion sputtering [58] clearly indicated that the segregation is confined to the one to five atomic layer region near the surface.

Segregation of carbon at Ni surfaces has been studied extensively [78, 79, 83–85]. Segregation studies at single crystal surfaces [78] and stepped surfaces [79] indicate that the C segregation exhibits three distinct equilibrium states at the surface in different temperature regions. From $\theta/(1-\theta)$ vs. $1/T$ plots, Isett and Blakely [79] obtained three different heats of segregation corresponding to different amounts of surface coverage, suggesting changes in surface chemical bonding.

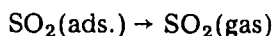
Ferrante [77] reported equilibrium segregation of Al in Cu–Al alloys (discussed in Section V.B.1.c) and obtained [76] Q values of 1.38 kcal/mole for Al segregation in the Cu–10 at.% Al alloy. Bonzel and Aaron [75] studied equilibrium surface segregation of Ag on a Cu–14.3 wt. % Al alloy. The Cu–Al alloy was plated with silver on one face and then equilibrated at various temperatures in UHV, while the composition of the other face was monitored with AES. From the temperature dependence of the equilibrium surface composition, they arrived at an enthalpy of adsorption for Ag on the Cu–Al alloy of 14.6–14.9 kcal/mole.

4. Surface reactions

Several examples of “gas–metal” as well as “gas–surface impurity” reactions have appeared in the literature. Reaction of oxygen with S segregated on Ni(111) surfaces was studied by AES in conjunction with mass spectrometry [86]. By studying the rate of growth of the oxygen Auger peak and the disappearance of the S peak at various temperatures and partial pressures of oxygen, Holloway and Hudson [86] have observed that the surface reaction consists of three steps, viz.



and



where σ represents an adsorption site for oxygen. Kinetic studies of the growth of surface oxygen and the decrease in S led them to conclude that the formation of $\text{SO}_2(\text{ads.})$ is the rate-controlling step, and that the reaction occurs by nucleation at a limited number of sulfur surface sites and outward spreading of the reaction zone.

AES in conjunction with LEED has been utilized for studying the interaction of O with C on a Mo(111) surface [60] and with CO on Pd(111) surfaces [59]. Adsorption and interaction of O and N on Nb surfaces have been studied by Farrell et al. [57].

B. METALLURGY AND MATERIALS SCIENCE

Chemical properties such as corrosion, stress corrosion, oxidation, and catalytic activity and mechanical properties such as fatigue, wear, adhesion, resistance to deformation processes, and surface cracking depend on surface properties. Similarly, grain boundary "chemistry" influences mechanical properties, such as low and high temperature ductility and fatigue, chemical properties, such as intergranular corrosion and stress corrosion cracking, and electrical properties. The near surface or grain boundary chemistry can be affected by penetration of external contamination or segregation from the bulk.

It is well known that free surfaces and interfaces are characterized by atomic structure and energies which are different from the bulk. The free energy of these surfaces is often reduced by adsorption or segregation of impurity or alloying elements from the bulk. When the segregation is in thermodynamic equilibrium with the bulk (i.e. not diffusion limited), it is viewed as equilibrium segregation. Since surface forces govern such segregation, the extent of segregation is expected to be very limited, at most a few atomic layers. Non-equilibrium segregation at surfaces and interfaces results when thermodynamic equilibrium is not established and occurs, for example, during freezing and solid state phase transformations, segregation resulting from drag of alloying elements by the vacancies during heat treatments, and concentration build-ups that occur during mechanical treatments. The non-equilibrium segregation is thus characterized by diffusion limitations, and its occurrence can either be short or large in extent from the surface or grain boundary. In several studies involving segregation, AES has provided non-destructive surface chemical analysis and proved to be extremely valuable compared to most other techniques which are limited by either large sampling depth and/or poor sensitivity. AES experiments in conjunction with ion sputtering have, in some cases, helped to distinguish equilibrium from non-equilibrium segregation.

In the following sections, several examples are presented in which AES has been used to relate surface and grain boundary chemistry to properties of materials.

1. Surface properties

a. Mechanical properties inferred from surface segregation studies

Boron segregation to grain boundaries or to carbide inclusions at the boundaries was thought to be at least partially responsible for high temperature fracture in precipitation-annealed (650–750°C range) steels containing boron. On the presumption that surface segregation would be similar to that at the grain boundary, Bishop and Riviere [87] conducted experiments to study the surface segregation of boron-doped Fe. They observed maximum

segregation rates for B in the 700–800°C range, where precipitation treatment is carried out in steels, and confirms the likelihood that B is one of the elements involved in embrittlement of steels. In addition to B, they also observed segregation of N and S on the surface of Fe.

The temperature dependence of surface segregation has been examined by AES in zircaloy specimens [88]. Surface segregation of carbon and subsequent metal carbide formation above 300°C was inferred from the occurrence of a C Auger peak and the detailed shape of the C peak. The formation of a brittle carbide surface layer is believed to contribute to the ductility minimum observed at certain strain rates in the 300–350°C range.

Surface segregation and formation of surface phases in alloys within limited temperature ranges strongly influence their behavior during mechanical processing. AES studies performed [89] on Al and Cu base alloys have substantially aided in understanding many processing problems, such as resistance to deformation in rolling and drawing, surface defects in finished products, and poor adhesion properties during final plating operations.

Thompson et al. utilized AES to study the role of lead [90] in the machining of steel. By measuring the composition, thickness, and coverage of the lead and oxide films on the chip and tool surfaces, they concluded that a discontinuous lead film 20–40 Å thick forms on both the tool and chip surfaces during the machining of a leaded steel and is responsible for reducing the metal–metal contact between the work material and the tool. The presence of appreciable quantities of oxygen on the chip surface is believed to result from surface oxidation caused at the machining temperatures.

b. Corrosion and oxidation

The addition of small amounts of Zr substantially improves corrosion properties of some systems. For example, as little as 100 ppm Zr added to liquid Bi prevents liquid metal corrosion of low alloy steel containers. It has also been found that preferential corrosion of Nb grain boundaries by liquid Li can be retarded by adding 1% Zr. The effect of Zr in inhibiting corrosion is believed to arise from the formation of stable compounds with C, N, and O.

AES studies were performed [91] on a commercial Nb–1% Zr alloy to examine the formation and stability of these surface compounds during heat treatment. Some of the results of this study are shown in Fig. 30. Prior to AES analysis, the specimen was cooled to room temperature after heating for a few minutes at the temperature designated on the abscissa. As the specimen temperature was raised progressively to higher values, observable surface segregation of oxygen first occurred in specimens cooled from 500°C and reached a maximum at about 1300°C. When specimens were held at higher temperatures, some oxygen diffused back into the bulk, while the remaining fraction as well as the segregated Zr appeared to be stable on the

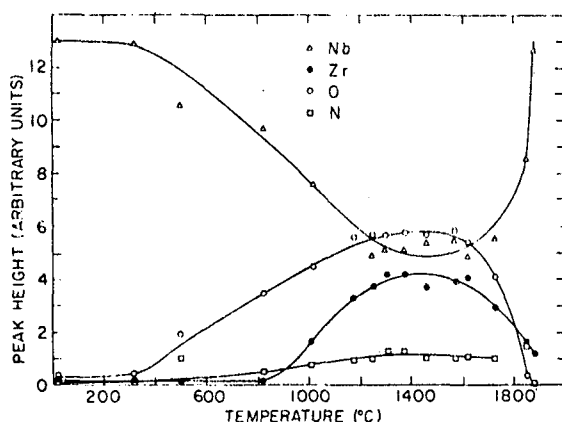


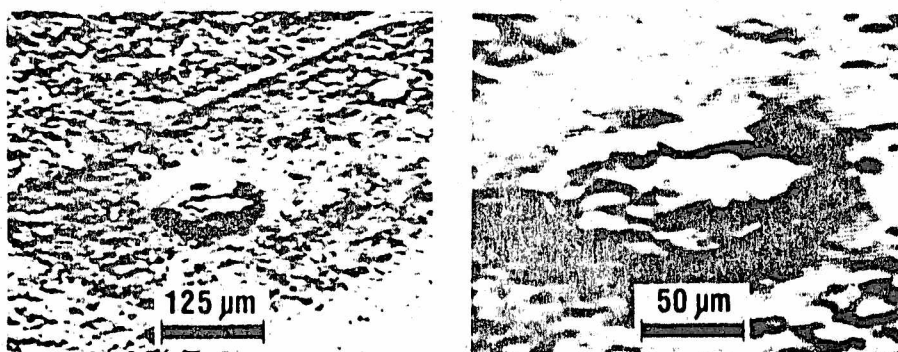
Fig. 30. Peak heights of Nb, Zr, O, and N as a function of the temperature from which the sample was cooled to room temperature. After Joshi et al. [91].

surface. The surface concentration of the irreversible and segregated Zr was estimated at about 30 at.%. Segregation of N was observed after heating to temperatures beyond 1000°C. At temperatures beyond 1500°C, Zr was desorbed from the surface, probably in the form of oxides. Sputter profiling measurements indicated that segregation of O, Zr, and N was limited to a few atomic layers. These measurements clearly indicate the formation of stable surface compounds at various annealing temperatures and thus explain the beneficial effect of Zr additions on the corrosion properties.

Wehner and co-workers [92] have studied surfaces of 304 stainless steel, Inconel, and CoCrAlY alloys corroded by fused salt eutectic mixtures of (a) NaCl + NaNO₃ and (b) KF + NaF + KNO₃ solutions. AES analysis and in-depth profiling gave compositional information of corrosion products on the surface and in the near surface region of the specimens. In some specimens which were corroded for a long time in mixture B, the corrosion products did not adhere well and could be peeled off easily. Scanning Auger analysis on these specimens provided chemical information near the reaction zones. Pitting and the formation of mesas and holes with a distinctive surrounding halo were studied in microscopic detail. An example of the type of information obtained in this study on 304 stainless steel specimens is given in Fig. 31. The Auger images were taken after sputter removing approximately 1500 Å. In addition, information on the compositional variation as a function of depth in various areas on the surface has led to a better understanding of the corrosion process.

Several studies on the initial stages of oxidation using AES have appeared in the literature. Ferrante [93] studied the oxidation of a Cu-19.6% Al alloy in 5×10^{-4} torr oxygen at 700°C and observed complete coverage of the surface by aluminum oxide. Studies of oxide growth at various tempera-

ABSORBED CURRENT MICROGRAPHS



AUGER IMAGES

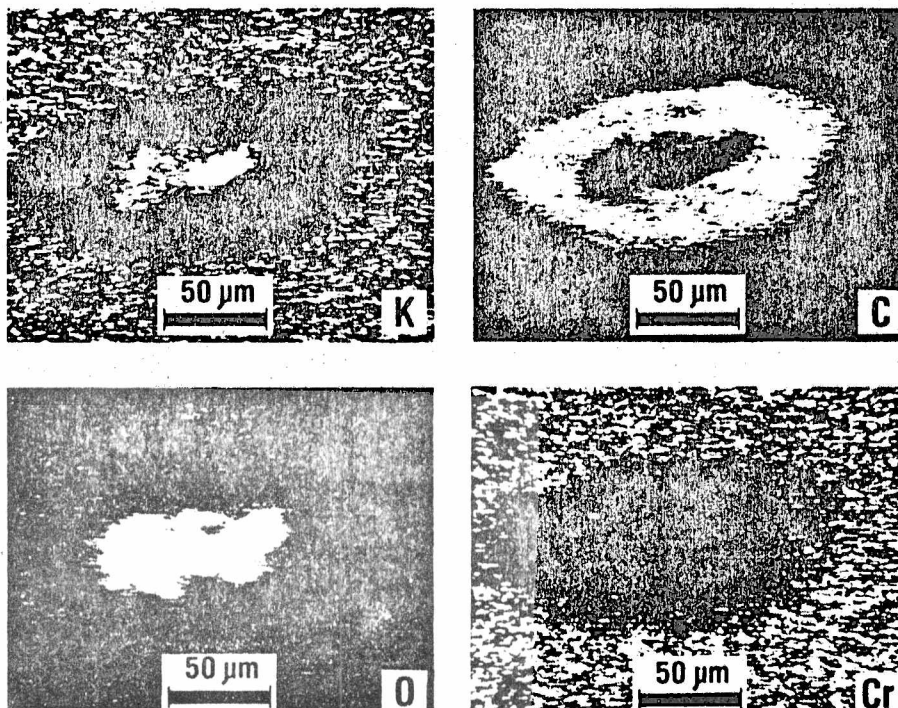


Fig. 31. Pit in 304 stainless steel after immersion in molten KF-NaF-NaNO_3 at 350°C for 7 days. After Wehner et al. [92].

tures indicated that a thermally activated diffusion process was important in oxide formation. Oxidation kinetics of Re in the $300\text{--}2200^\circ\text{K}$ range were studied in the 10^{-9} to 10^{-6} torr range of oxygen pressure using a quadru-

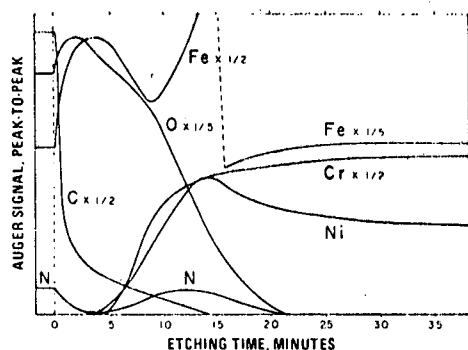


Fig. 32. Depth profile for a 304 stainless steel sample heated in air at 200°C for 2 h. Sputter rate = 5–10 Å/min. After Betz et al. [96].

pole mass spectrometer in conjunction with AES. In a different study, AES and ellipsometry were used to follow the growth of PbO on lead [94].

Studies on air oxidation of several commercial alloys [95,96] have been performed using AES. Betz et al. [96] have examined changes which occur at surfaces of 304 stainless steel, 321 stainless steel, and Inconel when exposed to air at various temperatures. Composition—depth profiles were obtained by AES and simultaneous sputtering. Results from a 304 stainless steel specimen oxidized at 200°C for two hours are shown in Fig. 32. Oxidation at temperatures below approximately 200°C caused formation of iron oxides within a narrow region near the surface, while oxidation at higher temperatures resulted in chromium-rich oxides. These results were explained on the basis that the chromium-rich oxide is the thermodynamically stable phase in the oxidation products of these alloys. The formation of an iron-rich oxide at low temperature occurs, because the kinetics of Cr migration to the surface is limited.

c. Adhesion, friction, and wear

Buckley [97] used a LEED—AES apparatus to study surface contamination and its influence on the adhesive properties of Fe single crystals. He showed that the effects of methane or ethane [98] on the Fe—Fe junction strength are minimal, while O [97] and H₂S [99] reduced the junction strength to values approaching zero. Similar studies were also performed in alloy systems. Ferrante and Buckley [100] found that surface segregation of Al occurs in Al—Cu alloys containing 1, 5, and 10 at. % Al. The segregated Al amounts to one atomic layer of ~100% Al. The enhanced adhesion observed for these alloy surfaces relative to pure copper was correlated [77,101] with the segregation of Al at free surfaces.

Adhesive properties of paint on galvanized steel surfaces has been studied as a function of pretreatment [102]. Auger analysis of steel showed that

surfaces cleaned in a kerosene—acetone—alcohol mixture were nearly free of surface carbon and exhibited excellent adhesion qualities. By performing AES analysis on several surfaces, Gjostein and Chavka [102] arrived at an empirical expression for an Adhesion Index (A.I.)

$$A.I. = (Zn) (O)/(C)$$

where the quantities in parenthesis are the Auger peak heights of the indicated surface species.

Auger measurements [103] from ground alumina substrates, which had been annealed in the 1400–1500°C range, demonstrated that Ca and Si segregated to the surface. Surfaces containing Ca and Si segregation exhibited good adhesion to Ta₂N—TiPdAu films, while etched specimens or annealed sapphire exhibited poor adhesion.

AES has succeeded in identifying contaminants in the plating industry which cause peeling, bulging, poor adhesion, or discoloration of platings. Electrodeposited Ni laminate material containing undesirably weak and fracture-sensitive Ni—Ni bonds was examined using an AES—SEM system [104,105]. Auger analysis of the fracture surfaces showed that Ag was a major constituent and definitely responsible for observed failures in structures fabricated by this technique.

AES data have led to a better understanding of wear properties [102] in friction materials. In a sintered Fe base brake material consisting of a wear additive MX, AES showed that the wear surface contained M in a concentration seven times larger than the bulk. The extent of segregation was estimated at 35 Å from an ion sputtering profile. These results demonstrate that the additive segregates to the wear interface in sufficient concentration to provide an effective wear interface.

In an effort to understand surface properties, such as corrosion, adhesion, wear, and wetting, Watterson and Simons [106] conducted AES investigations on the surface segregation of S, P, N, C, Sn, Sb, and Ca in heat-treated steels. Sulfur segregation was the most dominant feature, and the argon ion sputtering showed that the extent of segregation from the surface is very small. However, no direct correlations with any of the properties were reported in this study.

2. Grain boundary phenomena

Numerous mechanical properties and corrosion phenomena are related to grain boundary chemistry. Grain boundary embrittlement, intergranular corrosion, intergranular stress corrosion cracking, and grain growth are strongly influenced by impurity segregation to grain boundaries and have been successfully studied utilizing AES. The boundary chemistry is made amenable to study by obtaining intergranular fractures in these materials. Since the external surfaces so formed are envelopes containing grain boundary facets,

analysis of these fracture surfaces by AES is representative of grain boundary or near boundary chemistry. The fractures are usually carried out in a UHV and analyzed immediately to minimize contamination from the ambient. Pressures in the range of 10^{-9} torr or better are essential to prevent excessive contamination on the active surfaces. In most cases, fracture and analysis are preceded by a bakeout of the entire system. In this section, AES studies of fracture surface chemistry are reviewed and related to various properties. Also included are studies on some powder metallurgy materials in which the surface preparation of particles plays a dominant role in the properties of final sintered compacts.

a. Embrittlement in ferrous alloys

AES has been highly successful in identifying grain boundary segregation of impurities in many steels and other Fe-base alloys. The first experiments [107,108], on low alloy steels with a nominal composition of 3.5% Ni, 1.6% Cr, 0.4% C, and 300 ppm Sb by weight, clearly demonstrated that Sb segregates to grain boundaries during embrittling treatment. Enrichment of Cr and Ni at the grain boundaries was also detected. Segregation was not detected in steels fractured in the intergranular mode after a non-embrittling or de-embrittling treatment. The extent of segregation [109] was estimated by ion sputtering in conjunction with AES; it was shown that all impurity elements, including Sb [107–111], P [109,111,112], and Sn [111,113] were concentrated within a very narrow region (1–4 atomic layers) near the grain boundary (Fig. 33). Segregation of Ni near the grain boundaries extended [110,112,

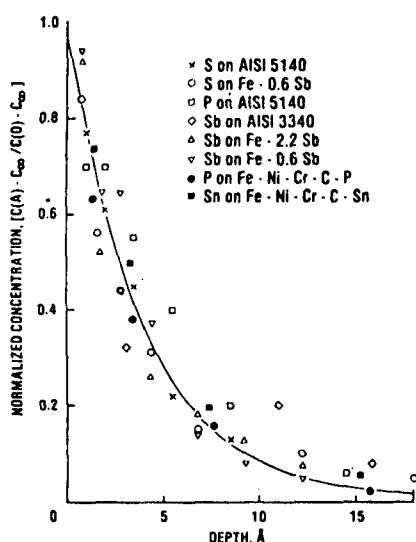


Fig. 33. Normalized concentration of segregated solute on fracture surface vs. average amount removed by ion sputtering. After Marcus et al. [111]. Reproduced by permission of the ASTM.

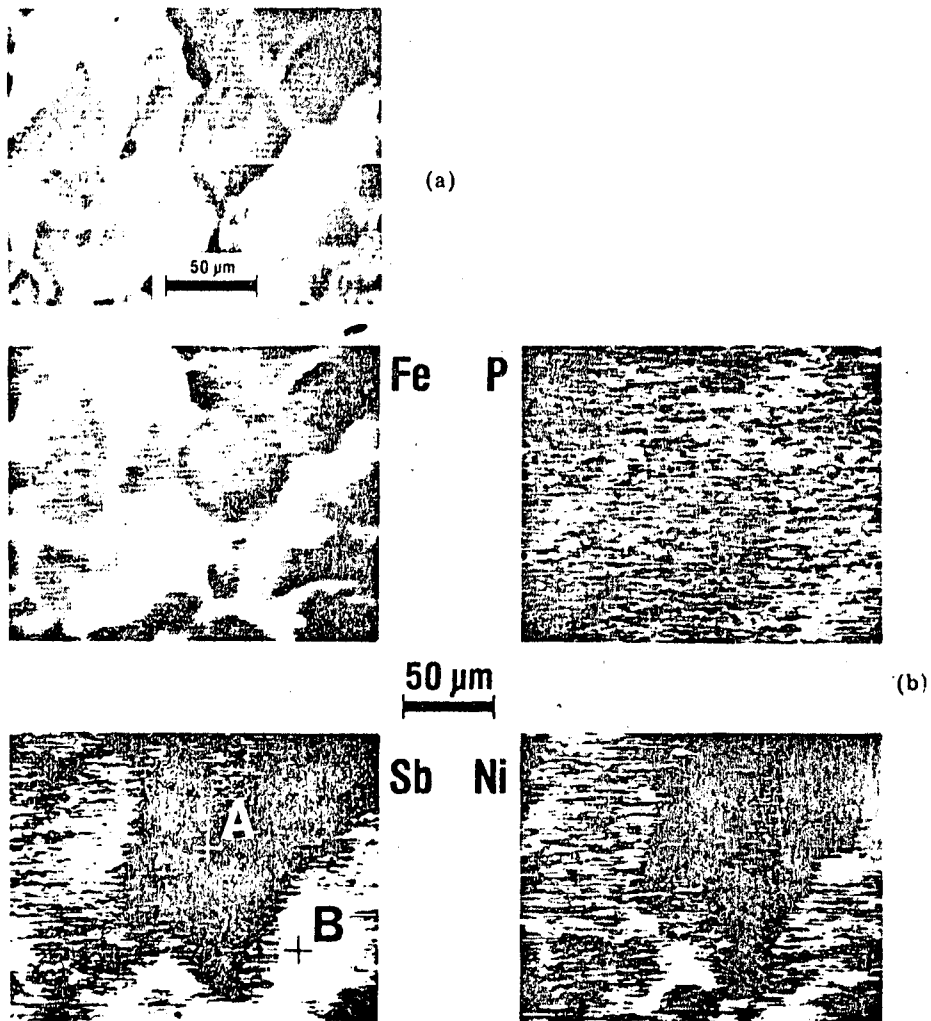


Fig. 34. (a) Specimen current micrograph showing the fracture surface of an embrittled 3340 steel, and (b) Auger elemental images of Fe, P, Sb and Ni obtained from the surface shown in (a).

over a larger range (as much as several hundred angstroms) and did not decrease exponentially with sputtering time; this result suggests [110] a segregation mechanism based on non-equilibrium processes.

The lateral distribution of segregated species on fracture surfaces from a 3340 steel has been examined with scanning AES [114]. These results, illustrated in Fig. 34, show that P segregates uniformly on all grain boundaries, and that Ni and Sb segregate preferentially on specific grain facets. Spectra obtained from two such facets are shown in Fig. 35. These observa-

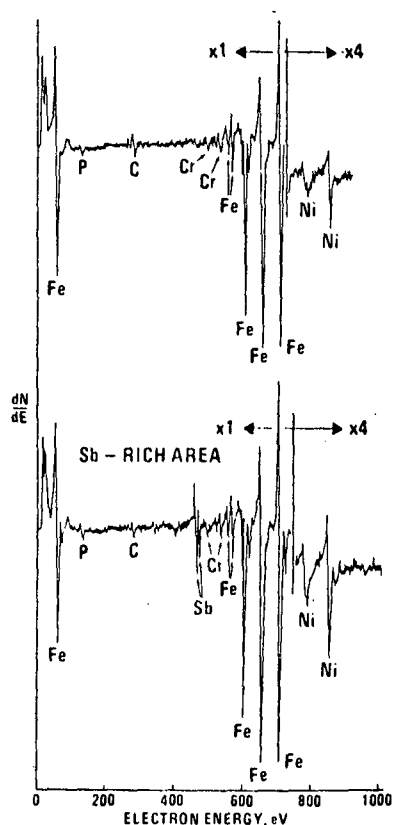


Fig. 35. Auger spectra obtained from the low Sb and Sb-rich grain boundary facets.

tions suggest a very strong dependence of segregation on grain boundary structure and energy. In most cases, the degree of embrittlement could be directly related to the observed segregation at grain boundaries; the variation in grain boundary composition as a function of the ductile to brittle transition temperature is shown in Fig. 36. Similar studies made in Ni—Cr—Mo—V steels [115] also indicate a direct correlation of segregation to the embrittlement.

The combined presence of Ni and Cr in low alloy steels leads to more segregation of Sb, P, or Sn to grain boundaries than when either is present alone [110,111]. The addition of Mo [111] to a Sb bearing steel only changes the kinetics of embrittlement, while extended aging at 480°C enhances segregation and consequent embrittlement. In a Sb steel containing additions of 0.1% Ti, however, Sb segregation was found to be diminished upon prolonged aging [116].

AES examination of grain boundary embrittlement in Fe—P and Fe—P—S alloys showed that P and S irreversibly segregated to grain boundaries in the

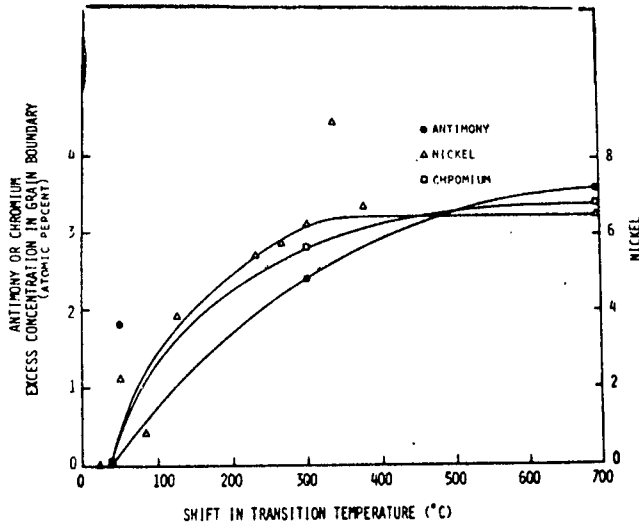


Fig. 36. Relation of severity of temper embrittlement to grain boundary concentrations of Sb, Ni, and Cr in 3340 steels. After Joshi and Stein [110]. Reproduced by permission of the ASTM.

entire ferrite range, while no segregation occurred in the austenite. It was also shown that, in the absence of C, the elements Ni and Cr are not required for the embrittlement and that the presence of P, S, or possibly Sb at the grain boundaries is sufficient to cause extreme brittleness in Fe. Irreversible embrittlement in Fe—Te alloys [118] was shown to be due to Te segregation to grain boundaries.

Segregation of Si, Sn, and S to grain boundaries of Fe was studied by Hondros and Seah [119] in an effort to measure their grain boundary activity directly. It was shown that enrichment ratios of 3, 462, and 10^4 , respectively, are inversely related to maximum solid solubility, a phenomenon that was found to be consistent with other measurements of interfacial activity.

b. Embrittlement in non-ferrous alloys

Tungsten made by powder metallurgical methods is often extremely brittle with ductile—brittle transition temperatures as high as 825°C. It was believed that the embrittlement was associated with the segregation of oxygen to grain boundaries, but AES studies [120] did not indicate any oxygen enrichment in the brittle materials. Instead, AES experiments have shown that the phosphorus concentration at grain boundaries is a strong function of the transition temperature as indicated in Fig. 37 [120]. The P concentration at grain boundaries was found to be a function of grain size of the material examined and in all cases the P enrichment was localized to $<20 \text{ \AA}$ near the grain boundary.

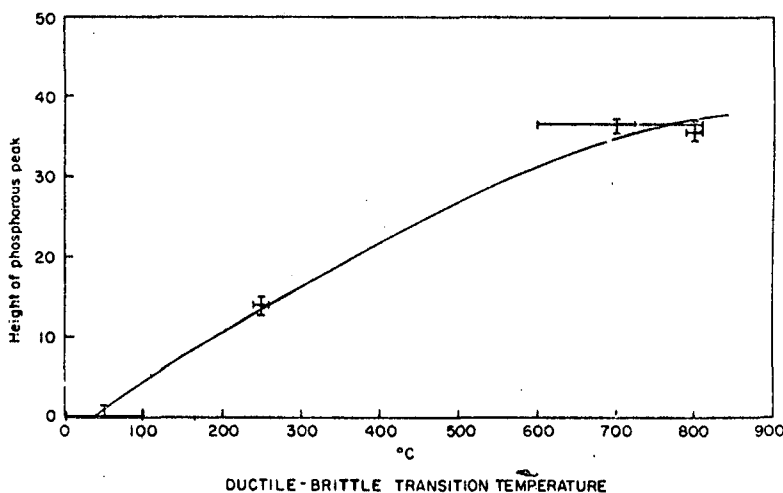


Fig. 37. Effect of P segregation to the grain boundaries on the ductile—brittle transition temperature of tungsten. After Joshi and Stein [120].

AES [121,122] was used to establish a correlation of embrittlement in copper, containing various amounts of Bi, with Bi segregation at grain boundaries. The concentration of Bi in the grain boundary region was estimated at 30 at.% and extended over a very limited region. In a different study, embrittlement in Cu containing 25–100 ppm Te was studied using AES [123]. A solution-treated material aged at 540°C for one day resulted in grain boundary segregation of Te and consequent embrittlement. Further aging resulted in a second phase formation in both the matrix and grain boundary region. This second phase formation resulted in de-embrittlement, which was believed to result from desegregation of Te from grain boundaries.

Polycrystalline Ni charged with hydrogen results in brittle, intergranular fractures when tested in slow tension. From AES studies, the embrittlement of Ni by hydrogen was correlated with segregation of hydrogen recombination poisons at the grain boundaries [124]. It was suggested that the entry of hydrogen into the Ni specimens occurs preferentially in the proximity of grain boundary intersections with the free surface. The Sb and Sn present at grain boundaries act as hydrogen recombination poisons and stimulate absorption of hydrogen by the metal.

In another AES study [125] on S-doped Ni base alloys, it was shown that embrittlement results from S segregation at grain boundaries in concentrations up to 12 at.%. It was also shown that ductility enhancement induced by doping the alloy with small amounts of elements such as Hf, Zr, and La was associated with a reduction in grain boundary sulfur concentration.

The role of TiC precipitation in the thermal embrittlement of 250 series maraging steels has been elucidated by AES [126]. It was shown that the

segregated TiC is highly localized near the prior austenite grain boundaries. Further loss in fracture toughness with aging was shown to result from a loss in cohesive strength at the TiC/matrix interface due to segregation of B.

c. Embrittlement in powder metallurgy materials

Under identical conditions of pressing and sintering, compacts of iron powders prepared by various methods differ in density and tensile strength. Differences in mechanical properties were believed to arise from variations in initial surface preparation techniques or from changes that occurred during sintering. The interface chemistry between particles can be examined with AES by in situ fracture which occurs primarily along interparticle interfaces. In a recent AES study [127], the density and tensile strength of various specimens were related to the fracture surface concentration of impurity elements; the results are presented in Fig. 38. The relationship between the concentration of impurity elements and the density of powder-metallurgy compacts was similar; only oxygen appears to be detrimental. Low density (also high strength) irons exhibited a shallow in-depth profile, while the lowest density iron exhibited a region of segregation extending well over 300 Å. In a scanning AES study [70] of a low-density Fe, it was shown that O, C, and Ca are localized in the same regions on the fracture surface. These observations suggest that the contamination in the low-density iron consists of O, C, and Ca in a compound form. The distribution of O and C were not highly correlated on the fracture surface of a high-density Fe specimen.

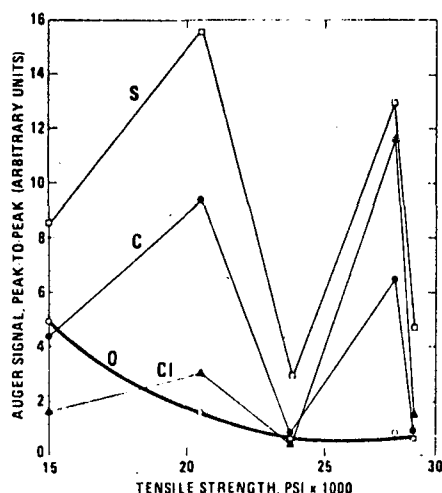


Fig. 38. Variation of S, Cl, C, and O at the fracture surface of powder metallurgy iron vs. tensile strength.

d. Intergranular corrosion

Austenitic stainless steels that have been solution-treated are often susceptible to grain boundary corrosion after heating in the 450–900°C temperature range. This phenomenon, known as sensitization, was strongly believed to result from precipitation of chromium-rich carbides at the grain boundaries. Since the carbides were chromium-rich, it was expected that the region adjacent to the grain boundaries would be depleted of Cr; impoverishment in Cr was hypothesized to be the reason for poor corrosion resistance. This explanation appeared satisfactory for explaining the corrosion behaviors in weakly oxidizing solutions, but does not account for observed intergranular corrosion of solution-treated steels which show no detectable carbide precipitation. Chaudron [128] and Armijo [129] have shown that high-purity alloys are immune to attack. These and other experiments indicate that Cr depletion and the strain theories [130] cannot account for all the observed properties. In order to understand the corrosion behaviors in austenitic stainless steels better, Joshi and Stein [131] conducted an AES study on freshly fractured surfaces of selected alloys and related the grain boundary chemistry to the corrosion behavior in strongly and weakly oxidizing solutions. The results of the study are briefly summarized below and in Table 2.

Sulfur, a common impurity element and sometimes an additive in stainless steels, segregates to grain boundaries during the high-temperature (~1050°C) non-sensitization treatment. When the steel is subsequently treated in the 600–850°C range, the grain boundaries undergo depletion of Cr and enrichment of Ni. The corrosion properties, measured as weight loss/cm²/h, in nitric–dichromate (strongly oxidizing) solutions relate very well with S concentration at grain boundaries and apparently have no relation to Cr depletion. The corrosion properties in H₂SO₄–CuSO₄ solutions, on the other hand, strongly depended upon Cr depletion, but not on S or Si segregation. The minimum Cr content at grain boundaries, required to provide good resistance to intergranular corrosion, was estimated at 13 wt.%. In other steels examined the segregation of P and N was observed and believed to cause poor corrosion resistance in nitric–dichromate solutions.

There is considerable evidence that intergranular corrosion under stress is influenced by impurities in many materials. AES studies on these materials in conjunction with stress corrosion studies is needed to assess the impurity effects fully. Another interesting area of application for AES studies is in materials where the penetration of liquid metals along grain boundaries seems to depend on the composition of the boundary.

e. Stability of grain structures

Powder metallurgy tungsten wire produced from WO₃, which is doped with potassium silicate and aluminum chloride prior to hydrogen reduction, is used extensively for filaments in incandescent lamps because of its resis-

TABLE 2

Auger spectroscopic analysis of 304 stainless steel fracture surfaces [131]

Treatment	C/Fe	Si/Fe	S/Fe	Cr/Fe	Ni/Fe	Corrosion rate (mg/cm ² /h)	Boiling nitric— dichromate solution ^a	Modified Strauss test ^b
(1) 2 h 1050°C, W.Q. ^d	0.0128	N.D. ^c	1.230	0.664	0.102	2.25	Negligible	Negligible
(2) 2 h 1050°C, W.Q. +2 h 850°C, W.Q.	0.177	0.066	0.588	0.515	0.111	0.84	0.016	0.016
(3) 2 h 1050°C, W.Q. +2 h 650°C, W.Q.	0.011	0.111	0.920	0.525	0.109	2.93	Negligible	Negligible
(4) 2 h 1050°C, W.Q. +2 h 600°C, W.Q.	0.0645	N.D. ^c	0.881	0.548	0.103	2.64	Negligible	Negligible
(5) 2 h 1050°C, W.Q. +3 days 650°C, W.Q.	0.283	N.D. ^c	0.850	0.459	0.119	0.87	0.447	0.447

^aWeight loss rate determined at the end of 14 h corrosion test in nitric—dichromate solutions.

^bWeight loss rate determined from a 60 h corrosion test.

^cNone detected.

^dW.Q. = water quenched.

tance to creep at high temperatures. The cause of this phenomenon has been attributed to an interlocked grain structure which is formed as a consequence of either mullite particles, as suggested by Walter [132], or bubbles, as suggested by Moon and Koo [133]. An AES study performed on the intergranular fracture surfaces of tungsten rods doped with Al, K, and Si showed that K was segregated at the grain boundaries. No Al or Si was detected, but a strong correlation between bubble density and K content was established [134]. The results demonstrate that the bubbles are formed by elemental K and that K, rather than mullite, is responsible for the interlocked grain structures. Additions of ~ 1000 ppm of MgO to Al_2O_3 are known to increase the sintering rates and substantially increase the density of sintered Al_2O_3 . The role of MgO was thought to result from reduced grain boundary motion caused by solute segregation at grain boundaries [135]. An AES study of intergranular fracture surfaces showed no large increase in Mg over bulk levels [136,137]; the grain boundary concentration was estimated at 0.4 at.% Mg^{2+} in a specimen containing 0.2 at.% Mg^{2+} in the bulk [138]. The only other element present in significant amounts at fracture surfaces was Ca. A closer examination [89] of the fresh fracture surfaces in a scanning Auger system indicated that the Mg signal arises from localized precipitates present at the grain corners where the Mg^{2+} content was estimated at 4 at.%. In Fig. 39(a), an optical micrograph of a relief polished section of slow-cooled Al_2O_3 sintered with MgO is shown, and in Fig. 39(b) the Mg Auger image of the fracture surface of a similar specimen demonstrates that the precipitates are indeed Mg-rich.

AES studies [137] in NiO-doped Al_2O_3 showed no significant segregation of the additive, but did exhibit heavy Ca segregation, which was observed in

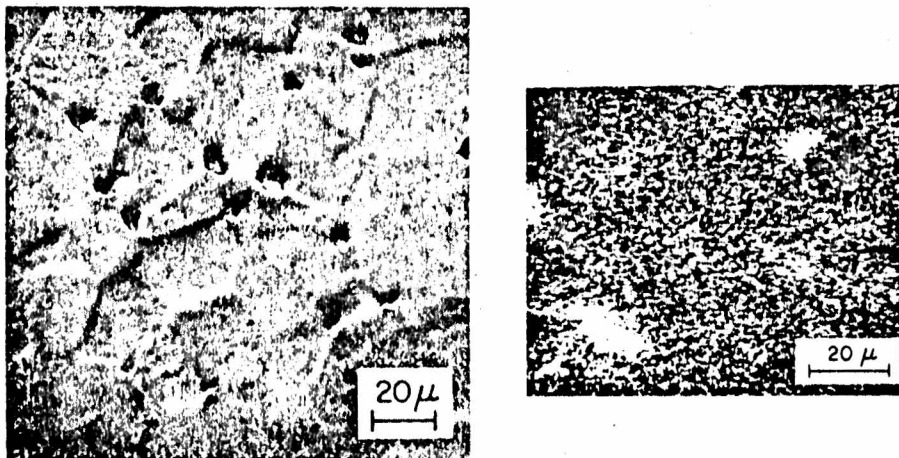


Fig. 39. (a) Micrograph of relief polished alumina, and (b) Mg Auger image obtained from a fracture surface of alumina. (Courtesy of W.C. Johnson, Ford Scientific Laboratory.)

CaO-doped Al_2O_3 , as well as commercially pure Al_2O_3 . Sputtering studies indicate that the segregated species were localized in the first 5–10 atomic layers near the boundaries.

Fracture studies of hot-pressed MgO doped with NaF and LiF have also been studied utilizing AES [137]. In the hot-pressed condition, the additives were present at the grain boundaries; after annealing only Ca and Ti were observed. Grain boundary chemistry changes affected by annealing were shown to be consistent with a liquid phase-assisted hot pressing mechanism and responsible for changes in physical properties.

C. CATALYTIC ACTIVITY

Catalytic activity of many materials is a surface phenomenon and hence a strong function of surface structure and chemistry. It is likely that surface impurities influence catalytic activity through induced changes in surface structure [139–141] as well as by more direct means. The surface chemistry in catalytic materials may be altered by adsorption from the environment, surface segregation from bulk, and contamination during usage.

Several Pt and Pt alloy catalyst surfaces have been studied using AES. After normal polishing and etching, Pt surfaces consist almost entirely of C and S to a depth of several atomic layers [142,143]. These are believed to be products of decomposition and can only be removed by excessive heating, ion bombardment, or heating in low oxygen pressures. A heat treatment of contaminated Pt [144] at 400°C in O_2 at 1 atm for 4 h removed the C and S from the surfaces. The Pt surface thus formed contained no more than a few monolayers of oxygen and was passive toward contamination in atmosphere that normally occurs on untreated Pt surfaces.

The kinetics of CO oxidation on a Pt(110) surface [145] was investigated using AES in conjunction with LEED and residual gas analysis. The experiments demonstrate that two different catalytic reaction mechanisms prevail in the oxidation process. At low temperatures, $100^\circ\text{C} < T < 200^\circ\text{C}$, CO remains adsorbed on the Pt surface resulting in a competitive adsorption by oxygen and an induction period for the onset of CO_2 formation which is a strong function of temperature. At high temperatures or in cases where oxygen was preadsorbed on Pt surfaces, the reaction with CO occurred immediately and was temperature-independent.

Catalytic platinum gauzes are often used in the oxidation of ammonia and in the synthesis of HCN. A 4% increase in HCN production and 20°C rise in temperature results when the catalyst, a Pt–10% Rh alloy, is treated with ~ 100 ppm H_2S for 110 h during continued HCN production. An examination of such a catalyst using AES [139] indicated that the surface consists of large amounts of C along with Rh, Ag, S, and N. Sputtering studies indicated that C extends over a great depth, while S and N are concentrated in the first few layers. This shows that treatment with H_2S does not produce bulk

contamination with S. Silver, the origin of which is unknown, was also present to depths on the order of several thousand angstroms. It was also noticed that Rh was present in excessive amounts near the surface compared with the bulk.

Copper catalysts that are used in a variety of oxidation and dehydrogenation reactions were examined [146] by AES to determine the cause of differences in their performance. The poorly performing catalyst was found to contain 4.9 at.% Pb near the surface, which was almost three times that of a good catalyst surface. Lead is a known poison for many copper catalysts and apparently migrated to the surface during the manufacturing operation. In a similar study [147] on a Pd-alumina catalyst used for selective hydrogenation of diolefins in an olefin-aromatic-paraffin stream, it was found that small amounts of Fe acted as a poison by preferentially masking the active Pd surface.

Surface composition, which can differ significantly from bulk composition with little or no external influence, plays an even more important role in alloy catalysis. AES analysis of Ni-Au alloy foil surfaces [148] indicated that Au enrichment occurs at the alloy surfaces upon thermal equilibration

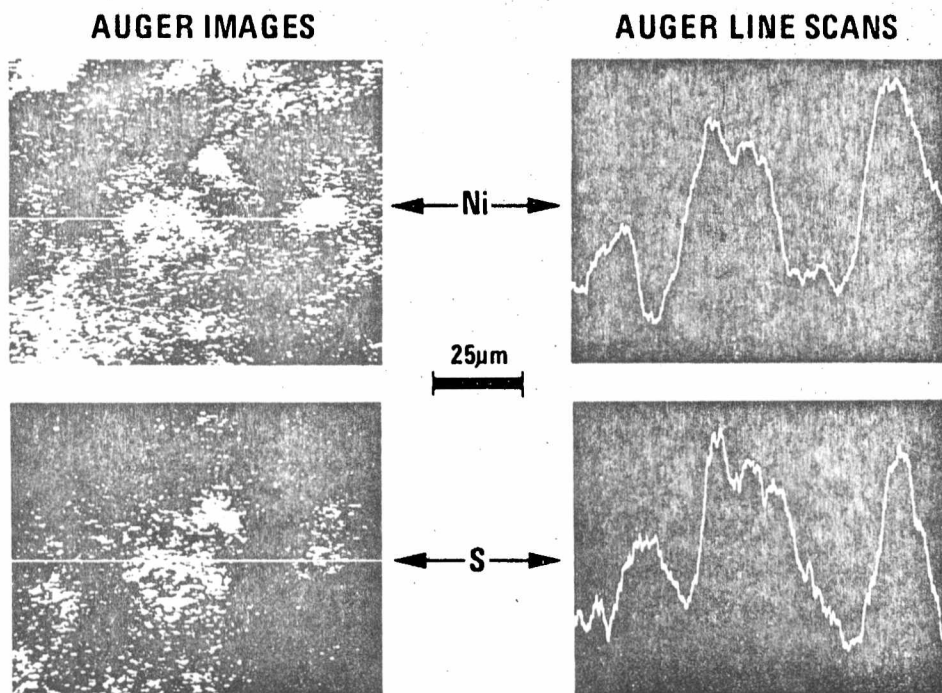


Fig. 40. Auger images and corresponding Auger line scans for Ni and S from spent methanation catalyst.

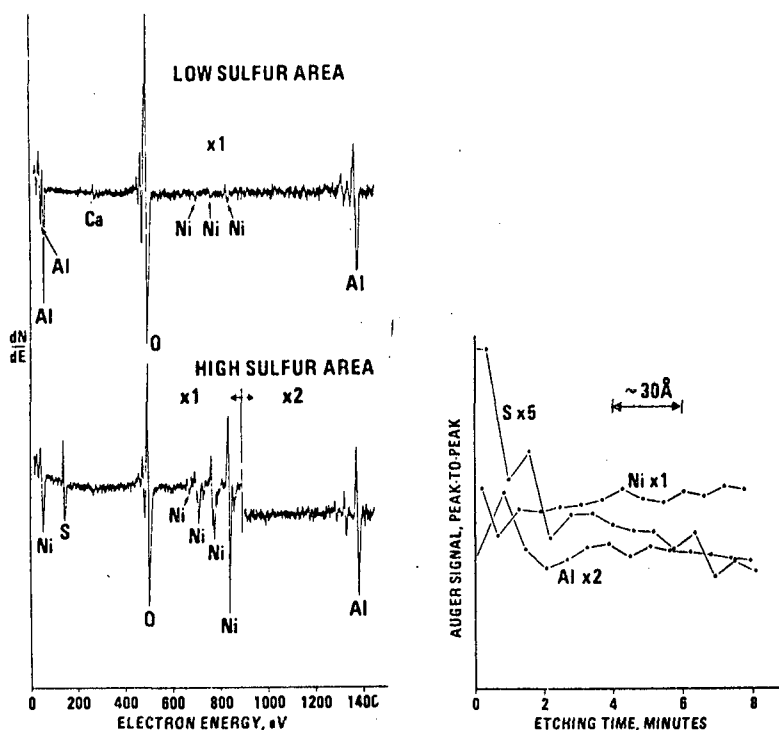


Fig. 41. Auger spectra from areas ($5 \mu\text{m}$ diam.) of high and low sulfur (concentration on the spent catalyst).

Fig. 42. Depth—composition profile of the spent catalyst.

at high temperature. Chemisorption of hydrogen or oxygen at room temperature caused the surface concentration of Ni to increase. Since the Ni—O and Ni—H bonds are stronger than Au—O and Au—H bonds, preferential migration of Ni to the surface from the near surface region is expected.

In a 50% Ni—50% Al alloy catalyst used in methanation of natural gas, AES experiments have shown [89] that deactivation resulted from coverage of the surface by a small amount of S. A scanning Auger system was used to study the actual sites of S enrichment at the surface. The Auger images (Fig. 40) of Ni, S, Al, and O clearly show that Ni and S are present in the same localized regions. The spectra of Fig. 41 taken from areas of high and low sulfur content also support this observation. These data suggest that S was either preferentially adsorbed or segregated to Ni-rich surfaces. Depth composition profiles obtained from the surface (Fig. 42) of the spent catalyst demonstrate that the S is localized within a depth of about 30 Å on the Ni surfaces.

D. SEMICONDUCTOR TECHNOLOGY

Semiconductor technology was one of the first areas for application of AES to failure analysis and is now one in which AES plays a critical role in process development. In many respects, semiconductor devices are ideal specimens for the AES technique. Thin film structures on these devices are well-defined in thickness and lateral extent. The depth profiling technique can be used to elucidate surface and interfacial contamination, as well as inter-diffusion with excellent in-depth resolution. Scanning Auger microscopy can be used to localize the area of examination on a bonding pad, an oxide window, a resistor, or any other feature of interest.

1. Failure analysis

Failure of a device can often be traced to impurity poisoning of a surface during a particular process step. For example, impurities such as hydrocarbons and alkalis left on the surface after cleaning can lead to poor thin film adherence or poisoning of the device. Incomplete removal of a photoresist also can cause poor adherence between metallic thin films. Similarly, incomplete removal of the passivation layer over a metallic contact pad can produce a bond with poor mechanical strength and/or a high resistance contact.

Thermal compression bond failure on gold-coated lead frames or bonding pads is most often caused by the formation of impurity metal oxides at the gold surface. These metal oxides usually form in the thermal annealing process step necessary for good thin film adherence. All active metallic elements (such as Fe, Ni, Cr, Ag, Cu, etc.) within the gold layer are potential bond inhibitors. Similarly, metallic components may diffuse to the surface from the underlying layers and form oxides at the gold surface. Usually, these oxide layers are less than a few hundred angstroms in thickness and thus a surface-sensitive technique is required for positive identification.

The role of AES in detecting and identifying the impurities detrimental to bonding is exemplified in a recent publication by Wagner et al. [149]. A thick gold film on an alumina substrate was examined and found to have a high surface concentration of copper oxide, even though the manufacturers had specified 99% purity. Wagner also showed that ultrasonic bonding of aluminum wires to electroplated gold failed "pull" tests because of impurities (C, Ca, Ag, Cd, and O) at the surface following thermal treatment of the device. It is important to point out that these impurities would not affect bond strength if they were uniformly distributed throughout the gold layer.

Figure 43 shows Auger spectra of gold-plated lead frames which had demonstrated both good and poor mechanical bonding strengths [150]. As indicated, the poor bonding characteristics were associated with the presence of thallium at the surface. Depth profile analysis demonstrated that the thallium was segregated within a few atomic layers of the surface. A com-

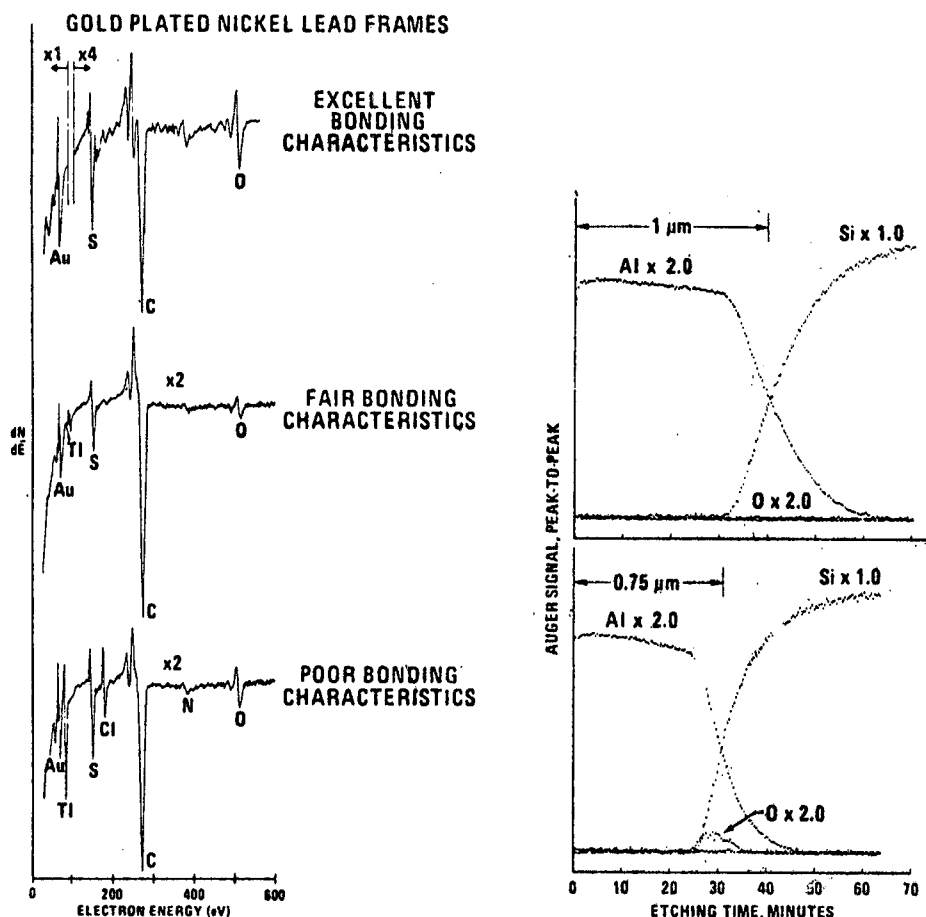


Fig. 43. Correlation of thallium Auger signal amplitude with bonding characteristics on gold-plated lead frames.

Fig. 44. Depth—composition profiles of Al—Si contacts; low resistance contact (top), and high resistance contact (bottom).

plete study showed that the mechanical bonding strength could be predicted by the amount (relative peak-to-peak height) of thallium present on the surface. After the cause of failure was determined, it was then possible to trace the source of thallium to the gold plating solution.

The formation of oxides at the surface or an interface can cause electrical as well as mechanical failure. Using AES, Morabito [151] has shown that zinc oxide at the surface of a gold-plated spring contact was the direct cause of high resistivity in the contact area. Further, the oxide layer was at most a few hundred angstroms thick and localized in the contact area.

T6

Depth—composition profiles of aluminum/silicon-alloyed contacts with good and poor electrical resistance characteristics are shown in Fig. 44. The depth profile demonstrates that at least a partial oxide layer existed at the aluminum/silicon interface in the poor contact area and very likely increased

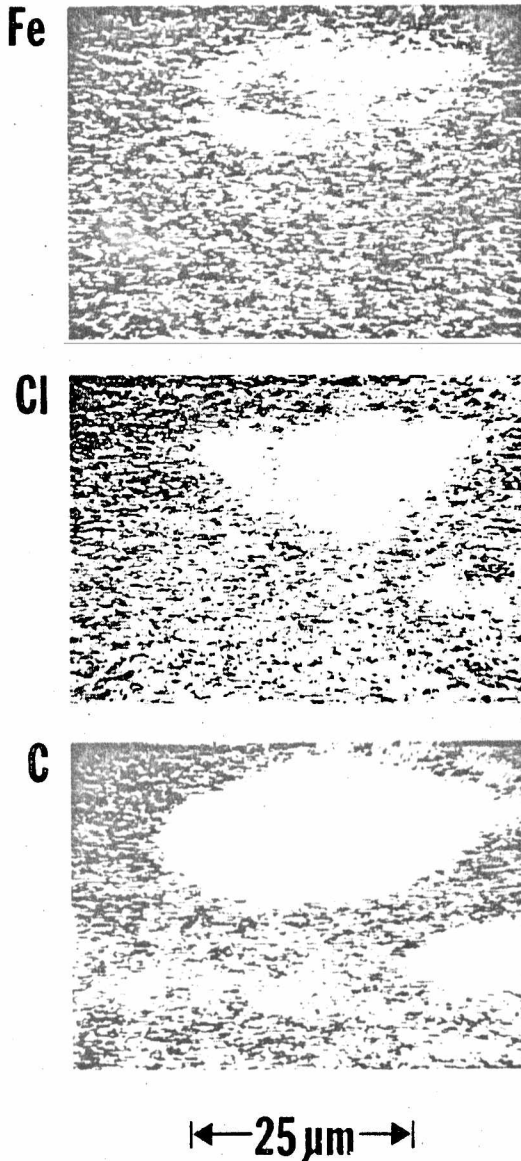


Fig. 45. Elemental analysis of particles on gold-plated lead frame showing Auger images for Fe, Cl, and C. After MacDonald [43].

37

the contact resistance. The source of contamination was traced to the accumulation of impurities from the vacuum environment on the silicon surface prior to aluminum evaporation.

An example of a scanning AES application in evaluating a bonding failure

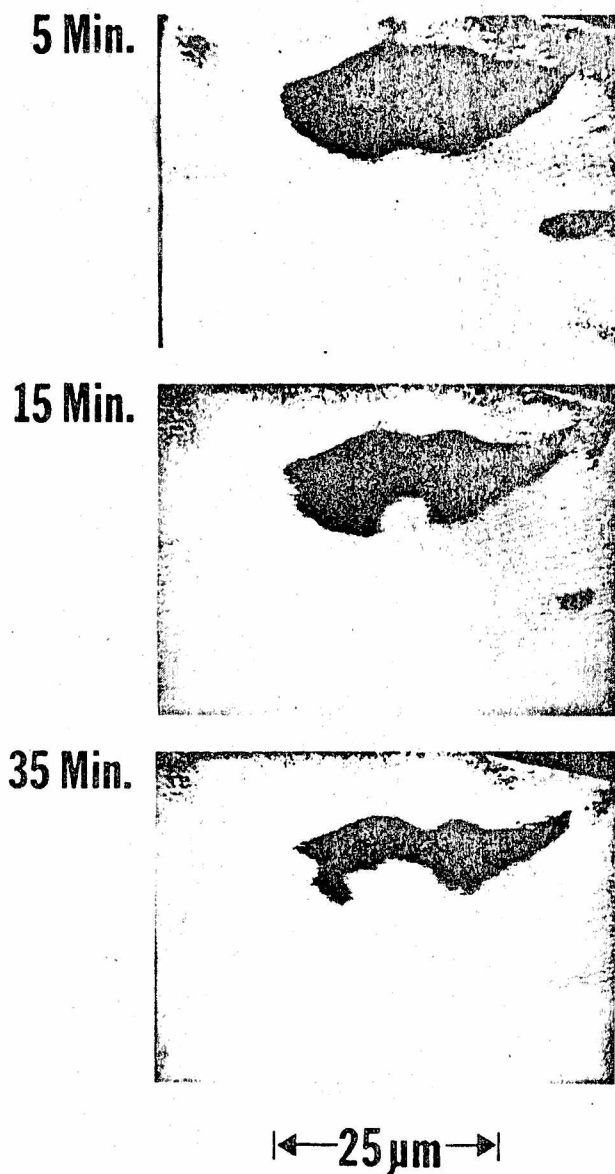


Fig. 46. Three-dimensional analysis of particles on a gold-plated lead frame. Au Auger images as a function of sputter etch time. After MacDonald [43].

is given in Fig. 45 which is a two-dimensional compositional map of a gold-plated beam lead frame [43]. As indicated, AES analysis revealed localized iron, chlorine, and carbon impurities at the surface. Three-dimensional analysis of the impurity particle is demonstrated in Fig. 46. Gold images taken after sputtering 5, 15, and 35 min ($\sim 700 \text{ \AA}$) define the particle geometry as a function of depth. The ability to identify particulate contamination and measure the thickness of the particle led to the particular process step in which the contamination was introduced.

2. Process evaluation

AES surface analysis and depth composition profiling provide a useful means for evaluating and developing specific device processes. The surface or interface composition may be characterized before and after a cleaning process. By direct comparison, the inter-diffusion characteristics important in achieving specific mechanical, electrical, and optical thin film properties can be characterized.

It has been shown [149] that contaminants such as Cl, F, and S left after final cleaning of MOS/LSI circuits can affect the operation of the final device. AES characterization of the surface was instrumental in the development of improved cleaning processes. From a depth-composition profile it was possible to show that the discoloration of a thin film metallization system used for terminating a tantalum nitride resistor was caused by copper and sulfur contamination of a palladium overlayer [151]. Since the profile showed that the copper and sulfur were removed from the palladium at similar rates during sputtering, it was concluded that copper and sulfur were chemically associated.

An example of depth-composition profile analysis of a thin film metallization system is shown in Fig. 47. This particular composite is made up of three separate metallic layers bonded to alumina. (Thin layers of chromium and titanium typically are used to promote gold adherence to ceramic surfaces.) The profile itself suggests what parameters are important and can be used as a visual aid for discussing the different kinds of evaluation that may be performed. For example, the test may be focused on the inter-diffusion of the chromium and titanium layers as a function of annealing temperature. In this case, several test specimens or even the actual package devices could be treated at different temperatures. The depth-composition profiles could then be compared for the penetration of chromium throughout the gold film or into the ceramic substrate. In another approach, the profile could be used as a quality control monitor of chromium film thicknesses for different production runs. Combining the test to include both thickness and Cr-Ti inter-diffusion could reveal preferred film thicknesses as a function of annealing temperature, thereby empirically arriving at an improved metallization system. Finally, the test could also be aimed at determining the maxi-

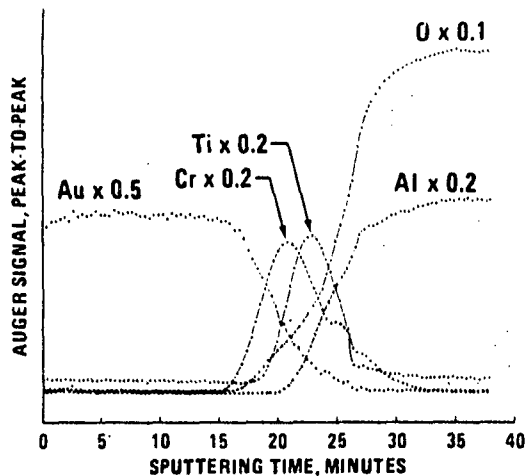


Fig. 47. Depth-composition profile of Au, Cr, and Ti metallization system on Al_2O_3 .

mum allowable contamination at the titanium-alumina interface. Correlating adhesion tests and/or contact resistance measurements with depth composition profiles of carbon and oxygen, for example, could serve as a quality control of ceramic cleaning procedures and predeposition environment.

Finn et al. [152] have shown that AES/X-ray diffraction studies can be used to study alloying and chemical reaction occurring at Pt/GaAs interfaces after device thermal treatment in the temperature range of 300–400°C. Their study showed that the inter-diffusion of Pt and GaAs was directly observable from AES depth profiles by comparing treated and untreated specimens. A depth profile of a sample treated at 400°C for one hour showed that Ga and As were present on the Pt surface and that Pt had diffused into the GaAs substrate. X-ray diffraction data showed that compounds of PtAs_2 , Pt_3Ga , and PtGa were formed after heat treatment.

In a depth-composition study of ohmic contacts, Robinson and Jarvis [153] examined nickel and gold-germanium thin films on GaAs substrates before and after alloying. Composition profiles from the surface showed that before annealing the 150 Å nickel and 340 Å gold-germanium films were well-defined on the GaAs substrate. Upon annealing (460°C for 40 sec), however, it was determined from the profiles that Ga, As, Au, and Ge had diffused to the nickel surface. The AES results, as well as scanning electron micrographs, indicated that the nickel overlayer was not a continuous and uniform coating after annealing. Additional process information about heated GaAs was gained from results which showed that differential out-diffusion of gallium depends on the crystalline orientation of the GaAs.

In a later study of ohmic contacts, Robinson [154] applied the same techniques and method to investigate the formation of palladium silicide on

single crystal silicon. In a comparison of X-ray diffraction data of a thick Pd_2Si layer and the low-energy silicon Auger spectrum, it was possible to associate distinguishable electron peaks with free silicon and silicon in the compound form of Pd_2Si . In total, the results indicated silicon enrichment at the surface and diffusion-limited formation of the Pd_2Si layer.

Acknowledgments

The authors express their appreciation to Drs. G.E. Riach, R.E. Weber, G.K. Wehner, R.L. Gerlach, and N.C. MacDonald for critical reading of the manuscript.

References

- 1 (a) P.W. Palmberg, in G.A. Somorjai (Ed.), *The Structure and Chemistry of Solid Surfaces*, Wiley, New York, 1969, p. 29-1. (b) D.F. Stein, R.E. Weber and P.W. Palmberg, *J. Metals*, 23 (1971) 39. (c) C.C. Chang, *Surface Sci.*, 25 (1971) 53. (d) P.W. Palmberg, in D.A. Shirley (Ed.), *Electron Spectroscopy*, North Holland, Amsterdam, 1972, p. 835. (e) R.E. Weber, *J. Cryst. Growth*, 17 (1972) 342. (f) T.E. Gallon and J.A.D. Matthew, *Rev. Phys. Technol.*, III 1 (1972) 31. (g) J.C. Riviere, *Contemp. Phys.*, 14 (1973) 513. (h) C.C. Chang, in P.F. Kane and G.B. Larrabee (Eds.), *Characterization of Solid Surfaces*, Plenum Press, New York, 1974, p. 509.
- 2 P. Auger, *J. Phys. Radium*, 6 (1925) 205.
- 3 J.J. Lander, *Phys. Rev.*, 91 (1953) 1382.
- 4 L.A. Harris, *J. Appl. Phys.*, 39 (1968) 1419.
- 5 R.E. Weber and W.T. Peria, *J. Appl. Phys.*, 38 (1967) 4355.
- 6 H. Hafner, J. Arol Simpson and C.E. Kuyatt, *Rev. Sci. Instrum.*, 39 (1968) 33; V.V. Zashkvara, M.I. Korsuuskii and O.S. Kosmackei, *Zh. Tekh. Fiz.*, 36 (1966) 132; H.Z. Sar-el, *Rev. Sci. Instrum.*, 38 (1967) 1210; E. Blauth, *Z. Phys.*, 160 (1957) 228.
- 7 P.W. Palmberg, G.K. Bohn and J.C. Tracy, *Appl. Phys. Lett.* 15 (1969) 254.
- 8 P.W. Palmberg, *J. Vac. Sci. Technol.*, 9 (1972) 160.
- 9 N.C. MacDonald, *Appl. Phys. Lett.*, 16 (1970) 76.
- 10 H.E. Bishop and J.C. Riviere, *J. Appl. Phys.*, 40 (1969) 1740.
- 11 J.F. Hannequin and P. Viaris de Lesegno, *Surface Sci.*, 42 (1974) 50; T.W. Haas, R.W. Springer, M.P. Hooker and J.T. Grant, *Phys. Lett. A*, 47 (1974) 317; R.G. Musket and W. Bauer, *Thin Solid Films*, 19 (1973) 69.
- 12 M.F. Chung and L.H. Jenkins, *Surface Sci.*, 22 (1970) 479.
- 13 W.N. Assad and E.H.S. Burhop, *Proc. Phys. Soc.*, 71 (1958) 369.
- 14 W.N. Assad, *Proc. Roy. Soc. Ser. A*, 249 (1959) 559; W.N. Assad, *Nucl. Phys.*, 44 (1963) 399, 415; 63 (1965) 337; 66 (1965) 494.
- 15 I. Bergstrom and C. Nordling, in K. Siegbahn (Ed.), *Alpha-, Beta-, and Gamma-Ray Spectroscopy*, Vol. II, North Holland, Amsterdam, 1965.
- 16 D.A. Shirley, *Phys. Rev. A*, 7 (1973) 1520.
- 17 P.W. Palmberg, G.E. Riach, R.E. Weber and N.C. MacDonald, *Handbook of Auger Electron Spectroscopy*, Physical Electronics Industries, Edina, 1972.
- 18 J.J. Vrakking and F. Meyer, *Surface Sci.*, 47 (1975) 50.

- 19 A.R. DuCharme and R.L. Gerlach, *J. Vac. Sci. Technol.*, 10 (1973) 188.
- 20 E.H.S. Burhop, *Proc. Cambridge Phil. Soc.*, 36 (1940) 43; A.M. Arthurs and B.L. Moiseiwitsch, *Proc. Roy. Soc. Ser. A*, 247 (1958) 550.
- 21 M.R.H. Rudge and S.B. Schwartz, *Proc. Phys. Soc.*, 88 (1966) 563.
- 22 R.L. Gerlach and A.R. DuCharme, *Surface Sci.*, 32 (1972) 329.
- 23 H.E. Bishop, *Brit. J. Appl. Phys.*, 18 (1967) 703.
- 24 K. Gato, K. Ishikawa, T. Koshikawa and R. Shimizu, *Appl. Phys. Lett.*, 24 (1974) 358.
- 25 T.E. Gallon, *J. Phys.*, 5 (1972) 822.
- 26 F.J. Szalkowski and G.A. Somorjai, *J. Chem. Phys.*, 56 (1972) 6097.
- 27 C.D. Wagner and P. Biloen, *Surface Sci.*, 35 (1972) 82.
- 28 C.D. Wagner, American Chemical Society Meeting, Houston, Texas, Nov. 1974.
- 29 S.P. Kowalczyk, R.A. Pollak, L. Ley and D.A. Shirley, *Phys. Rev. B*, 8 (1973) 2387.
- 30 T.W. Haas, J.T. Grant and G.J. Dooley, in F. Ricca (Ed.), *Adsorption-Desorption Phenomena*, Academic Press, New York, 1972, p. 359.
- 31 J.P. Coad, *Phys. Lett. A*, 35 (1971) 185.
- 32 R.J. Fortner and R.G. Musket, *Surface Sci.*, 28 (1971) 339.
- 33 T.W. Haas and J.T. Grant, *Phys. Lett. A*, 30 (1969) 272.
- 34 G.G. Amelio, *Surface Sci.*, 22 (1970) 301.
- 35 H.D. Hagstrum, *Phys. Rev.*, 150 (1966) 495.
- 36 G.E. Becker and H.S. Hagstrum, *Surface Sci.*, 30 (1972) 125.
- 37 E.N. Sickafus, *J. Vac. Sci. Technol.*, 11 (1974) 308.
- 38 D. Pines, *Elementary Excitations in Solids*, Benjamin, New York, 1964.
- 39 W.M. Mularie and W.T. Peria, *Surface Sci.*, 26 (1971) 125.
- 40 K.K. Spangenberg, *Vacuum Tubes*, McGraw-Hill, New York, 1948.
- 41 N.C. MacDonald and J.R. Waldrop, *Appl. Phys. Lett.*, 19 (1971) 315.
- 42 D.J. Pocker and T.W. Haas, *J. Vac. Sci. Technol.*, 12 (1975) 370.
- 43 N.C. MacDonald, in D. Beaman and B. Siegel (Eds.), *Electron Microscopy: Physical Aspects*, Wiley, New York, 1974.
- 44 P.W. Palmberg, *Anal. Chem.*, 45 (1973) 549A.
- 45 P.H. Holloway, to be published.
- 46 R.E. Weber and A.L. Johnson, *J. Appl. Phys.*, 40 (1969) 314.
- 47 M.L. Tarnag and G.K. Wehner, *J. Appl. Phys.*, 44 (1973) 1534.
- 48 L.E. Davis and A. Joshi, to be published.
- 49 S. Thomas, *J. Appl. Phys.*, 45 (1974) 161; P.W. Palmberg and T.N. Rhodin, *J. Phys. Chem. Solids*, 29 (1968) 1917.
- 50 J.T. Grant, T.W. Haas and J.E. Houston, *J. Vac. Sci. Technol.*, 11 (1974) 227; J.E. Houston, *Rev. Sci. Instrum.*, 45 (1974) 897; J.T. Grant, M.P. Hooker and T.W. Haas, *Surface Sci.*, 46 (1974) 672.
- 51 R.L. Gerlach and R. Hedtke, Physical Electronics Industries, Inc., Eden Prairie, Minnesota, private communication.
- 52 W. Farber and P. Braun, *Vak. Tech.*, to be published.
- 53 G.K. Wehner, this volume, Chap. 1.
- 54 P.W. Palmberg, *Surface Sci.*, 25 (1971) 598.
- 55 J.V. Florio and W.D. Robertson, *Surface Sci.*, 18 (1969) 398.
- 56 R.G. Musket and J. Ferrante, *J. Vac. Sci. Technol.*, 7 (1970) 14.
- 57 H.H. Farrell, H.S. Isaacs and M. Strongin, *Surface Sci.*, 38 (1973) 31.
- 58 A. Joshi and M. Strongin, *Scr. Met.*, 8 (1974) 413.
- 59 G. Ertl and J. Koch, in F. Ricca (Ed.), *Adsorption-Desorption Phenomena*, Academic Press, New York, 1972, p. 345.
- 60 R.M. Lambert, J.W. Linnett and J.A. Schwartz, in F. Ricca (Ed.), *Adsorption-Desorption Phenomena*, Academic Press, New York, 1972, p. 381.

- 61 S. Thomas and T.W. Haas, *J. Vac. Sci. Technol.*, 9 (1972) 840.
- 62 E. Bauer, H. Poppa, G. Todd and F. Bonczek, *J. Appl. Phys.*, 45 (1974) 5164.
- 63 L.E. Davis, L.L. Levenson and J.J. Melles, *J. Cryst. Growth*, 17 (1972) 354.
- 64 J.C. Tracy and P.W. Palmberg, *Surface Sci.*, 14 (1969) 274.
- 65 B.W. Byrum, *Rev. Sci. Instrum.*, 45 (1974) 707.
- 66 L.A. Harris, *J. Appl. Phys.*, 39 (1968) 1428.
- 67 L.H. Jenkins and M.F. Chung, *Surface Sci.*, 24 (1971) 125.
- 68 N.J. Taylor, *J. Vac. Sci. Technol.*, 6 (1969) 241.
- 69 M. LaGues and J.L. Domange, *Surface Sci.*, 47 (1975) 77.
- 70 A. Joshi, to be published.
- 71 C.C. Chang and G. Quintana, *J. Electron Spectrosc. Relat. Phenom.*, 2 (1973) 363.
- 72 S. Danyluk, G.E. McGuire, K.M. Koliwad and M.G. Yang, *Thin Solid Films*, 25 (1975) 483.
- 73 H.S. Wildman, J.K. Howard and P.S. Ho, *J. Vac. Sci. Technol.*, 12 (1975) 75.
- 74 R.T. Whipple, *Phil. Mag.*, 45 (1954) 1225.
- 75 H.P. Bonzel and H.B. Aaron, *Scr. Met.*, 5 (1971) 1057.
- 76 J. Ferrante, *Scr. Met.*, 5 (1971) 1129.
- 77 J. Ferrante, *Acta Met.*, 19 (1971) 743.
- 78 J.C. Shelton, H.R. Patil and J.M. Blakely, *Surface Sci.*, 43 (1974) 493.
- 79 L.C. Isett and M. Blakely, *J. Vac. Sci. Technol.*, 12 (1975) 237.
- 80 K. Kunimori, T. Kawai, T. Kondow, T. Onishi and K. Tamaru, *Surface Sci.*, 46 (1974) 567.
- 81 J.J. Bellina and B.B. Rath, AIME Meeting, Pittsburgh, Pennsylvania, May 20, 1974.
- 82 D. McLean, *Grain Boundaries in Metals*, Oxford University Press, London, 1957.
- 83 J.M. Blakely, J.S. Kim and H.C. Potter, *J. Appl. Phys.*, 41 (1970) 2693.
- 84 J.P. Coad and J.C. Riviere, *Surface Sci.*, 25 (1971) 609.
- 85 E.N. Sickafus, *Surface Sci.*, 19 (1970) 181.
- 86 P.H. Holloway and J.B. Hudson, *Surface Sci.*, 33 (1972) 56.
- 87 H.E. Bishop and J.C. Riviere, *Acta Met.*, 18 (1970) 813.
- 88 G.J. Dooley, III, *J. Vac. Sci. Technol.*, 9 (1972) 145.
- 89 Analytical Services Laboratory, Physical Electronics Industries, Inc., Eden Prairie, Minnesota.
- 90 R.W. Thompson, D.T. Quinto and B.S. Levy, Inland Steel Co., East Chicago, private communication.
- 91 A. Joshi, M.N. Varma and M. Strongin, *Met. Trans.*, 5 (1974) 861.
- 92 E.M. Sparrow, J.W. Ramsey, G.K. Wehner, and co-workers, Rep. No. NSF/RANN/SE/GI-34871/PR/74/2, 1974.
- 93 J. Ferrante, NASA Tech. Note, TND 7479, 1973.
- 94 N.J. Chow, J.M. Eldridge, R. Hammer and D. Dong, IBM, T.J. Watson Research Center, private communication.
- 95 C.T.H. Stoddart and E.D. Hondros, *Nat. Phys. Sci.*, 237 (1972) 90.
- 96 G. Betz, G.K. Wehner, L.E. Toth and A. Joshi, *J. Appl. Phys.*, 45 (1974) 5312.
- 97 D.H. Buckley, NASA Tech. Note, TND 5756, 1970.
- 98 D.H. Buckley, NASA Tech. Note, TND 5322, 1970.
- 99 D.H. Buckley, *Int. J. Nondestr. Test.*, 2 (1970) 171.
- 100 J. Ferrante and D.H. Buckley, NASA Tech. Note, TND 6095, 1970.
- 101 D.H. Buckley, *J. Adhesion*, 1 (1969) 264.
- 102 N.A. Gjosten and N.G. Chavka, *J. Test. Eval.*, 1 (1973) 183.
- 103 R.C. Sundahl, *J. Vac. Sci. Technol.*, 9 (1972) 181.
- 104 J.R. Waldrop and H.L. Marcus, *J. Test. Eval.*, 3 (1973) 194.
- 105 H.L. Marcus, J.R. Waldrop, F.T. Schuler and E.F.C. Cain, *J. Electrochem. Soc.*, 119 (1972) 1348.

- 106 K.F. Watterson and G.W. Simmons, Paper presented before the GI Committee of ASTM, Williamsburg, Virginia, December 6-8, 1972.
- 107 H.L. Marcus and P.W. Palmberg, Trans. AIME, 245 (1969) 1164.
- 108 D.F. Stein, A. Joshi and R.P. LaForce, ASM Trans. Quart., 62 (1969) 776.
- 109 P.W. Palmberg and H.L. Marcus, ASM Trans. Quart., 62 (1969) 1016.
- 110 A. Joshi and D.F. Stein, ASTM-STP, 499, 1972, p. 59.
- 111 H.L. Marcus, L.H. Hackett and P.W. Palmberg, ASTM-STP, 499, 1972, p. 90.
- 112 R. Viswanathan, Met. Trans., 2 (1971) 809.
- 113 H.G. Suzuki and M. Ono, Presented at the Japan Institute of Metals, Kanazawa, October 1971.
- 114 A. Joshi, Scr. Met., 9 (1975) 251.
- 115 R. Viswanathan and T.P. Sherlock, Met. Trans., 3 (1972) 459.
- 116 B.J. Schulz and C.J. McMahon, Jr., ASTM-STP, 499, 1972, p. 104.
- 117 P.V. Ramasubramanian and D.F. Stein, Met. Trans., 3 (1972) 2939.
- 118 J.R. Rellick, C.J. McMahon, Jr., H.L. Marcus and P.W. Palmberg, Met. Trans., 2 (1971) 1492.
- 119 E.D. Hondros and M.P. Seah, Scr. Met., 6 (1972) 1007.
- 120 A. Joshi and D.F. Stein, Met. Trans., 1 (1970) 2543.
- 121 A. Joshi and D.F. Stein, J. Inst. Metals, 99 (1971) 178.
- 122 B.D. Powell and H. Mykura, Acta Met., 21 (1973) 1151.
- 123 H.L. Marcus and N.E. Paton, Met. Trans., 5 (1974) 2135.
- 124 R.M. Latinision and H. Oppenhauser, Met. Trans., 5 (1974) 483.
- 125 W.C. Johnson, J.E. Doherty, B.H. Kear and A.F. Giamei, Scr. Met., 8 (1974) 971.
- 126 W.C. Johnson and D.F. Stein, Met. Trans., 5 (1974) 549.
- 127 A. Joshi, J. Wildermuth and D.F. Stein, Int. J. Powder Met., 11 (1975) 137.
- 128 G. Chaudron, EURAEC-976, Quart. Rept. 6, October-December, 1963.
- 129 J.S. Armijo, Corrosion, 24 (1968) 24.
- 130 M.A. Streicher, J. Electrochem. Soc., 106 (1959) 161; H. Coriou, J. Hurl and G. Plante, Electrochim. Acta, 5 (1961) 105.
- 131 A. Joshi and D.F. Stein, Corrosion, 28 (1972) 321.
- 132 J.L. Walter, Trans. AIME, 239 (1967) 272.
- 133 D.M. Moon and R.C. Koo, Met. Trans., 2 (1971) 2115.
- 134 H.G. Sell, D.F. Stein, R. Stickler, A. Joshi and E. Berkey, J. Inst. Metals, 100 (1972) 275.
- 135 P.J. Jorgenson and J.H. Westbrook, J. Amer. Ceram. Soc., 47 (1964) 332.
- 136 H.L. Marcus and M.E. Fine, J. Amer. Ceram. Soc., 55 (1972) 568.
- 137 W.C. Johnson, D.F. Stein and R.W. Rice, Proc. Bolton Landing Conf., August, 1974.
- 138 D.F. Stein, J. Vac. Sci. Technol., 12 (1975) 268.
- 139 L.D. Schmidt and D. Luss, J. Catal., 22 (1971) 269.
- 140 J.J. McCarroll, T. Edmonds and R.C. Pikehly, Nature (London), 223 (1969) 1260.
- 141 G.A. Somorjai, J. Catal., 23 (1972) 453.
- 142 P.W. Palmberg, Proc. Int. Mater. Conf., 4th, Univ. Calif., Berkeley, June, 1968, 1969, p. 29-1.
- 143 G.A. Somorjai, Catal. Rev., 7 (1972) 87.
- 144 T.P. Pignet, L.D. Schmidt and N.L. Jarvis, J. Catal., 31 (1973) 145.
- 145 H.P. Bonzel and R. Ku, J. Vac. Sci. Technol., 9 (1972) 663.
- 146 M.M. Bhasin, J. Catal., 34 (1974) 356.
- 147 M.M. Bhasin, J. Catal., (1975) to be published.
- 148 F.L. Williams and M. Boudart, J. Catal., 30 (1973) 438.
- 149 N.K. Wagner, A.R. Hart and D.W. McQuitty, Government Microelectronics Conf., Boulder, Colorado, June, 1974.
- 150 N.C. MacDonald and G.E. Riach, Electron. Packaging Prod., 13 (1973) 50.

64

222

- 151 J.M. Morabito, Thin Solid Films, 19 (1973) 21.
- 152 M.C. Finn, H.Y.P. Hong, W.T. Lindley, R.A. Murphy, E.B. Owens and A.J. Strauss, presented at the 15th Electronics Materials Conference, Las Vegas, August 1973.
- 153 G.Y. Robinson and N.L. Jarvis, Appl. Phys. Lett., 21 (1972) 507..
- 154 G.Y. Robinson, Appl. Phys. Lett., 25 (1974) 158.

AN AES ANALYSIS OF OXIDE FILMS ON IRON

M. SEO*, J.B. LUMSDEN and R.W. STAEBLE

*Department of Metallurgical Engineering, The Ohio State University,
 Columbus, Ohio 43210, U.S.A.*

Received 30 September 1974; revised manuscript received 12 February 1975

The Auger spectra of the iron oxides have been investigated. The relative amplitudes of the Auger lines from oxygen and iron have been determined for FeO, Fe₃O₄, α -Fe₂O₃, γ -Fe₂O₃, and FeOOH. It was found that the amplitude ratio $s_{\text{O}}/s_{\text{Fe}}$ of the O (510 eV)/Fe (703 eV) lines was, to a first approximation, directly proportional to the ratio of oxygen and iron in the chemical formula. Structure was observed in the spectra resulting from the Fe M_{2,3} VV transition. Different spectra were observed for Fe, FeO, Fe₃O₄, Fe₂O₃, and FeOOH; however, the same spectra were obtained for α - and γ -Fe₂O₃.

1. Introduction

There have been numerous investigations of the protective oxide film formed on iron exposed to both gaseous environments [1-3] and to aqueous solutions [3-6]. It has been well established that the high temperature oxidation of iron (up to approximately 570°C) results in the formation of a two layer film consisting of Fe₃O₄ and Fe₂O₃; at higher temperatures a three layer film of FeO, Fe₃O₄, and Fe₂O₃ is formed.

The oxide film formed at low temperatures is less well characterized with several different structures having been observed in diffraction patterns from the films [7-10]. Saleman and Pattinson [11] have noted changes in the Auger valence band spectra of iron when a clean surface is exposed to oxygen at room temperature; they give no interpretation. Seo, Lumsden, and Staehle [12] have observed similar changes in spectra from the passive film; they suggest that one type of structure in the spectra can be attributed to Fe₂O₃ and a second type to Fe₃O₄. Recently Veda and Shimizu [13] have also conjectured that different low energy spectra can be attributed to Fe₂O₃ and Fe₃O₄; however, their interpretation is still unclear.

There is no general agreement on the nature of the oxide film formed on iron in aqueous solutions. Thermodynamics [14] as well as experimental results [3,15,16] can be used to support either a two phase or a single phase model; the interpretation depends upon the investigator.

In the work reported herein AES has been used to investigate the oxide films

Present address: Electrochemistry Laboratory, Faculty of Engineering, Hokkaido University, Sapporo, Japan.

formed on iron in both gaseous and aqueous environments. The profiling technique [17] has been utilized to define the various regions of stoichiometry in the films, and the changes in the valence band spectra of iron have been further clarified.

2. Experimental

The iron specimens used in this study were vacuum melted electrolytic rods. 5.1 mm in diameter and 1.0 cm in length having a purity of 99.96%. They were annealed in an argon atmosphere at 750 °C for 3 h and then electropolished in a 20:1 glacial acetic acid and 70% perchloric acid solution.

Magnetite, Fe_3O_4 , haematite, $\alpha\text{-Fe}_2\text{O}_3$, and wustite, Fe_xO ($0.84 < x < 0.95$) were formed by gaseous oxidation. This was performed in a continuous flow system with the specimen contained in a quartz tube. The temperature was maintained within $\pm 2^\circ\text{C}$.

Lepidocrocite, $\gamma\text{-FeOOH}$, was prepared by anodic deposition. The film was deposited on Pt at 300 mV (SCE) in a 0.15 N $(\text{NH}_4)_2\text{SO}_4$ solution containing ferrous ions [18]. Lepidocrocite was converted into $\gamma\text{-Fe}_2\text{O}_3$ by exposure to an oxygen flow at 25 °C for 5 days after heating in a vacuum at 180 °C for one day.

Passive films were prepared by anodic polarization of iron exposed to an equilibrium mixture of 0.15 N sodium borate 0.15 N boric acid solution (pH 8.4). This system was chosen because it has been widely studied and the electrochemistry and kinetics have been well characterized [19].

The Auger analysis was carried out in a stainless steel, ultra-high vacuum system which was pumped to a base pressure of 8×10^{-10} torr or better using sorption, ion and titanium sublimation pumps. No bakeout was used in order to avoid changing the composition of the films.

Ion bombardment was performed at a base pressure of 2×10^{-4} torr using purified argon. After the admission of argon the system was pumped with the titanium sublimation pump a minimum of five hours before measurements were made to eliminate the possibility of contamination by active residual gases. A 600 eV ion beam was used having an ion current density of approximately $1 \mu\text{A}/\text{cm}^2$. On the basis of ellipsometric film thickness measurements outside of the vacuum system, the sputtering rate was estimated to be 3–5 Å/min; therefore a value of 4 Å/min was used.

Spectra were taken using a Varian cylindrical mirror analyzer with a coaxial electron gun. Assuming an isotropic emission of electrons from a point source on a surface, the transmission of the analyzer is 1.7% of those electrons emitted into the solid angle centered at the source and bounded by the surface. A 2 kV, 50 μA electron beam was used having a diameter of approximately 50 Å. The modulation frequency was 17 kHz. The modulation amplitude used to take the valence band spectra of Fe ($M_{2,3}$ VV transition) was 0.5 V (p–p) all other spectra were taken using 2 V (p–p) modulation. The electron beam was incident normally on the sample sur-

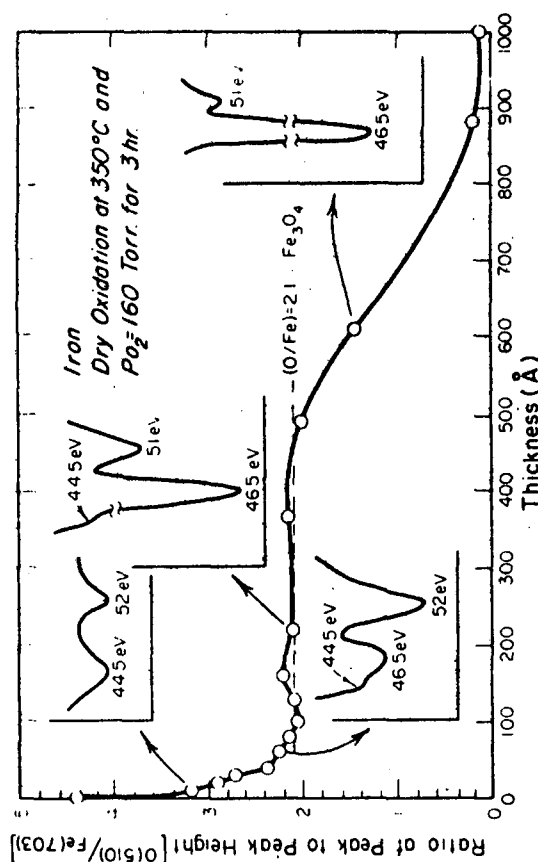


Fig. 1. The ratio of oxygen to iron peak heights versus depth and the low energy iron spectra at various depths for an Fe_3O_4 film on iron.

face which was positioned approximately 0.25 inches in front of the analyzer.

3. Results

Fig. 1 shows the peak height ratio of the oxygen 510 eV line to the iron 703 eV line for a film formed by oxidizing iron at 350 °C for 3 h in 160 torr O_2 . An X-ray analysis of the specimen indicated that the film was predominantly Fe_3O_4 but consisted of approximately 10% $\alpha\text{-Fe}_2\text{O}_3$. The plateau region where the O/Fe = 2.1 ± 0.1 has been assumed to be the region of stoichiometry. Also shown in fig. 1 are the spectra resulting from the $M_{2,3}$ VV transition at various depths. The spectra associated with this transition which were obtained from the surface and near-surface layers contain lines at 44.5 eV and 52 eV. As the plateau region is approached a third line appears at 46.5 eV. In the plateau region lines are observed at 46.5 eV and 51 eV with a shoulder remaining at 44.5 eV. Beyond the plateau the peak to peak height of the 46.5 eV line increases as the metal substrate is approached corresponding to a decrease in the 52 eV line.

The results for the oxide formed at 500 °C with an oxygen flow of one atmosphere for 10 days are shown in fig. 2. Unlike the other iron specimens this was a 10 μm iron foil mounted on platinum. An X-ray analysis indicated that the foil was totally oxidized and composed of $\alpha\text{-Fe}_2\text{O}_3$. After removal of the near-surface layers, the O(510)/Fe(703) peak height ratio was found to be 2.5 ± 0.1 . The spectra for

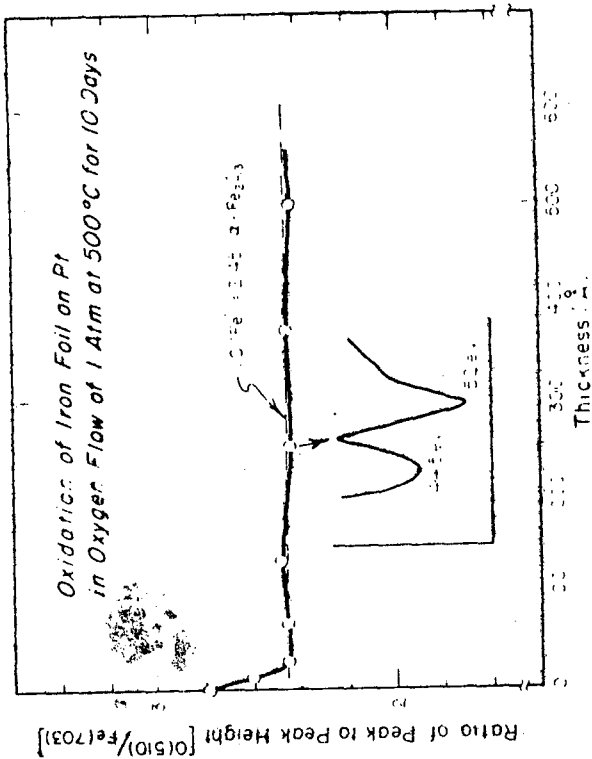


Fig. 2. Depth profile and valence band spectrum from α -Fe₂O₃.

the $M_{2,3}VV$ transition remained unchanged with depth; two lines were observed - one at 44.5 eV and one at 52.5 eV. Wustite was formed by oxidizing iron at 650 °C with an oxygen partial pressure of 240 torr for 3 hr. The Auger analysis of this oxide is given in fig. 3. There are two

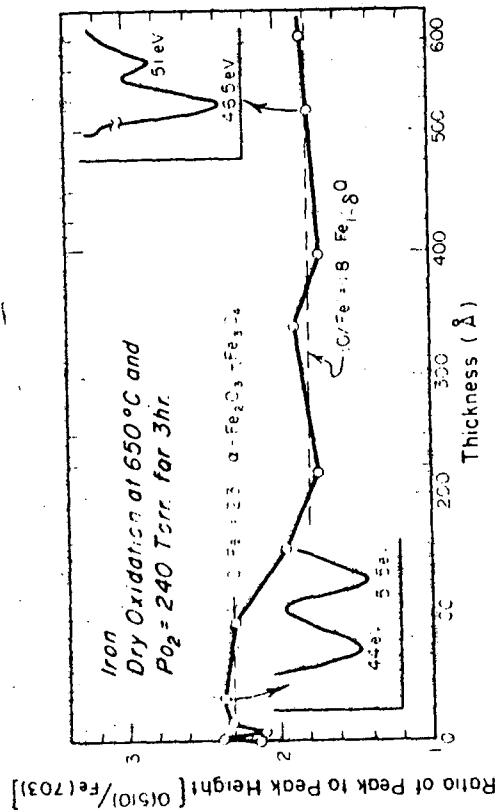


Fig. 3. The low energy iron spectra and peak height ratios from wustite.

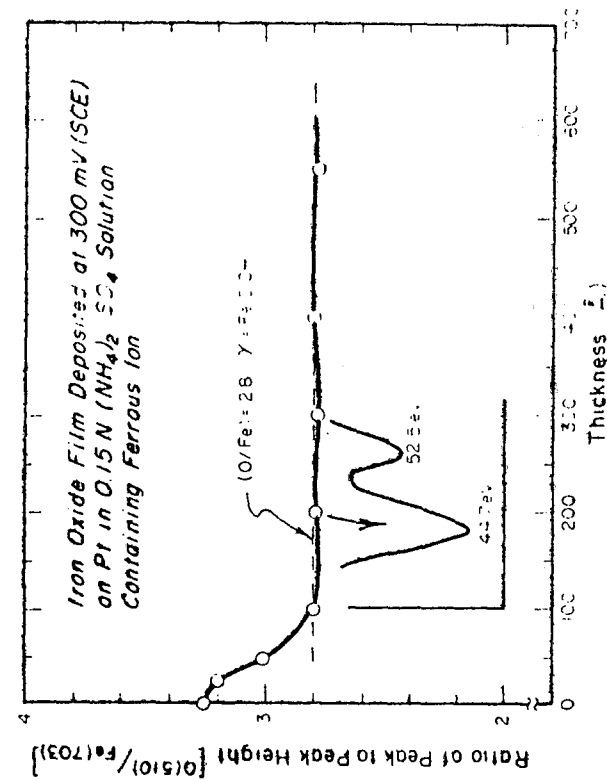


Fig. 4. Depth profile and valence band spectrum from γ -FeOOH.

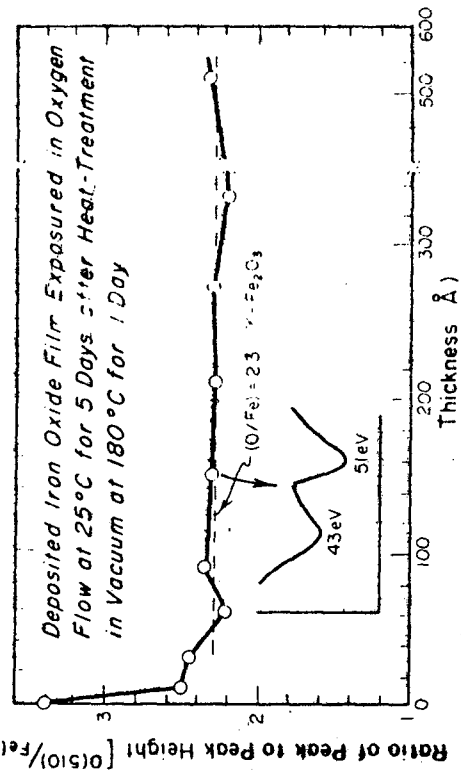


Fig. 5. Depth profile and valence band spectrum from γ -Fe₂O₃.

plateaus, one existing for approximately 100 Å with O(510)/Fe(703) = 2.3 and a second, which is FeO, with O(510)/Fe(703) = 1.8 ± 0.1. The low energy iron spectra consisted of 44.0 eV and 51.5 eV lines in the first plateau region and 46.5 eV and 51 eV lines in the second region.

The depth profiles for γ-Fe₂O₃ and lepidocrocite are shown in figs. 4 and 5 with oxygen to iron peak height ratios of 2.3 ± 0.1 and 2.8 ± 0.05 respectively. The low energy spectra for γ-Fe₂O₃ contained lines at 43.0 eV and 51.0 eV, while those for γ-FeOOH had lines at 44.7 eV and 52.5 eV. These spectra remained unchanged with depth.

All of the above oxides contained only oxygen and iron in the stoichiometric regions; however, carbon, nitrogen and sulfur were detected in small amounts on the surface and in the near-surface layers. The concentrations of these substances decreased rapidly with depth. They were no longer detectable beyond 25–50 Å beneath the surface.

To assess the possible effects of ion bombardment, residual gases, and the electron beam, the samples were left undisturbed (no ion or electron bombardment) for 12 h after the plateau region had been reached. No changes in the spectra were observed. In addition, the valence band spectra were taken at electron beam energies of 1, 2, and 3 keV; the peaks did not shift when the beam energy was changed.

Figs. 6 and 7 give the results for the passive film which was formed in the borate buffer solution. This is a nonstoichiometric oxide film (fig. 6) approximately 50 Å in thickness containing small quantities of carbon, boron, and sulfur. The changes in the low energy spectra of this film have been reported in a previous paper [12]

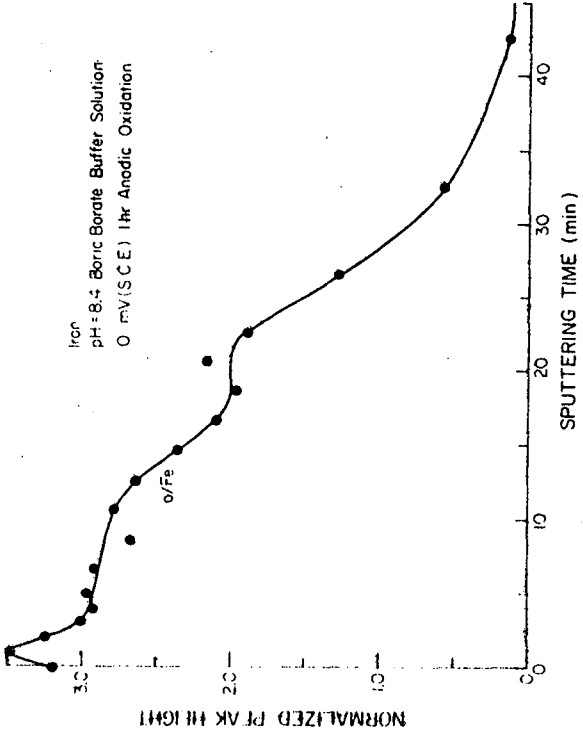


Fig. 6. Composition of the passive film formed on iron exposed to a borate buffer solution.

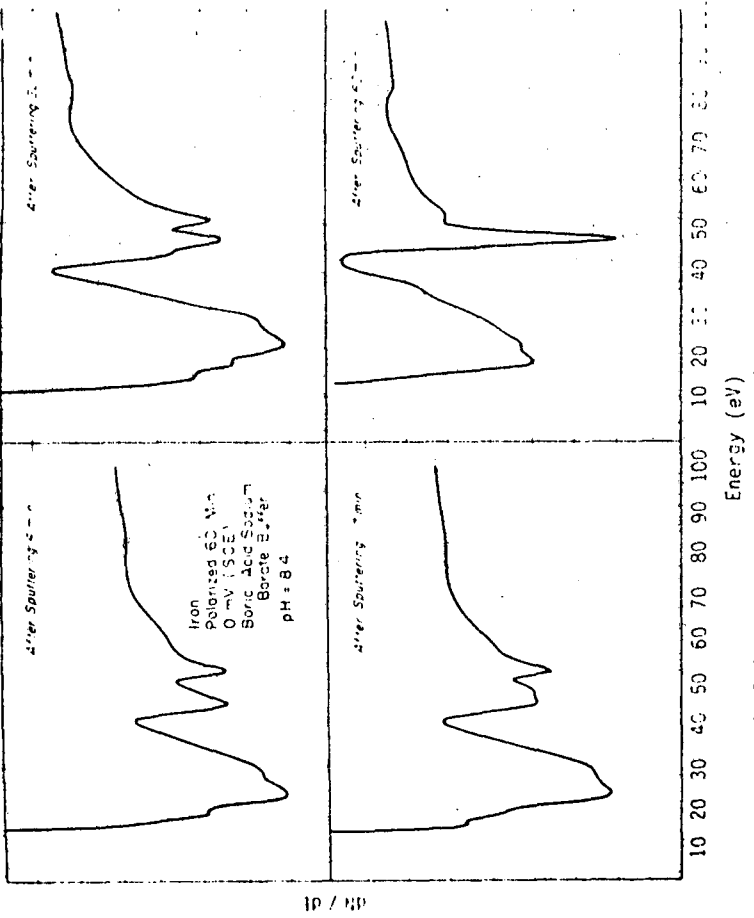


Fig. 7. Valence band spectra obtained from the passive film.

and are shown in fig. 7. The spectra from the surface and near-surface layers have peaks at 51.9 eV and 44.0 eV. A third line at 46.2 eV appears when O(510)/Fe(703) is less than 2.3. Upon further removal of the film the 44.0 eV line increases substantially in amplitude and the 51.9 eV line remains unchanged. When the O(510)/Fe(703) is approximately 2.0, the 46.2 eV peak begins to increase in intensity corresponding to a decrease in the 51.9 eV peak. This trend continues until the surface is free of oxygen at which point only the 46.2 eV line remains.

4. Discussion

Two significant conclusions follow from these results: (1) AES is quantitative with respect to the iron oxides (2) the spectra resulting from the Fe M_{2,3} VV transition can be used to identify the oxide phase.

The possibility of obtaining quantitative data from AES spectra was first discussed by Weber and Johnson [20]. They showed that the derivative of the *N(E)* curve is a linear function of the elemental concentration provided that there is no change in peak shape or shift in energy. No such changes were observed in the

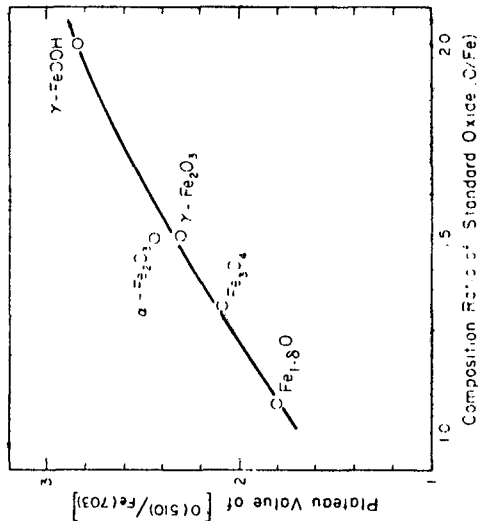


Fig. 5. The oxygen 510 eV peak height from iron oxides versus the oxygen to iron ratio in their chemical formula.

O 510 eV or the Fe 703 eV lines.

The quantitative nature of these results is summarized in fig. 8. Here the O(510)/Fe(703) peak height ratios of the plateau values, which are assumed to be the regions of stoichiometry, versus O/Fe in the chemical formula is given. To a first approximation this relationship is linear.

A summary of the chemical shifts is given in table 1. This gives the energies of the two lines observed in the valence band spectra, Fe₁ and Fe₂, of iron in its various oxides. Also given is the energy difference of the peaks, Fe₂-Fe₁, and the peak-to-peak height ratio Fe₂/Fe₁ as measured from the maximum between the two lines. These three quantities are not identical for any two oxides.

The energies of the lines in the valence band spectra are the same for α- and γ-Fe₂O₃ and FeOOH within error; the error is estimated to be ±1 eV although the reproducibility was ±0.5 eV. The distinguishing features between the Fe₂O₃ and FeOOH spectra is the amplitude of Fe₁ (~44.5 eV). The amplitude of this line is

Table 1
Energies of the Auger peaks resulting from the Fe_{2,3} VV transitions for iron oxides

Oxide	Fe ₁	Fe ₂	Fe ₂ -Fe ₁	Fe ₂ /Fe ₁ (p.p.h.)
γ-FeOOH	44.7 eV	52.5 eV	7.8 eV	0.44
α-Fe ₂ O ₃	44.5	52.0	7.5	1.67
γ-Fe ₂ O ₃	43.0	51.0	8.0	1.83
Fe ₃ O ₄	46.5	51.0	4.5	0.36
FeO	46.5	51.0	4.5	0.28

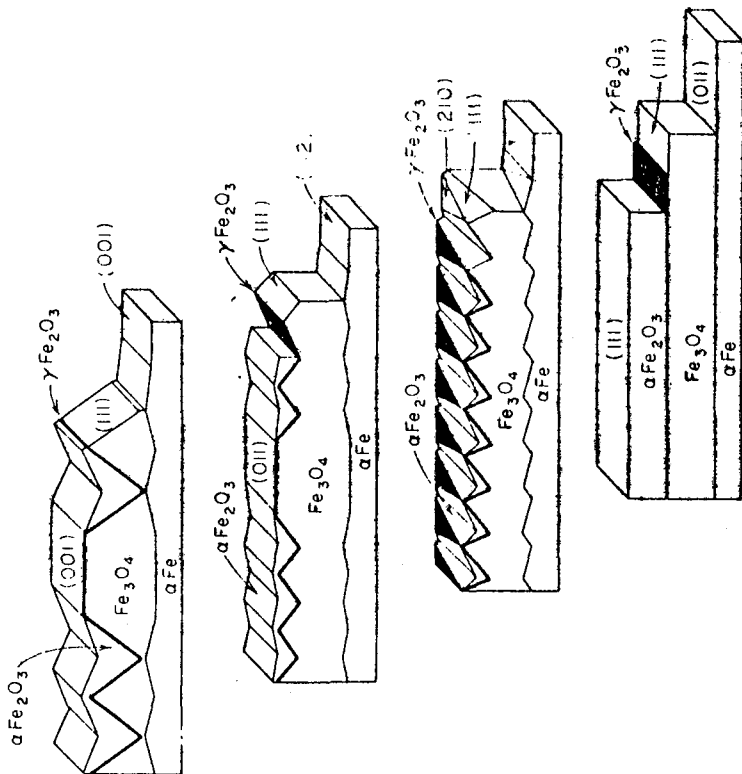


Fig. 9. Structure of the oxide film formed on iron at 350 °C (Boggs et al. [2]).

more than twice that of Fe₂ (~51.5 eV) for FeOOH. Whereas, the amplitude of Fe₁ is less than Fe₂ for Fe₂O₃. The line Fe₁ is very sensitive to oxygen content: the amplitude of this line is always greater than that of Fe₂ in spectra from the near surface layer where the O/Fe ratio is large: this is observed for all oxides formed by gaseous oxidation and those formed in aqueous solution as well.

The energies of Fe₁ (46.5 eV) and Fe₂ (51.0 eV) are the same for Fe₃O₄ and Fe_xO; both spectra also have a shoulder at 44 eV. The spectra from these two oxides differ in the amplitude ratio as indicated in table 1.

The AES results are in excellent agreement with the high temperature oxidation studies of others. Boggs et al. [2] have investigated the oxidation of iron at 350 °C. As shown in fig. 9, they found that the oxide was arranged in layers with Fe₂O₃ as the outer layer and Fe₃O₄ in contact with the metal. In general the interface between the two oxides and the oxide-metal interface were rough. Channing and Grlam [21] have used Mössbauer spectroscopy to investigate the fraction of Fe₂O₃ and Fe₃O₄ in the oxide as a function of oxidation time. They investigated the temperature range 475–500 °C and found that the amount of Fe₂O₃ never exceeded 10% of

the total film after three hours of oxidation. The valence band spectra and the peak height ratios of the AES results for the oxide formed at 350 °C indicate that it consists principally of stoichiometric Fe_3O_4 with a thin surface layer of Fe_2O_3 . The lack of the plateau region near the surface is a result of the Fe_2O_3 layer being non-stoichiometric or a result of a rough interfacial region. The slow decrease of the O/Fe ratio as the iron substrate is approached indicates the presence of roughening. The surface had a very high oxygen content relative to iron. This can be rationalized as resulting from contamination since a large carbon line and small sulfur and nitrogen lines were observed.

The outer portion of the film formed at 650 °C was quite brittle and nonadherent. It was dislodged from the surface by tapping the sample before placing it in the vacuum system. Two plateau regions were observed for the remaining film. The oxygen to iron ratio in the first region was between that obtained for Fe_2O_3 and Fe_3O_4 indicating a mixture of these oxides with a nonplanar interface. The second plateau region was Fe_xO .

The peak height ratio of oxygen relative to iron in the surface layers of the passive film was approximately that observed for $\gamma\text{-FeOOH}$. Also, the valence band spectra in this region resembled that of FeOOH . As reported in an earlier paper [12] the 46.5 eV and 51 eV lines were also observed indicating a possible two-phase film. Small amounts of boron and sulfur, which were incorporated in the film from the solution, were confined to the surface and near-surface layers. The origin of the carbon in the film is not clear. However, that close to the substrate most certainly has its origin in the metal. The slow drop in the O/Fe ratio with depth is probably an artifact of sputtering. Such an effect can be expected if submonolayer oxygen coverage exists since the rate of change of coverage during sputtering is proportional to the coverage.

One of the inherent uncertainties in the profiling technique is the possible occurrence of differential sputtering. This arises because elemental sputtering yields are different, which results in an altered surface layer enriched in the element with the lower sputtering yield [22].

Most studies of this phenomenon have been concerned with alloy systems where the general observation has been that the effect is small [23–27]. In investigations of compounds, the oxygen to silicon ratio in the surface layers of SiO_2 has been found to change from 2:1 to 3:1 after sputtering [28] while no differential sputtering was observed for MgO [29].

It is not possible to make a definitive statement concerning the existence of differential sputtering of the compounds used in this investigation. If differential sputtering were occurring and the elemental sputtering yields were the same for each compound, the same type of linear dependence as shown in fig. 8 would result. The initial decrease of the O/Fe ratio with depth (sputtering time) can be interpreted as a transient change in the surface composition to the equilibrium concentration where the surface coverage of oxygen and iron are such that the sputtered material has the same concentration as the bulk. Alternatively one would expect this behavior for Fe

and Fe_3O_4 since these are layered films with the outer layer having a higher oxygen content than that of the stoichiometric region. In the case of FeOOH , which was deposited from solution, and Fe_2O_3 the higher oxygen content of the surface layers can be rationalized by postulating the existence of the hydrated oxide on the surface. Such an oxide could result after exposure to the atmosphere.

5. Conclusion

AES has been used to investigate the oxide films formed on iron in gaseous and aqueous environments. The stoichiometric regions of five oxides have been identified. AES has been shown to be quantitative for the iron oxides with the ratios of the peak-to-peak heights of the oxygen 510 eV line and the iron 703 eV line approximately proportional to the oxygen to iron ratio in the chemical formula. Structure has been observed in the low energy iron line which results from the $\text{M}_{2,3}$ VV transition. The structure is different for each oxide making identification possible.

Acknowledgement

Support from the American Iron and Steel Institute contract No 61-244 and the National Science Foundation contract =DMR 74-08061 is gratefully acknowledged.

References

- [1] O. Kubaschewski and B.F. Hopkins, *Oxidation of Metals and Alloys*, 2nd ed. (Academic Press, New York, 1962).
- [2] W.E. Boggs, R.H. Kachik and G.E. Pellissier, *J. Electrochem. Soc.* 116 (1969) 424.
- [3] M. Cohen, *J. Electrochem. Soc.* 121 (1974) 191C.
- [4] K.J. Vetter, *Electrochemical Kinetics: Theoretical and Experimental Aspects* (Academic Press, New York, 1962).
- [5] N. Sato and K. Kudo, *Electrochimica Acta* 16 (1971) 447.
- [6] J. Kruger and J.P. Calvert, *J. Electrochem. Soc.* 114 (1967) 43.
- [7] A.J. Pignocco and G.E. Pellissier, *Surface Sci.* 7 (1967) 261.
- [8] K. Moliere and F. Portele, in: *The Structure and Chemistry of Solid Surfaces*, Ed. G.A. Somorjai (Wiley, New York, 1969).
- [9] A.J. Melmed and J.J. Carroll, *J. Vacuum Sci. Technol.* 10 (1973) 164.
- [10] P.B. Sewell, D.F. Mitchell and M. Cohen, *Surface Sci.* 33 (1972) 535.
- [11] M. Suleman and E.B. Pattinson, *Surface Sci.* 35 (1973) 75.
- [12] M. Seo, J.B. Lumsden and R.W. Staehle, *Surface Sci.* 42 (1974) 337.
- [13] K. Veda and R. Shimizu, *Surface Sci.* 43 (1974) 77.
- [14] C. Wagner, *Ber. Bunsenges. Physik. Chem.* 72 (1968) 1197.
- [15] J. O'M Bockris, M. Gershaw and V. Brusic, *Symp. Faraday Soc.* 4 (1970) 177.
- [16] F.C. Ho and J.L. Ord, *J. Electrochem. Soc.* 119 (1972) 139.
- [17] P.W. Palmberg, *J. Vacuum Sci. Technol.* 9 (1971) 160.

- [18] J.L. Leibenguth and M. Cohen, *J. Electrochem. Soc.* **119** (1972) 987.
- [19] R.P. Frankenthal, *Electrochim. Acta* **16** (1971) 1845 (and references therein).
- [20] R.E. Weber and A.L. Johnson, *J. Appl. Phys.* **40** (1969) 314.
- [21] D.A. Channing and M.J. Graham, *Corrosion Sci.* **12** (1972) 271.
- [22] J.W. Coburn and E. Kay, *CRC Critical Rev. Solid State Sci.* **4** (1974) 561.
- [23] M.L. Tarrg and G.K. Wehner, *J. Appl. Phys.* **42** (1971) 2449.
- [24] M. Ono, Y. Takusu, K. Nakayama and T. Yamashira, *Surface Sci.* **26** (1971) 313.
- [25] K. Nakoyama, M. Ono and H. Shimizu, *J. Vacuum Sci. Technol.* **9** (1972) 749.
- [26] T. Quinto, V.S. Sundaram and W.D. Robertson, *Surface Sci.* **28** (1971) 504.
- [27] H. Shimizu, M. Ono and K. Nakayama, *Surface Sci.* **36** (1973) 817.
- [28] A. Turos, W.F. van der Weg, D. Sigurd and J.W. Mayer, *J. Appl. Phys.* **45** (1974) 2777.
- [29] V.E. Henrich and J.C.C. Fan, *Surface Sci.* **42** (1974) 139.

AUGER ANALYSIS OF THE ANODIC OXIDE FILM ON IRON IN NEUTRAL SOLUTION*

M. SEO and ^N~~M.~~ SATO

Electrochemistry Laboratory, Faculty of Engineering, Hokkaido University,
Kita 13, Nishi 8, Kita-ku, Sapporo 060, Japan

and

J. B. LUMSDEN and R. W. STAHLF

Department of Metallurgical Engineering, The Ohio State University,
Columbus, OH 43210, U.S.A.

Abstract—The composition depth-profile of anodic oxide films on iron at various potentials in a boric acid–sodium borate solution of pH 8.4 was measured by the sequential use of Auger electron spectroscopy (AES) and sputter-etching. It was found that the anodic oxide film consisted mainly of oxygen and iron with minor impurities such as boron, sulphur and carbon. The composition ratio of boron or sulphur to oxygen exhibited a maximum value at a certain depth in the outer layer of the film and the maximum value of (B/O) increased with increasing potential up to 500 mV (SCE). The film formation mechanism is discussed from the observed dependence of boron content in the film.

INTRODUCTION

STUDIES of the anodic oxide film on iron in neutral boric acid–sodium borate solution have been carried out by many researchers. Nagayama and Cohen¹ made electrochemical measurement of the anodic oxide film on iron and proposed a two layer model consisting of an inner magnetite and an outer ferric oxide. The recent application of ellipsometry to this system has succeeded in the direct measurement of the thickness and the optical constant of the anodic oxide film. Noda *et al.*² proposed a model consisting of anhydrous ferric oxide as an inner layer and hydrated ferric oxide as an outer layer as a result of using a cathodic reduction technique combined with ellipsometry.

Recently, the sequential use³ of Auger Electron Spectroscopy (AES) and sputter-etching of solid surfaces has made possible the measurement of the composition profile of a surface layer in depth; the composition gradient of surface layer in depth can be determined by repeated sputtering with Ar⁺ ion-bombardment followed by Auger analysis. The application of this technique to the anodic oxide film on metals should bring forth further an understanding of the passivation phenomena.

In the present paper the composition profile in depth of the anodic oxide film on iron in neutral boric acid–sodium borate solution was examined by the sequential use of AES and sputter-etching and these Auger results were compared with the results² previously obtained by ellipsometry and coulometry.

*Manuscript received 24 January 1976; in revised form 20 February 1976.

EXPERIMENTAL METHOD

Preparation of specimen

The iron specimen used in this study was a vacuum melted electrolytic rod, 0.2 in. in dia. and 0.4 in. in length (purity 99.96%), which was annealed in an atmosphere of argon at 750°C for 3 h and then electropolished in a solution of glacial acetic acid and 70% perchloric acid (20 : 1). The electrolyte solution used was an equivolume mixture of 0.15N $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 0.15N H_3BO_3 (pH 8.4), which was de-aerated in a solution reservoir by prepurified argon before introduction into an electrolytic cell. The electropolished specimen was cathodically reduced in this solution at $5 \mu\text{A}/\text{cm}^2$ for 30 min to remove any oxide films from its surface. The solution was changed after cathodic reduction, and the specimen was oxidized potentiostatically at a desired anodic potential for 1 h to form the anodic oxide film on it. The specimen thus anodically oxidized was rapidly removed from the cell, washed with double-distilled water, dried with anhydrous methanol under argon atmosphere and stored in a glass tube filled with prepurified argon to prevent from further oxidation in air. The cylindrical surface of rod specimen was used for AES measurement.

AES measurement

The AES chamber consisted of a cylindrical mirror analyser (Varian) with a co-axial electron gun, an ion-bombardment gun, and an ultra-high vacuum system. The specimen was set on a sample holder in this chamber, in which prepurified argon had been filled at a pressure higher than the atmospheric pressure. After rough-pumping with zeolite-filled cryosorption pumps, the chamber was evacuated to a vacuum of 10^{-8} Torr or better, using ion and titanium sublimation pumps. No bake out of the chamber was used, in order to avoid changing the composition of the films.

Spectra were taken by using a 2 keV, 50 μA primary electron beam and a 2 V modulation amplitude with a frequency of 17 KHz. Argon ion-bombardment was performed at a pressure 8×10^{-4} Torr, using prepurified argon. After the admission of argon the chamber was pumped with the titanium sublimation pump to eliminate the possibility of contamination by active residual gases.

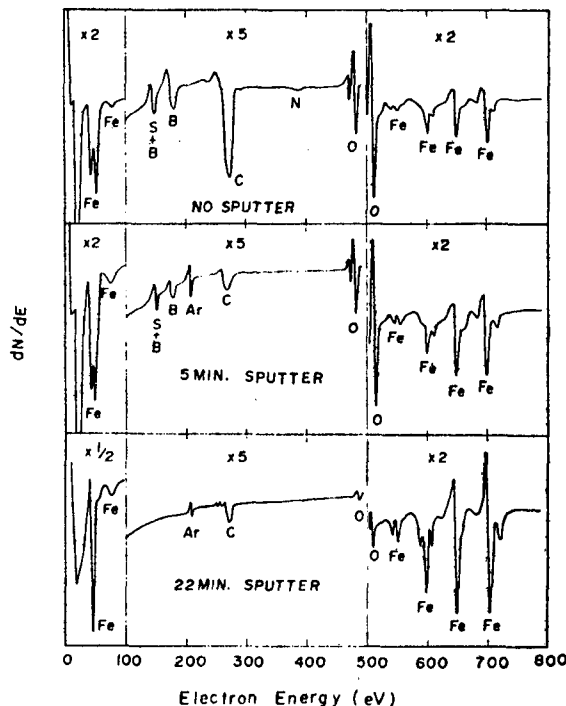


FIG. 1. The Auger spectra of the anodic oxide film formed on iron at $-300 \text{ mV}(\text{SCE})$ for 1 h in the boric acid-sodium borate solution. The sensitivity of the lock-in amplifier was so changed that all the Auger spectra was represented in a single figure.

Auger analysis of the anodic oxide film on iron in neutral solution

A 500 eV ion beam was used for ion-bombardment at an ion current density less than $1 \mu\text{A}/\text{cm}^2$. The sputtering rate of the anodic oxide film on iron was estimated to be $1 \sim 1.5 \text{ \AA}/\text{min}$ by comparing the time required for the film to be sputtered completely and the film thickness measured by ellipsometry.

EXPERIMENTAL RESULTS AND DISCUSSION

Auger spectra of anodic oxide films on iron

Figure 1 shows the Auger spectra of iron specimen anodically oxidized at -300 mV (SCE) for 1 h. The anodic oxide film consists mainly of oxygen and iron with minor impurities such as boron, sulphur and carbon. The Auger peak observed at *ca.* 155 eV in Fig. 1 can be regarded as an overlapped peak of boron and sulphur since recent Auger results⁶ have revealed that the Auger peak of boron in the film splits into two peaks (157 and 178 eV) and the lower energy peak is close to the sulphur Auger peak (152 eV). An appearance of the argon Auger peak (215 eV) during sputtering results from argon penetration in the film due to argon ion bombardment. The composition of the anodic oxide film changes with sputtering time. A low energy iron Auger peak (47 eV) of pure metallic iron corresponding to $M_{2,3}$ VV transition splits into two peaks (43 and 51.5 eV) as a result of the formation of the anodic oxide film; the height and location of two peaks change with sputtering time. This chemical shift will be discussed later in detail.

Composition depth-profile of anodic oxide films formed at various potentials

The peak to peak height (p.p.h.) for each component in the anodic oxide film on iron was plotted versus sputtering time to observe the composition profile in depth. The major Auger peaks of oxygen (510 eV) and iron (703 eV) were used to monitor their concentrations in the film. To eliminate experimental errors caused by a fluctuation of Auger operational condition, it is desirable to normalize the observed p.p.h. of each component as a ratio to the p.p.h. of iron. Figures 2 and 3 show the normalized composition profiles of the anodic oxide films formed in the potential range from -630 to 750 mV (SCE) for 1 h; the maximum active dissolution current density in the polarization curve of iron in the boric acid-sodium borate solution of pH 8.4 appears at -630 mV (SCE) and the passivity of iron, which starts at -500 mV (SCE), extends over a wide potential range up to $+900 \text{ mV}$ (SCE).

The ratio of oxygen p.p.h. of iron p.p.h. $(\text{O}/\text{Fe})_{\text{p.p.h.}}$, initially decreases with sputtering time, but there is a plateau region where it remains almost constant before the film is completely sputtered. The presence of the plateau suggests that the film has a constant composition region in its thickness, provided that a preferential sputtering⁸ of the film components does not occur. The plateau value of $(\text{O}/\text{Fe})_{\text{p.p.h.}}$ for the anodic oxide film formed at -500 and -300 mV (SCE) is 2.1 ± 0.1 . According to previous AES results⁶ of standard iron oxide films, it is magnetite, Fe_3O_4 , which corresponds to the ratio, $(\text{O}/\text{Fe})_{\text{p.p.h.}} = 2.1$. The film formed at potentials above 0 mV (SCE) has a wide plateau in which $(\text{O}/\text{Fe})_{\text{p.p.h.}}$ slightly decreases with sputtering time, and the mean value of $(\text{O}/\text{Fe})_{\text{p.p.h.}}$ in the plateau region increases from 2.7 to 3.2 as the potential is more noble, which corresponds to the composition of $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ($n = 0.6 \sim 1.8$). The gradual change of $(\text{O}/\text{Fe})_{\text{p.p.h.}}$ across the film/iron substrate interface may suggest the possibility of extensive oxygen diffusion into the iron substrate, although an alternative explanation may be made by the knock-on effect⁷ of

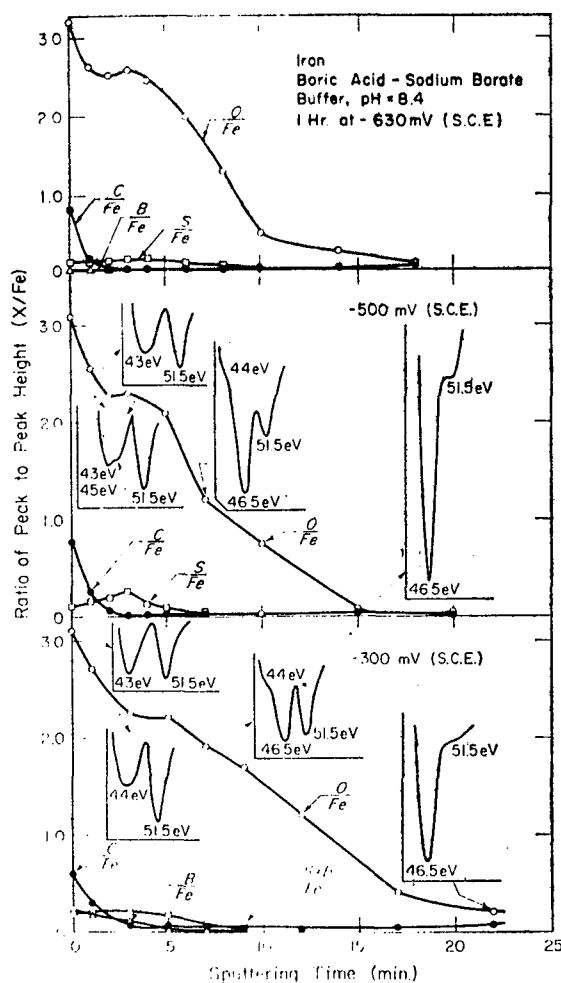


FIG. 2. The normalized composition profiles of the films formed on iron at relatively less noble potentials in a range from -630 to -300 mV(SCE) for 1 h and the chemical shift of low energy Auger peaks of iron.

ion-bombardment or by the heterogeneous sputtering of the film which also makes its interface unclear.

The values of $(C/Fe)_{p.p.h.}$ in the composition profile decreases exponentially with sputtering time and increases again when the iron substrate is exposed. Almost no boron was observed in the films formed at -630 and -500 mV (SCE). Some amount of boron, however, was observed in the films formed at potentials more noble than -300 mV (SCE), and its content increases as the potential rises up to $+500$ mV (SCE), although the presence of boron is limited to an outer layer of the film. The distribution of boron and sulphur in the film is different from that of carbon. The difference in distribution may be more evident in terms of $(B/O)_{p.p.h.}$, $(S/O)_{p.p.h.}$, and $(C/O)_{p.p.h.}$.

Auger analysis of the anodic oxide film on iron in neutral solution

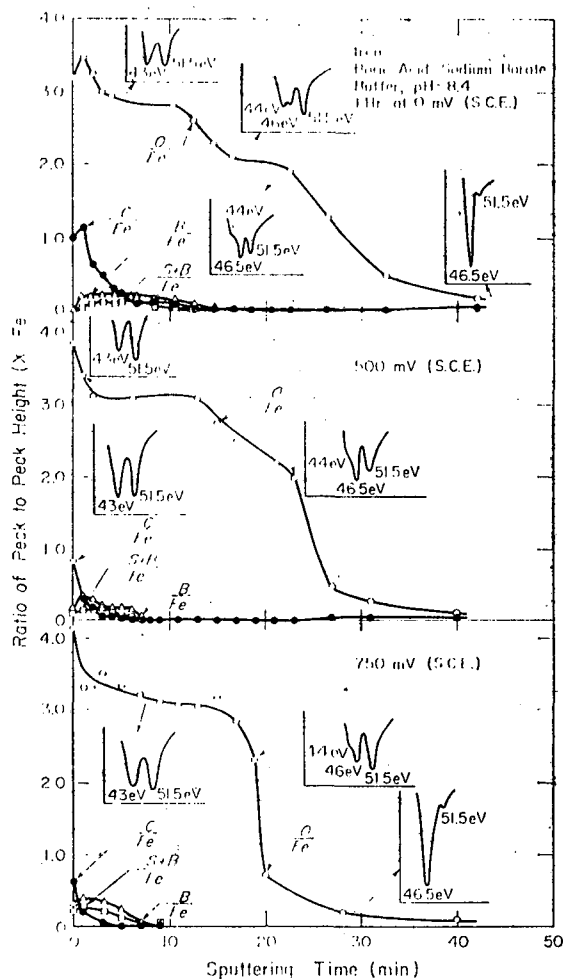


FIG. 3. The normalized composition profiles of the films formed on iron at relatively more noble potentials in a range from 0 to 750 mV(SCE) for 1 h and the chemical shift of low energy Auger peaks of iron.

as shown in Fig. 4. The presence of maximum values of $(B/O)_{p.p.h.}$ and $(S/O)_{p.p.h.}$ at a certain depth in the film means that sulphur as well as boron has come from the solution, whereas carbon has come from another source, for example, air, anhydrous methanol used for washing the specimen or residual gas in Auger chamber. The maximum values of $(B/O)_{p.p.h.}$ in the films were plotted versus an anodic potential in Fig. 5. The increase in maximum value of $(B/O)_{p.p.h.}$ up to +500 mV (SCE) is in accordance with the increase in the outer layer thickness of film; the film thickness has been measured by ellipsometry.² Figure 5 also shows that boron is contained in the film formed in the active dissolution region. Such a potential dependence of boron in the film may be related to the film formation mechanism which will be discussed later.

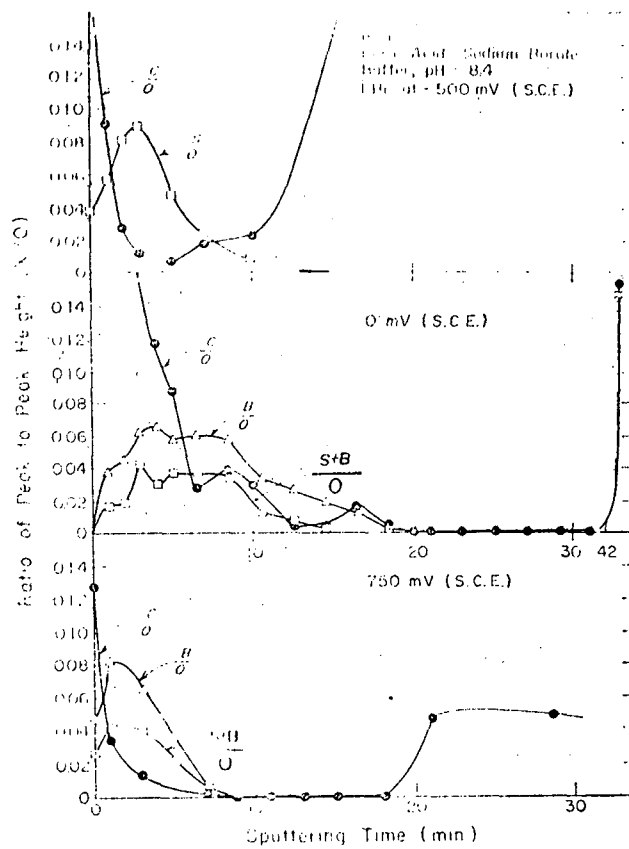


FIG. 4. The distribution of boron, sulphur and carbon in the films formed on iron at different potentials, -500, 0, and 750 mV(SCE).

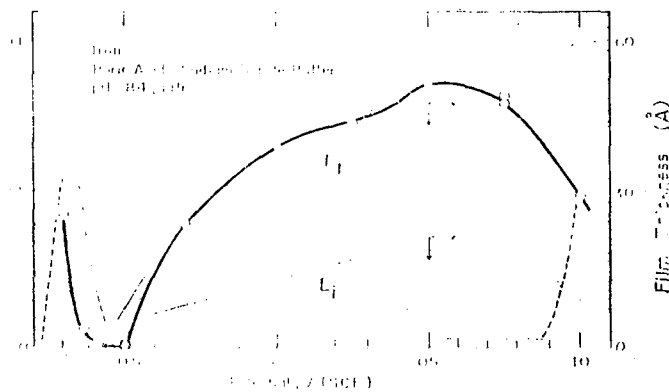


FIG. 5. The potential dependence of the maximum value of $(B/O)_{p.p.h.}$ in the films; the dotted line shows polarization curve of iron, and L_t and L_i indicate respectively the total film thickness and the inner layer thickness obtained by ellipsometry.

Chemical shift of low energy Auger peak of iron in anodic films

Figures 2 and 3 show the chemical shift of low energy Auger peaks of iron in the anodic oxide films formed in the potential range from -630 to 750 mV (SCE) for 1 h. A modulation voltage of 0.5 V was used for an accurate measurement of the low energy Auger peaks of iron. Two low energy Auger peaks at $43 \sim 44$ eV and 51.5 eV were always observed in an initial sputtering stage of the film. As the composition of the film approaches to $(\text{O}/\text{Fe})_{\text{p.p.h.}} = 2.2$, a third peak appears at $46 \sim 46.5$ eV besides the two peaks at 44 and 51.5 eV. After the composition of the film attained to $(\text{O}/\text{Fe})_{\text{p.p.h.}} = 2.2$, the peak height of 46.5 eV increases rapidly, whereas the peak height of 51.5 eV decreases reversely and the peak of 44 eV disappears completely.

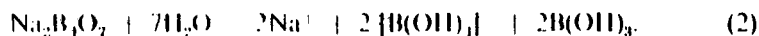
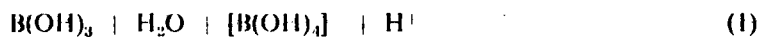
According to previous Auger results⁶ concerning standard iron oxide films, $(\text{O}/\text{Fe})_{\text{p.p.h.}} = 2.2$ corresponds to an intermediate composition between $\gamma\text{-Fe}_2\text{O}_3$ [$(\text{O}/\text{Fe})_{\text{p.p.h.}} = 2.3$] and Fe_3O_4 [$(\text{O}/\text{Fe})_{\text{p.p.h.}} = 2.1$]. The presence of two peaks ($43 \sim 44$ and 51.5 eV) means that iron ions in the film are trivalent, whereas the presence of two peaks (46.5 and 51.5 eV) means that iron ions in the film are divalent. It is thus possible to determine the distribution of Fe^{2+} and Fe^{3+} in the film from the chemical shift of low energy Auger peak of iron. It can be seen from Figs 2 and 3 that a significant amount of Fe^{2+} is contained in the inner layer of the film formed at potentials below 0 mV (SCE) but that Fe^{3+} ions remain only at the film/iron interface for the film formed at potentials above 500 mV (SCE).

Revie, Baker and Bockris¹⁰ have recently reported that the anodic oxide film on iron, which was transferred from an electrochemical cell to an Auger chamber without any damage, had only one low energy peak of 51.5 eV. Thus their results¹⁰ appear to differ from our results. Leygraf and Ekelund⁸ have suggested that the low energy Auger peaks of $43 \sim 44$ eV and 51.5 eV are related to Fe^{2+} and Fe^{3+} , respectively. According to their suggestion, Revie, Baker and Bockris¹⁰ concluded that the anodic oxide film contains Fe^{2+} and no Fe^{3+} . Ertl and Wandelt,⁹ however, have recently found that the $43 \sim 44$ eV peak corresponds to the cross-Auger transition between $M_{2,3}$ level of iron and $2p$ level of oxygen, whereas the 51.5 eV peak corresponds to the cross-Auger transition between $M_{2,3}$ level of iron and $3d$ level of iron. Therefore, the interpretation made by Revie, Baker and Bockris¹⁰ for the 51.5 eV peak seems to be doubtful.

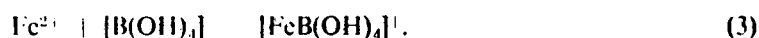
Formation mechanism of anodic oxide films on iron

The film formed at the lowest passive potential (-500 mV) contains no boron, whereas the film formed at higher potentials contains some amount of boron, the presence of which is however limited to the outer layer. This suggests that the formation mechanism of the outer layer is different from that of the inner layer. Markovac and Cohen¹¹ found that an anodic-deposited film on platinum in a boric-borate solution containing ferrous ions contains a large amount of boron. Our Auger results¹² with a deposited film formed under the same condition as that of Markovac and Cohen¹¹ showed that the distribution of boron in depth is constant and $(\text{B}/\text{O})_{\text{p.p.h.}}$ is 0.18 . The presence of boron in the outer layer of the anodic oxide films, therefore, proves that the outer layer is formed by anodic oxidation of ferrous ions dissolved from the iron specimen in an initial period of passivation.

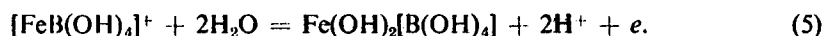
It is known^{1,3} that boric acid and sodium borate in the solution are dissociated according to the following equations.



Dissociated ion, $[\text{B(OH)}_4]^-$, can react with ferrous ion to form ferrous borate complex ions such as $[\text{FeB(OH)}_4]^+$,



Ferrous borate complex ion $[\text{FeB(OH)}_4]^+$ may be oxidized anodically to form a deposited oxide film of which the composition may be represented by $\text{FeOH}[\text{B(OH)}_4]_2$ or $\text{Fe(OH)}_2[\text{B(OH)}_4]$ as shown in equations (4) and (5).



The presence of boron in the film formed at the active dissolution region (-700 mV) may suggest that the film consists of a hydrated ferrous borate oxide deposited such as $\text{FeOH}[\text{B(OH)}_4]_2$.

The absence of boron in the inner layer of the anodic oxide film, on the contrary, may prove that the inner layer is formed by a direct anodic oxidation of iron. Noda, Kudo and Sato,² using ellipsometry and coulometry concluded that the inner layer of the anodic oxide films on iron is $\gamma\text{-Fe}_2\text{O}_3$, in which almost all the overpotential of film formation exists; its thickness increases linearly with the potential. It is difficult to estimate from the AES results the region of a phase oxide with constant composition for the inner layer, because of diffuse profile of composition in depth of the film. The Auger results, however, suggest that the film formed at potentials below 0 mV contains a significant amount of ferrous ion and has a narrow constant composition region corresponding to Fe_3O_4 . Thus it can be estimated that the inner layer of the film formed at potentials below 0 mV (SCE) is Fe_3O_4 , if it is a phase.

Recent electrochemical analysis by Sato, Kudo and Nishimura¹⁴ has revealed that the inner layer of the film formed at potentials below the Flade potential (-150 mV (SCE) in pH 8.4 solution), which is close to 0 mV (SCE), consists of Fe_3O_4 . Wagner¹⁵ has ascribed the passivity of iron to a thin film of iron-deficient magnetite with the limiting composition in the range from Fe_3O_4 to $\gamma\text{-Fe}_2\text{O}_3$ and he has interpreted the Flade potential as the potential at which the composition of the oxide is equal to the intermediate composition between two the limiting compositions. The Auger results of the anodic oxide films on iron is consistent with Wagner's interpretation.

CONCLUSION

The composition depth-profile of anodic oxide films on iron at various potentials

in a boric-borate solution of pH 8.4 was measured by a sequential use of AES and sputter-etching.

The outer layer of the anodic oxide film contains a significant amount of boron, which increases as the potential rises up to 500 mV (SCE), suggesting that the outer layer is formed by anodic oxidation of ferrous ion dissolved from the iron specimen during an initial period of passivation.

The inner layer of the films was found to contain no boron. This may suggest that the inner layer is formed by a direct anodic oxidation of metallic iron. From the measurement of chemical shift of low energy iron Auger peak, a significant amount of ferrous ion was found to be contained in the inner layer of the films formed at potentials below 0 mV (SCE), which is close to the Flade potential. The inner layer of the films formed at potentials below the Flade potential was thus estimated to be an iron oxide containing ferrous ion, probably magnetite. The inner layer of the films formed at potentials above 500 mV (SCE) was estimated to be a ferric oxide such as $\gamma\text{-Fe}_2\text{O}_3$ because no ferrous ion was found in the film except in a region very close to the film/iron interface.

Acknowledgement—This work was conducted in a Japan-USA collaborative research project supported by JSPS (Japan Society of Promotion of Science) and NSF (National Science Foundation in USA). The authors wish to acknowledge the financial support of JSPS and NSF.

REFERENCES

1. M. NAGAYAMA and M. COHEN, *J. electrochem. Soc.* **109**, 781 (1962).
2. T. NODA, K. KUDO and N. SATO, *J. Japan Inst. Metals* **37**, 951, 1088 (1973).
3. P. W. PALMBERG, *J. Vacuum Sci. Technol.* **9**, 160 (1971).
4. M. SEO, J. B. LUMSDEN, R. W. STAEBLE and N. SATO, *Corros. Sci.*, to be submitted.
5. H. SCHIMIZU, M. ONO and K. NAKAYAMA, *J. appl. phys.* **46**, 460 (1975).
6. M. SEO, J. B. LUMSDEN and R. W. STAEBLE, *Surface Sci.* **50**, 541 (1975).
7. J. W. COBURN, Extended abstract, p 235; 148th Fall Meeting of the Electrochl. Soc., Texas (1975).
8. S. EKELUND and C. LEYGRAF, *Surface Sci.* **40**, 179 (1973).
9. G. ERBL and K. WANDELT, *ibid.* **50**, 479 (1975).
10. R. W. REVIE, B. G. BAKER and J. O'M. BOCKRIS, *J. electrochem. Soc.* **122**, 1460 (1975).
11. V. MARKOVAC and M. COHEN, *ibid.* **114**, 678 (1967).
12. M. SEO, J. B. LUMSDEN and R. W. STAEBLE, unpublished data.
13. M. FISCHER, W. GRUNER and G. REINHARD, *Corros. Sci.* **15**, 279 (1975).
14. N. SATO, K. KUDO and R. NISHIMURA, Extended abstract, 1-29; 6th Int. Congr. on Metallic Corrosion, Sydney (1975).
15. C. WAGNER, *Ber. Bunsenges. phys. Chem.* **77**, 1080 (1973).



Authorized Reprint from
Special Technical Publication 596
Copyright
American Society for Testing and Materials
1916 Race Street, Philadelphia, Pa. 19103
1976

J. B. Lumsden¹ and R. W. Staehle¹

Composition of Protective Films Formed on Iron and Stainless Steels

REFERENCE: Lumsden, J. B. and Staehle, R. W., "Composition of Protective Films Formed on Iron and Stainless Steels," *Surface Analysis Techniques for Metallurgical Applications*, ASTM STP 596, American Society for Testing and Materials, 1976, pp. 39-51.

ABSTRACT: The composition of passive films formed on austenitic stainless steels have been determined using Auger electron spectroscopy. The films were found to be enriched in chromium which is consistent with the understanding of the relative insolubility of chromium compared to that of iron and nickel. However, the films were depleted in both silicon and molybdenum which are thermodynamically more stable than chromium in the solutions used. Thus, it is not possible to rationalize the improved resistance to acid solutions and solutions containing chlorides obtained by the addition of silicon and molybdenum to stainless steels using a selective-dissolution-enrichment model.

KEY WORDS: spectroscopy, iron, stainless steels, protective coatings, chemical analysis

Metals owe their chemical integrity to the presence of thin layers of reaction products on the surface. The amount of protection afforded by these layers depends upon their insolubility, adherence, and defect structure. This film is sometimes called a passive film; a metal is said to be passive if it is thermodynamically unstable under the conditions to which it is exposed, but, nevertheless, corrodes at a very low rate.

Faraday [1]² was one of the first to investigate this phenomenon when he studied the corrosion of iron in nitric acid. He found that iron dissolves rapidly in dilute nitric acid; however, in concentrated nitric, where according to thermodynamics iron should also dissolve, the metal becomes stable and is unattacked. Figure 1 shows the attacked and

¹ Adjunct assistant professor and professor, respectively, Department of Metallurgical Engineering, The Ohio State University, Columbus, Ohio 43210.

² The italic numbers in brackets refer to the list of references appended to this paper.

82

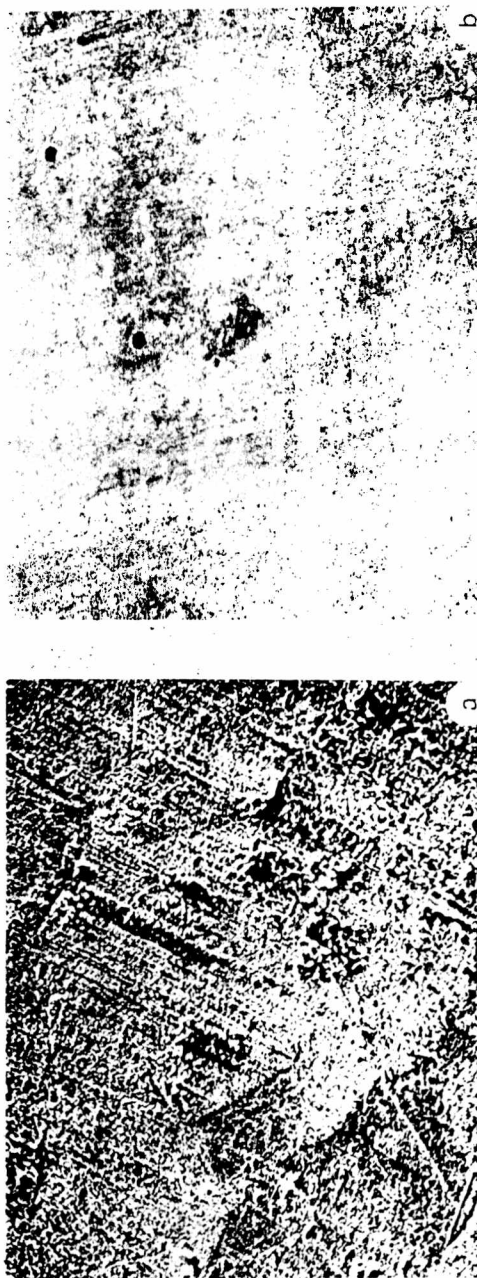


FIG. 1—Effects of dilute (a) and concentrated nitric acid (b) on iron.

unattacked surface of iron in dilute and concentrated nitric acid. The Auger electron spectroscopy (AES) analysis of these surfaces (Fig. 2) shows that in both cases the product layer film has the same composition, thus indicating the complexity of the phenomenon.

This work is particularly concerned with rationalizing the role of alloy species with respect to their critical influences on the protective quality of the films on stainless steel. Alloying iron with chromium and nickel to form austenitic stainless steel renders it passive under a wide range of environmental conditions including dilute nitric acid solutions. The addition of silicon and molybdenum produces a further resistance to attack in acid solutions and a substantial improvement in resistance to pitting in chloride containing environments [2,3].

For the various alloying elements to exert a significant effect, presumably they should be associated with the protective film. Rhodin [3-5] determined film compositions by chemical analysis of the isolated film. He used a film stripping procedure in which an aggressive reagent (an anhydrous methanol-bromine solution) was employed to attack the metal and float the film away. The improved corrosion behavior of stainless steels was found to correlate with the enrichment of silicon and molybdenum in the surface films.

The technique utilized here to obtain film compositions is AES, which permits the relative amounts of chemical species in the surface layers to be determined. Barnes et al [6] have used AES to determine the surface

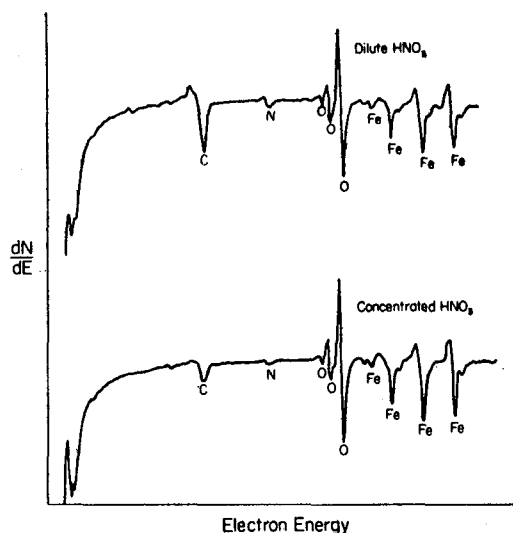


FIG. 2—Auger electron spectroscopy spectra from the attacked and unattacked iron surfaces on Fig. 1.

composition of stainless steels containing molybdenum. It was found in these studies that mill processing (the exact nature of the surface treatment was unknown) produced a surface concentration of molybdenum which was a factor seven larger than that of the bulk. In contrast, the study reported herein considers the formation of films resulting from exposure to aqueous environments.

Experimental

The alloys used were the austenitic stainless steels AISI Types 304, 316, 347, and a duPont experimental alloy, SP-2, which is a silicon modified Type 316L stainless steel. Compositions are given in Table 1.

The specimens were first vacuum annealed and then metallographically polished down to $0.3\ \mu\text{m}$ and passivated. One passivation procedure was identical to that used by Rhodin. It consisted of first pickling the specimens in 10 percent nitric acid (HNO_3)-2 percent hydrofluoric acid (HF)-1 percent hydrochloric acid (HCl) at 80°C for 1 min. After rinsing the specimens in demineralized double distilled water, the passive films were formed by treating the pickled surface in 5 percent HNO_3 -0.5 percent potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) at 60°C for 30 min. In order to examine the effect of the dichromate ion on the protective film, the specimens were also passivated by immersion in the 5 percent HNO_3 solution without the $\text{K}_2\text{Cr}_2\text{O}_7$.

In order to examine the influence of chloride ions, passive films were formed potentiostatically in a pH 7, 1.0 M sodium chloride (NaCl) + 0.1 M sodium sulfate (Na_2SO_4) solution. After mechanical polishing, the specimens were reduced cathodically and then polarized at 0 mV against the saturated calomel electrode (SCE). The solution was open to the air.

Comprehensive reviews of AES have been given elsewhere [7,8]; therefore, this technique will not be discussed here. The AES spectra were taken using a cylindrical mirror analyzer with a coaxial electron gun. A 2 keV, 50 μA electron beam was used having a diameter of approximately 50 Å. The modulation amplitude was 2 V peak to peak, and a frequency of 17 kHz was used.

The composition profiles of the passive films were obtained by the sequential application of sputtering by argon ion bombardment and AES analysis [9]. Ions of 600 eV energy and current densities in the $10^{-6}\ \text{A}/\text{cm}^2$ range were used. The estimated sputtering rate was 2 to 4 Å/min. A base pressure of 8×10^{-10} torr or less was always used. A typical spectrum is shown in Fig. 3.

Results

The AES results for the specimens passivated in the HNO_3 - $\text{K}_2\text{Cr}_2\text{O}_7$ solution are shown in Figs. 4, 5, 6, and 7. Peak-to-peak heights versus sputtering time are given for the silicon (92 eV), columbium (167 eV),

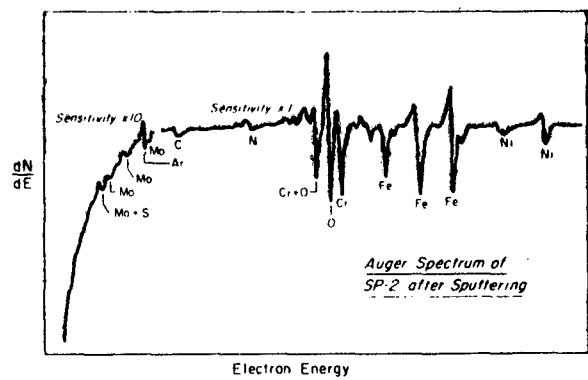


FIG. 3 Auger electron spectroscopy spectrum of passive film on Type SP-2 after sputtering.

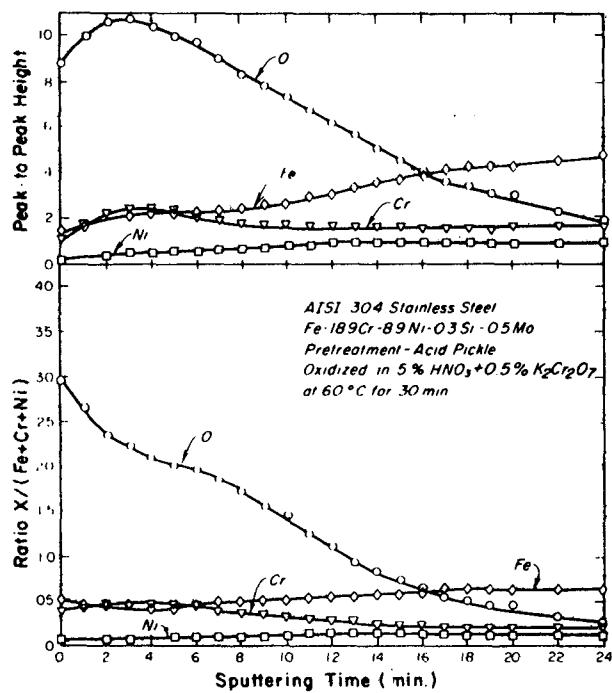


FIG. 4—Depth-composition profile of the film on Type 304 stainless steel passivated in a nitric acid-dichromate solution.

SURFACE ANALYSIS TECHNIQUES

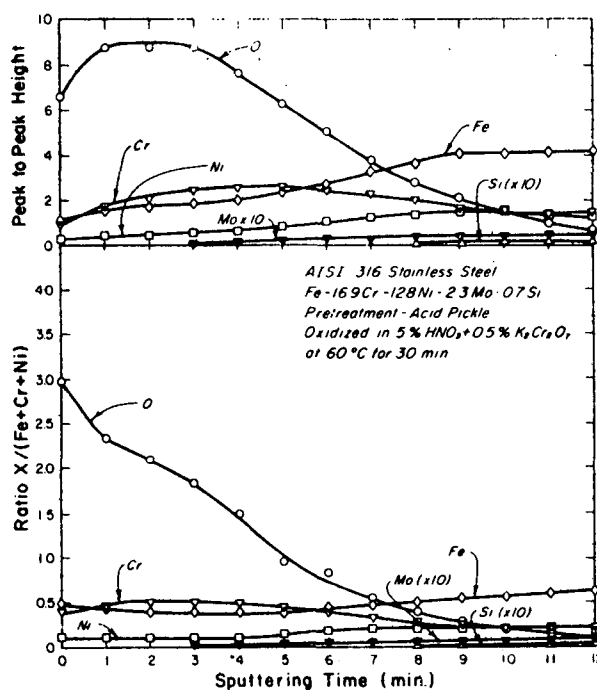


FIG. 5—Depth-composition profile of the film on Type 316 stainless steel passivated in a nitric acid-dichromate solution.

molybdenum (186 eV), oxygen (510 eV), chromium (529 eV), iron (703 eV), and nickel (848 eV) lines; also given are the normalized peak heights versus sputtering time, where the peak-to-peak heights of each of the above lines have been divided by the sum of the peak-to-peak heights for iron and nickel.

The results indicate that there was no enrichment of the molybdenum or silicon in the film. In fact, a depletion of these elements is observed. They were not detected in the surface or near surface layers of the films even at a sensitivity level ten times that used to obtain the remaining portion of the spectrum; likewise, there was no enrichment of columbium in the film on Type 347. This too was not detected until the metal substrate was

TABLE I—Composition of stainless steel alloys, percent.

	Cr	Ni	Si	Mo	Cb
Type 304	18.9	8.8	0.33	0.46	...
Type 316	16.9	12.8	0.66	2.3	...
Type 347	18.7	11.0	0.41	...	0.59
Type SP-2	18.8	9.2	2.5	2.4	...

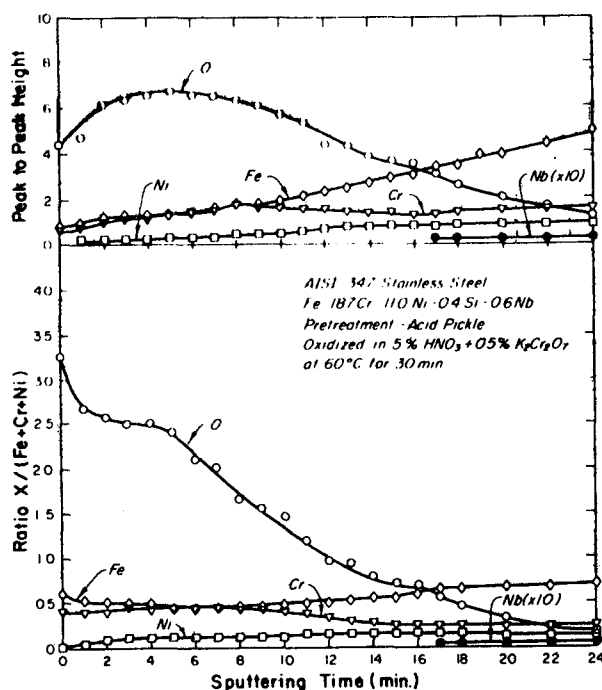


FIG. 6—Depth-composition profile of the film on Type 347 stainless steel passivated in a nitric acid-dichromate solution.

approached. The results also show that there was a substantial enrichment of chromium in the films. The peak-to-peak heights of the chromium line is greater than that of iron at several points within the films on all four alloys. Comparing the ratio of the normalized iron peak amplitude to chromium at the maximum chromium level in the film with the same ratio at the last point of the profile, an "enrichment factor" can be defined. This factor has the value of 3.5, 3.5, 3.2, and 3.3 for Types 304, 316, 347, and SP-2, respectively. The normalized nickel line changes little throughout the profile.

The compositions of the films formed in the 5 percent HNO_3 solution without the dichromate ions are shown in Figs. 8, 9, 10, and 11. These results are very similar to the previous ones. The differences are that the chromium enrichment was somewhat less and the normalized oxygen peak heights are also less. The enrichment factors in this case are 2.7, 2.7, 2.4, and 2.8 for Types 304, 316, 347, and SP-2, respectively. But here again no enrichment of molybdenum nor silicon was observed in the films, and the surface layers were depleted of these elements.

Figure 12 shows the current density-potential curve for Types 304, 316, and SP-2 in the sulfate-chloride (SO_4 -Cl) solution. This shows the increase in the range of stability as the molybdenum and silicon contents

SURFACE ANALYSIS TECHNIQUES

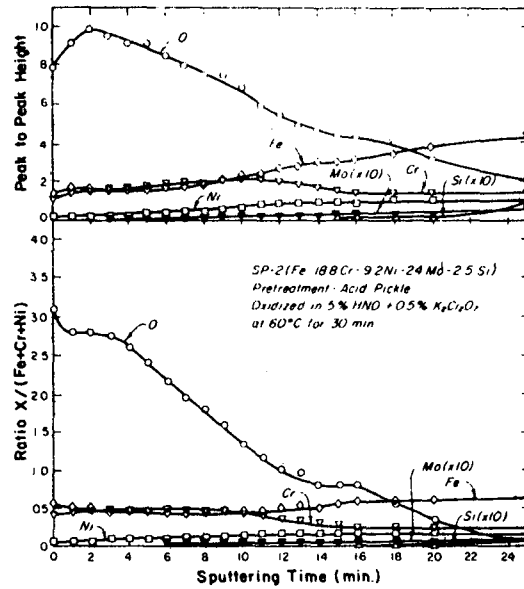


FIG. 7—Depth-composition profile of the film on Type SP-2 stainless steel passivated in a nitric acid-dichromate solution.

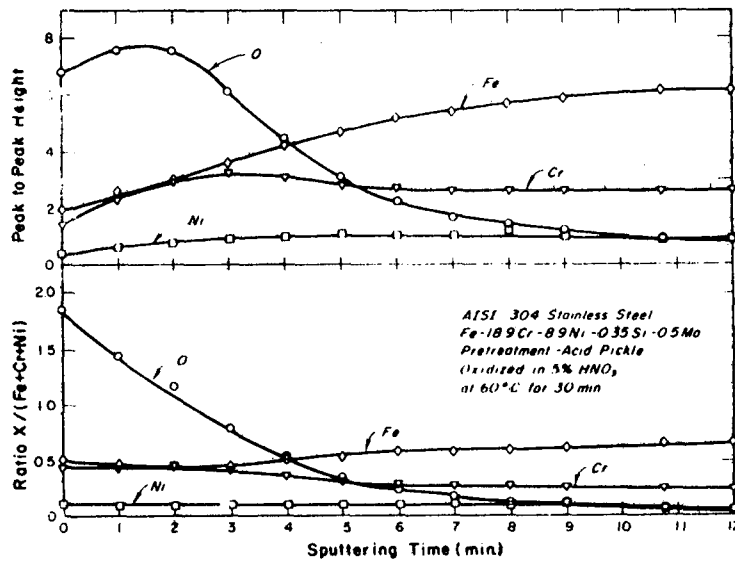


FIG. 8—Depth-composition profile of the film on Type 304 stainless steel passivated in nitric acid.

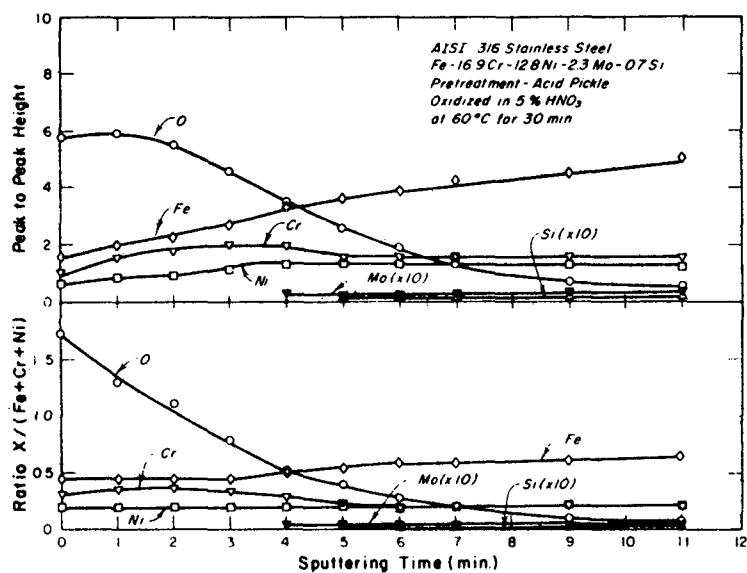


FIG. 9—Depth-composition profile of the film on Type 316 stainless steel passivated in nitric acid.

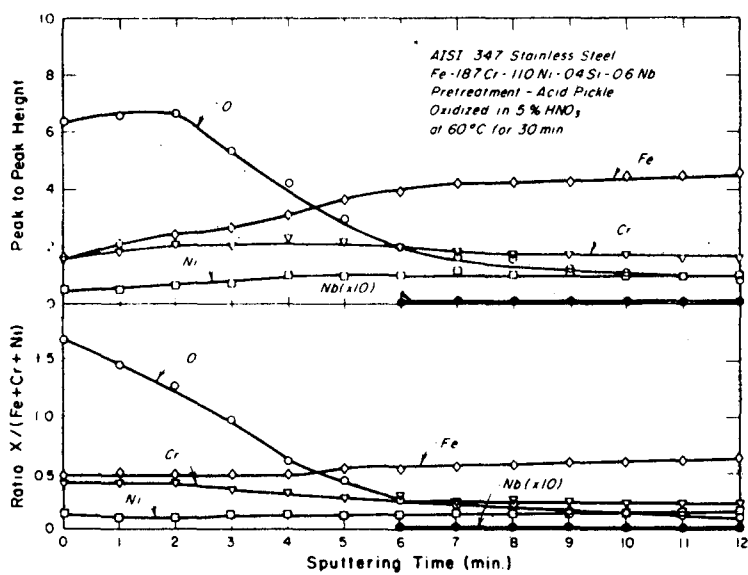


FIG. 10—Depth-composition profile on the film on Type 347 stainless steel passivated in nitric acid.

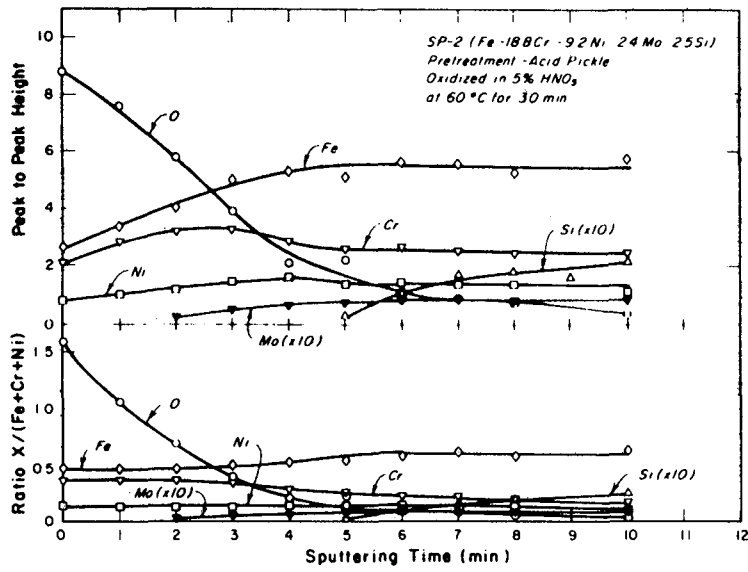


FIG. 11—Depth-composition profile of the film on Type SP-2 stainless steel passivated in nitric acid.

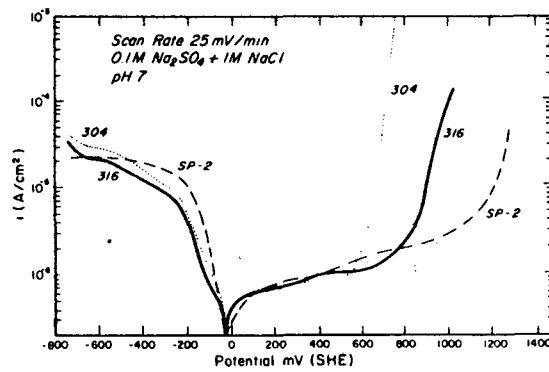


FIG. 12—Current density-potential curve for Types 304, 316, and SP-2 stainless steels exposed to a sulfate-chloride solution.

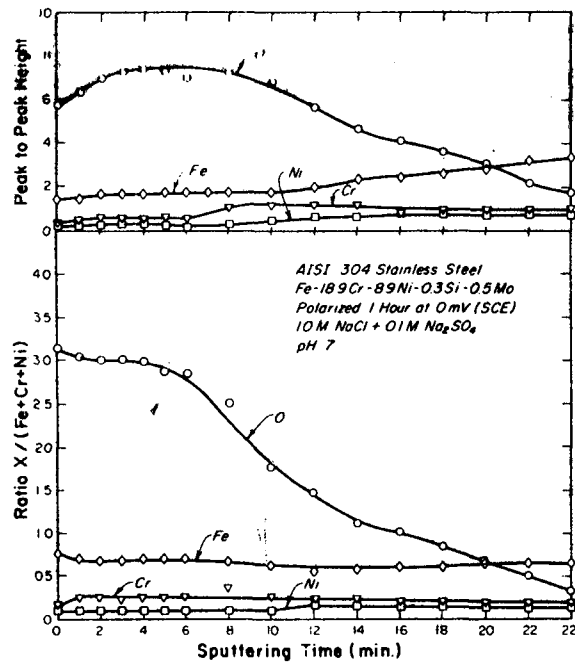


FIG. 13—Depth-composition profile of the film on Type 304 stainless steel passivated by potentiostatic polarization in a sulfate-chloride solution.

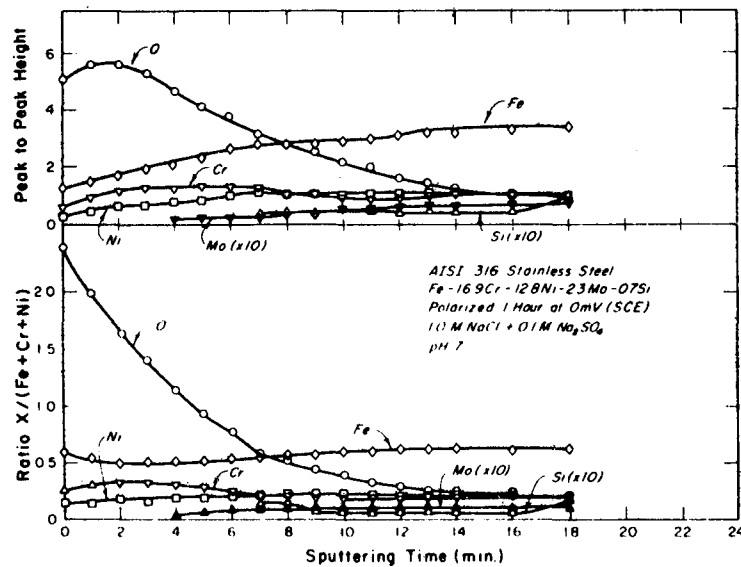


FIG. 14—Depth-composition profile of the film on Type 316 stainless steel passivated by potentiostatic polarization in a sulfate-chloride solution.

SURFACE ANALYSIS TECHNIQUES

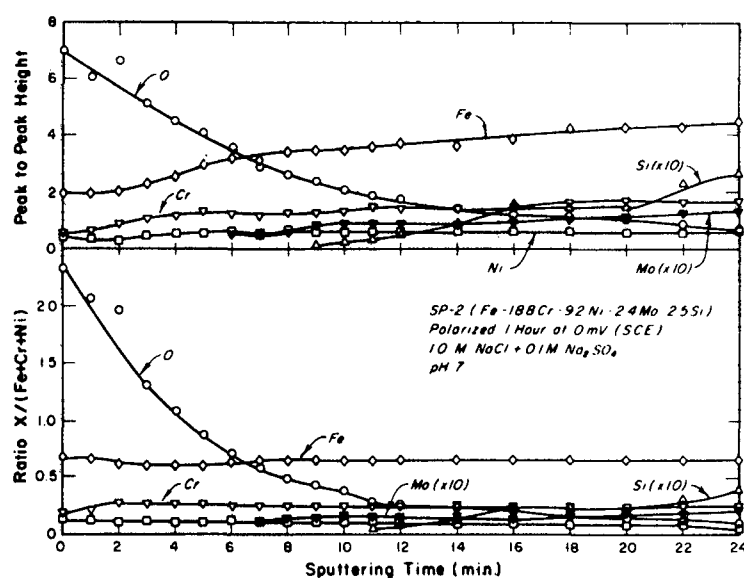


FIG. 15—Depth-composition profile of the film on Type SP-2 stainless steel passivated by potentiostatic polarization in a sulfate-chloride solution.

are increased. The AES results for the films formed in this solution are given in Figs. 13, 14, and 15. Only a slight enrichment of chromium is observed in the film on Type 304. The compositional behavior of silicon and molybdenum is identical to those observed in the previous two cases.

Discussion

The following are significant observations made using AES to analyze passive films on stainless steels.

1. There appears to be no enrichment of molybdenum or silicon in the surface film.
2. Chromium is enriched in the surface layers of the protective films which result from passivation in HNO₃ and HNO₃ plus K₂Cr₂O₇ solutions.
3. There is little, if any, chromium enrichment in films formed potentiostatically in a pH 7 SO₄²⁻-Cl⁻ solution.
4. The normalized nickel content remains essentially constant through the film.
5. The films formed by electrochemical polarization and in the HNO₃ solution containing the dichromate ion appear to have higher oxygen levels than those films formed in the HNO₃ solution without the dichromate ion.

The enrichment of chromium is consistent with the understanding of the

relative insolubility of chromium compared to that of iron and nickel in these environments and has been predicted in previous studies [10]; however, these results cannot be explained simply from thermodynamic considerations since silicon and molybdenum are both more stable than chromium at low pH's and these elements do not enrich in the film.

These results are substantially different from those obtained by Rhodin using a chemical analysis technique. He found a factor of 10 enrichment in silicon compared to the percentage in the alloy. In the case of molybdenum, he found an enrichment ranging from approximately 2 for Type 316 to slightly more than 10 for Type SP-2. He further found that the enrichment of silicon and molybdenum in the film corresponded to a depletion of iron. No enrichment of chromium was observed. In the case of Type 347, columbium enriched in the film by a factor of nine. None of these phenomena were observed using AES to determine film composition. Also the higher chromium levels found after passivation in the dichromate solutions could explain the increased improvement in pitting resistance following the treatment compared to that for alloys passivated in HNO_3 solutions without dichromate ions [3].

Considering the compositions of the films on Type 316 and SP-2, one must be concerned about the role of molybdenum and silicon since they do have a major influence on suppressing the pitting behavior; however, the AES analysis of these films gives no evidence that molybdenum and silicon are present to any substantial extent in the films on Type 316 and SP-2. Indeed, these elements are depleted in the outer layers of the film; therefore, it appears one must look in other directions for rationalizing the role of molybdenum and silicon.

Acknowledgments

The authors gratefully acknowledge support from the National Science Foundation, Grant No. DMR74-08061.

References

- [1] Faraday, M., *Philosophical Magazine*, Vol. 9, 1836, pp. 57, 122, 153.
- [2] Streicher, M. A., *Journal of the Electrochemical Society*, Vol. 103, 1956, p. 375.
- [3] Nielsen, N. A. and Rhodin, T. M., *Zeitschrift für Elektrochemie*, Vol. 62, 1958, p. 707.
- [4] Rhodin, T. N., *Corrosion*, Vol. 11, 1956, p. 465t.
- [5] Rhodin, T. N., *Corrosion*, Vol. 12, 1956, p. 123t.
- [6] Barnes, G. J., Aldag, A. W., and Jerner, R. C., *Journal of the Electrochemical Society*, Vol. 116, 1972, p. 684.
- [7] Chang, C. C., *Surface Science*, Vol. 25, 1971, p. 53.
- [8] Palmberg, P. W. in *Electron Spectroscopy*, D. A. Shirley, Ed., North-Holland, Amsterdam, 1972.
- [9] Palmberg, P. W., *Journal of Vacuum Science and Technology*, Vol. 9, 1972, p. 160.
- [10] Evans, U. R., *Research*, Vol. 6, 1953, p. 130.

The Composition of Passive Films on Ferritic Stainless Steels

A. E. Yaniv

Israel Ministry of Defense, Scientific Department, Tel-Aviv, Israel

and J. B. Lumsden and R. W. Staehle*

Department of Metallurgical Engineering, The Ohio State University, Columbus, Ohio 43210



Reprinted from JOURNAL OF THE ELECTROCHEMICAL SOCIETY
Vol. 124, No. 4, April 1977
Printed in U.S.A.
Copyright 1977

The Composition of Passive Films on Ferritic Stainless Steels

A. E. Yaniv

Israel Ministry of Defense, Scientific Department, Tel-Aviv, Israel

and J. B. Lumsden and R. W. Staehle*

Department of Metallurgical Engineering, The Ohio State University, Columbus, Ohio 43210

ABSTRACT

Auger electron spectroscopy has been used to investigate the influences of pH, Cl⁻ addition, and potential on the composition of passive films on Fe-Cr-Mo ferritic stainless steels. It was found that the improved corrosion resistance properties obtained by the addition of molybdenum cannot be explained by its enrichment of the protective film. Molybdenum was not found in the film even at those potential and pH values at which its oxide is the stable species. However, the relative iron and chromium content in the film followed predictions based on their solubilities in aqueous solutions. These results also indicate changes in bonding in the film as a function of distance from the substrate.

The development of high purity Fe-Cr-Mo ferritic stainless steels of low interstitial content stimulated the commercial use of ferritics after the results of several studies demonstrated the excellent corrosion resistance of this class of alloys. The improved corrosion resistance is derived mainly from the addition of molybdenum.

The beneficial effect of molybdenum on austenitic stainless steels in increasing its resistance to attack by chloride and acid solutions has been known for many years. Molybdenum- and silicon-containing austenitic stainless steels were investigated by Streicher (1) and by Rhodin *et al.* (2, 3). Bond and Lizlovs (3-7) have extensively studied the corrosion properties of molybdenum-containing ferritic stainless steels exposed to chloride solutions. Besides a substantial increase in pitting potential, the addition of 5% Mo to 13, 18, and 25% Cr alloys produces over an order of magnitude decrease in the critical current density. Further, the effect of molybdenum depends upon the chromium level: the higher the chromium content the greater the effect. Thus, molybdenum interacts synergistically with chromium. The function of Mo, or for that matter Cr, in improving resistance to halide solutions is not understood.

Ambrose and Kruger (8) have presented evidence that Mo increases the passivation rate; they suggest that in the presence of chloride ions the film is constantly breaking down and being repaired. Whether or not pitting occurs depends upon the rate at which the film repairs itself. Uhlig explains the beneficial effects of Mo and Cr using a competitive adsorption model (9). He rationalizes the effects of Cr by its greater affinity for oxygen than Fe and that of Mo by its lower affinity for chloride than Cr.

Rhodin (2,3) found that the improved corrosion behavior of the austenitic stainless steels correlated with the enrichment of silicon and molybdenum and the depletion of iron in the surface films. He used a film-stripping procedure in which an aggressive reagent (an anhydrous methanol bromide solution) was employed to attack the metal and float the film away. The isolated film was then chemically analyzed. However, Lumsden and Staehle (10, 11), using Auger electron spectroscopy (AES), found no enrichment of molybdenum or silicon in the films on these alloys. To the contrary, a depletion was observed.

The work reported herein was undertaken to determine correlations between film composition and its protective quality. Auger electron spectroscopy was used to determine film compositions on Fe-Cr-Mo ferritic stainless steels as a function of pH and chloride content.

Experimental

The alloys used were high purity ferritic stainless steels provided by Climax Molybdenum Company with chromium contents of 13, 17, and 25% and with varying additions of molybdenum. They were prepared by induction melting and vacuum casting. The chemical compositions are given in Table I. The surfaces studied were mechanically polished by standard metallographic techniques (12) to $\frac{1}{4}$ μ m diamond paste. Prior to polarization, the specimens were washed in a mild detergent, rinsed in double distilled water, and finally cleaned ultrasonically in methanol.

Polarization was carried out in a glass cell of standard design (13), which was open to the air. Initially, polarization curves were determined potentiodynamically at a scan rate of 0.55 mV/sec to establish the active, passive, and transpassive regions.

Films were formed potentiostatically in 1N H₂SO₄, 1N Na₂SO₄ + H₂SO₄ (pH 3), 1N NaCl + H₂SO₄ (pH 3.45), and pH 14 NaOH at 60, -150, -150, and -700 mV (NHE), respectively. Prior to anodic polarization the specimens were cathodically polarized at -750 mV (NHE) for 1 hr. The alloys were passivated for 1 hr.

Table I. Composition and heat-treatment of the ferritic stainless steels used

Alloy	Cr	Mo	C	N	Ni	Condition (°C, 1 hr WQ)
1	13.68	0.08	0.003	0.004		815
2	13.14	1.04	0.005	0.004		815
3	13.60	1.88	0.002	0.004		815
4	12.95	3.48	0.003	0.004		980
5	13.04	4.77	0.003	0.003		980
6	17.35	<0.01	0.002	0.003		815
7	17.35	1.14	0.003	0.004		815
8	17.61	2.02	0.004	0.004		815
9	17.58	3.52	0.005	0.004		815
10	17.38	4.75	0.004	0.004		980
11	25.66	0.002	0.002	0.015		815
12	25.26	2.05	0.002	0.017		815
13	25.25	5.25	0.002	0.013		980
14	25.66	0.002	0.002	0.015	0.13	980
15	26.15	0.99	0.003	0.016	0.1	980
16	25.26	2.05	0.002	0.017	0.13	980
17	25.58	3.49	0.002	0.015	0.13	980
18	25.25	5.24	0.002	0.013	0.13	980

* Electrochemical Society Active Member.

Key words: passivity, corrosion, molybdenum, Auger electron spectroscopy.

After removal from the electrolyte, the specimens were washed in double distilled water and placed immediately in the vacuum system.

Polarization in a NaOH pH 14 solution was carried out in an open-to-the-air polypropylene beaker using a Hg/HgO/NaOH reference electrode and a zirconia bridge. The reference electrode was constructed of a platinum wire embedded in a shrinkable Teflon tube which was mounted in the end of a zirconia tube. The zirconia tube contained mercury and HgO on the bottom covered with a mixture of ZrO_2 particles and NaOH. A bridge was made of a $\frac{1}{4}$ in. Teflon tube filled with the same mixture as the reference electrode and closed on both ends with a porous ZrO_2 plug.

Selected specimens were also passivated in a HNO_3 solution using the same procedure as that employed by Nielsen and Rhodin (2, 3). The surface preparation consisted of first mechanically polishing as above followed by pickling in a 10% HCl solution at 80°C for 1 min. Then the surfaces were passivated by immersion in a 5% HNO_3 solution at 60°C for 30 min. The alloys were subsequently rinsed in demineralized, double distilled water.

Auger analysis was performed using a Varian cylindrical mirror analyzer (14) with a coaxial electron gun. Before analysis the system was pumped to 8×10^{-10} Torr or less using nonmechanical pumping. No bakeout was used in order to avoid changing the composition of the films.

The composition of the passive films was determined using the profiling technique (15, 16). This consists of simultaneous etching by argon ion bombardment and AES analysis. A 600 eV ion beam was used having an ion current density of approximately $1 \mu A/cm^2$. The Auger spectra were taken using a 2 kV, 50 μA electron beam (static) having a diameter of approximately 50 μm . A 17 kHz modulation frequency was used with a modulation amplitude of 2V (p-p).

Results

The composition profiles are given as plots of normalized peak heights vs. sputtering time. The Auger peak heights have been normalized to the sum of those for iron and chromium in order to compensate for any change in surface and experimental conditions which affect the Auger signal. Due to the uncertainty in the sputtering rate, the sputtering time is given rather than the thickness of the film removed; however, the rate of film removal has been estimated to be approximately 3 Å/min before submonolayer coverage is reached. This was determined by sputtering and Auger analyzing oxide films which were formed by exposing iron to chromate solutions. The thickness was determined using an ellipsometer. After coverages of less than a monolayer are attained, the sputtering rate decreases exponentially since the rate at which an element is sputtered is proportional to its surface concentration.

Preliminary experiments were carried out to find the effect of the mechanical surface preparation on the film composition. A chromium deficiency was found in the film.

Figure 1 gives the composition of the passive film formed on the Fe-25.25Cr-5.24Mo alloy which had been exposed to the pH 3 sulfuric acid solution and polarized to a potential of -150 mV (NHE) for 1 hr. The Auger peaks used for all profiles were the O 510 eV, Fe 703 eV, Cr 529 eV, Mo 221 eV, S 152 eV, C 272 eV, and Cl 181 eV lines.

The results given in Fig. 1 are typical of those obtained for all the alloys exposed to the pH 3 solution. In addition to oxygen and the alloying elements, sulfur was present in appreciable amounts but was localized in the outermost layers and was easily sputtered off. Carbon, which was present in large quantities on the surface, was rapidly removed and reached a level slightly above its content in the steels after 5-10 min of sputtering. Its presence on the surface was probably due to atmospheric contamination. The relative amount

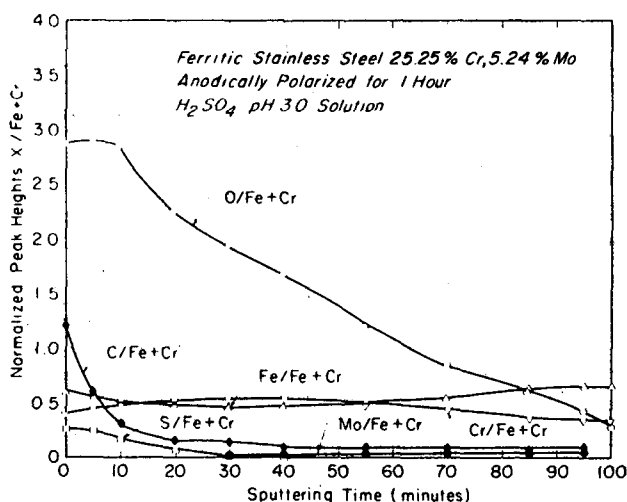


Fig. 1. Normalized Auger peak heights vs. sputtering time for the passive film on Fe-25Cr-5Mo ferritic stainless steel.

of molybdenum in the film was the same as that described in previous publications (10, 11), i.e., no molybdenum in the outermost layers of the films and no enrichment in the films. Finally, chromium enriches the film with a corresponding depletion of iron.

The effects of heat-treatment on the anodic film composition were evaluated using alloys 11, 12, 14, and 16 in Table I. No effect was observed, but it should be emphasized that only 25% Cr steels heat-treated at 815° and 980°C were available.

The surfaces of the alloys which were polarized in the pH 3.45 chloride solution were examined optically and no attack was observed. The lowest pitting potential, 295 mV (NHE), was obtained for the Fe-13Cr alloy. The potential applied to the alloys exposed to the chloride solution was -150 mV (NHE). This potential is well below the pitting potential of all of the alloys used in this investigation.

The analysis of the film formed on the Fe-25.25Cr-5.24Mo alloy at -150 mV (NHE) exposed for 1 hr to a H_2SO_4 -1.0N NaCl solution is shown in Fig. 2. The compositions were similar to those obtained for films formed in the pH 3 solution without chloride. In all cases the enrichment of chromium in the passive film was observed reaching the highest value for the 25% Cr steels and proportionally lower for the 17 and 13% Cr steels (Fig. 3). Molybdenum was not detected in the surface and near-surface layers nor did it enrich. Chlorine was detected in the surface and near-surface

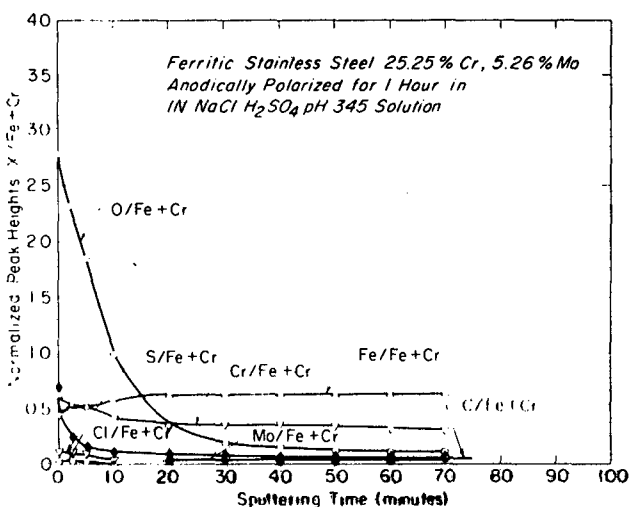


Fig. 2. Composition of passive film formed on Fe-25Cr-5Mo alloy after anodic polarization in a pH 3.45 chloride solution.

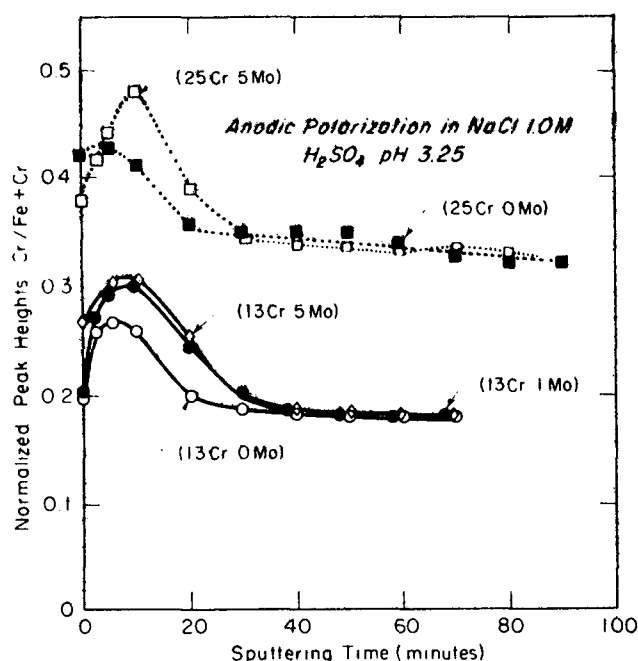


Fig. 3. Relative chromium composition of passive films on ferritic stainless steels formed by anodic polarization in a pH 3.45 chloride solution.

layers only. Also, there was no significant difference in the thickness of the passive film on the alloys as deduced from the sputtering time necessary to reach the substrate.

Typical results for alloys exposed to 1N H₂SO₄ are given in Fig. 4. This is the composition profile of the film on Fe-25.25Cr-5.24Mo which had been polarized at 60 mV (NHE) for 1 hr. Chromium enrichment was found to coincide with a decrease in the iron content in the film. The molybdenum content was the same as that observed previously.

For comparison, an AES analysis was performed on surfaces which had been passivated by immersion in nitric acid. The film compositions resulting from passivation in nitric acid (Fig. 5) differed from those formed anodically only in the chromium content. Whereas anodic polarization resulted in films with varying amounts of chromium enrichment depending upon the chromium content of the alloy, the amount of chromium enrichment which resulted from passivation in nitric acid did not change in either the 17% or the 25% Cr steels with or without molybdenum; the 13%

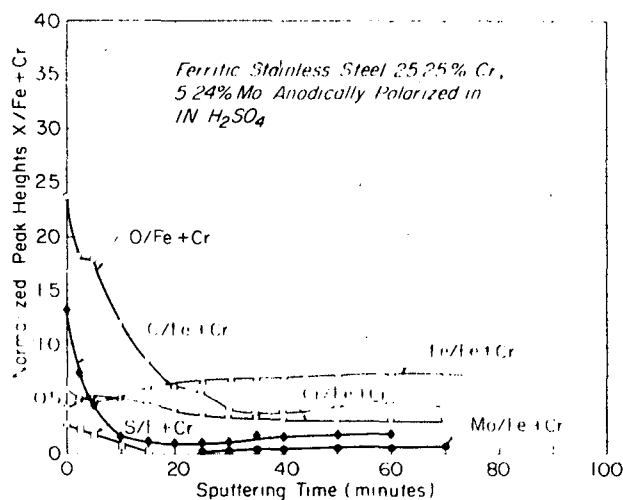


Fig. 4. Auger results for the passive film on Fe-25Cr-5Mo formed by anodic polarization in 1N H₂SO₄.

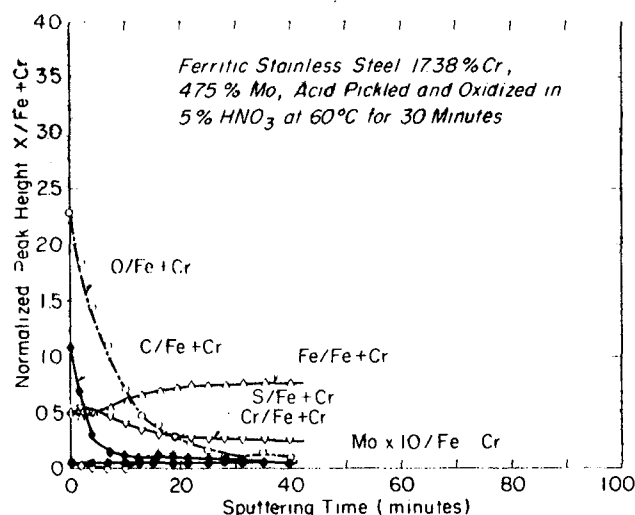


Fig. 5. Passive film composition on 17Cr-5Mo ferritic stainless steel after passivation in 5% HNO₃ at 60°C for 30 min.

Cr steels were attacked by the 10% nitric acid solution.

The films formed on 13, 17, and 25% Cr alloys (with 0 and 5% Mo) exposed to the pH 14 NaOH solution were analyzed. In every case a depletion of Cr and an absence of Mo was observed in the films. An enrichment in iron was found corresponding to the chromium depletion. As the film was sputter etched, the iron and chromium contents uniformly approached the alloy levels. This is shown in Fig. 6.

The effects of potential were determined for alloys exposed to the H₂SO₄-NaCl solution. Figure 7 shows the film composition of the 18% Cr 5% Mo alloy obtained by polarization in the transpassive region at 1250 mV (NHE). For all of the alloys investigated there was a depletion of chromium in the film and an enrichment of iron relative to the bulk composition. Molybdenum was detectable in the surface layers of the film on those alloys in which it was present; however, the depletion-enrichment type of behavior of chromium and iron was independent of its existence in the alloy. Figure 8 shows the Auger results for the 25% Cr 5% Mo stainless steel which had been polarized cathodically at -1150 mV NHE. The film compositions on the ferritic stainless steels which had been polarized cathodically were identical to those resulting from polarization in the transpassive region.

Thus, these results suggest that cathodic polarization changes the surface composition of the alloy. It is not conclusive, however, that the observed film is that

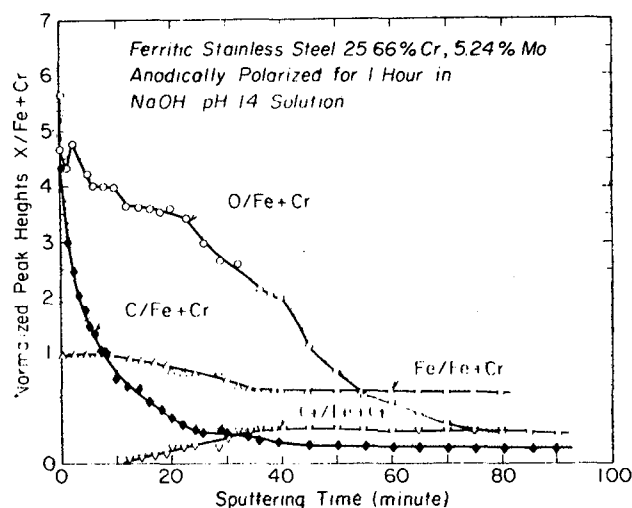


Fig. 6. Composition of the film formed in a pH 14 NaOH solution.

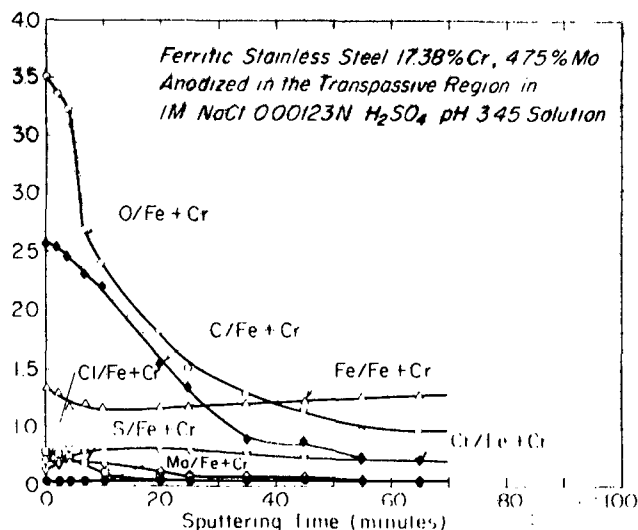


Fig. 7. Auger results for the film formed on 17% Cr 5% Mo stainless steel polarized in the transpassive region.

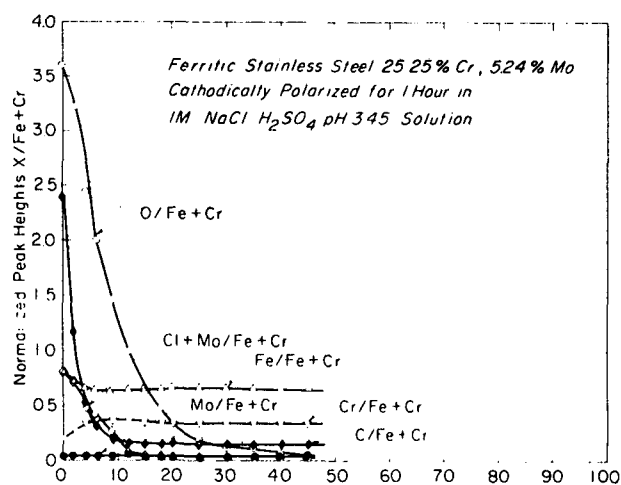


Fig. 8. Effects of cathodic polarization of the film composition on 25% Cr 5% Mo alloy.

which exists on the alloy in solution. If the air-formed film is removed by cathodic reduction, then oxidation would occur when the alloy is taken out of solution and exposed to the air. However, the air-formed film on the alloys used in this investigation is always enriched in chromium; therefore, air oxidation of an unaltered surface would not produce a film depleted of chromium.

Figures 9-13 show the Auger spectra at various depths in the passive film on the Fe-25.25Cr-5.25Mo alloy which had been passivated in the HNO₃ solution. Each figure has two spectra. One is the complete spectrum showing all of the Auger lines from the constituents of the film; the other is the low energy or valence band spectrum from iron. For the latter, two of the electrons involved in the Auger transition are in the valence band. Thus, these Auger electrons are very sensitive to changes in bonding. Figure 9 shows the spectra which result after 5 min of sputtering. The film for the most part is an iron oxide with only a small amount of Cr. The valence band spectrum shown is that of iron; this is the type of spectrum which results when iron is in the ferric state as reported previously (17). The spectra in Fig. 10 were taken after 10 min of sputtering. Here, a substantial amount of Cr appears in the film; whereas the oxygen and iron content remains approximately the same as that in the previous spectrum. Molybdenum also begins to become detectable. The lower energy peak in the valence band spectrum has shifted in energy; this is the same type of valence band

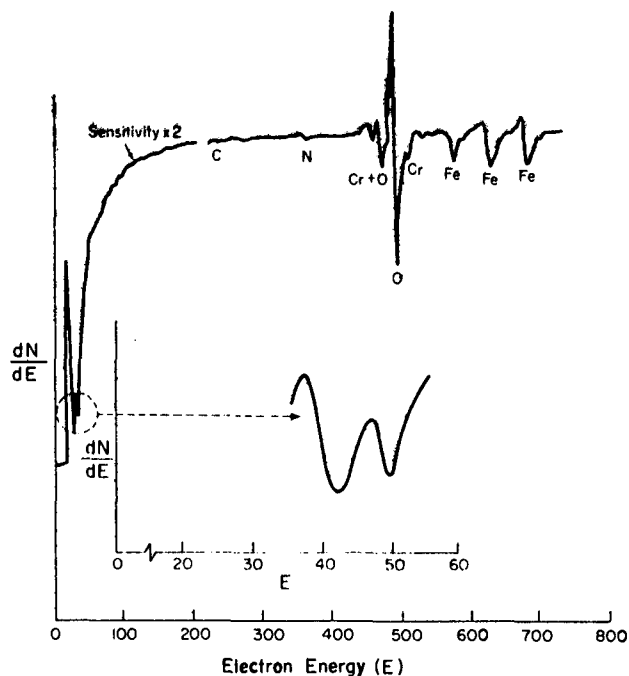


Fig. 9. Auger spectra of the passive film on Fe-25Cr-5Mo after 5 min of sputtering.

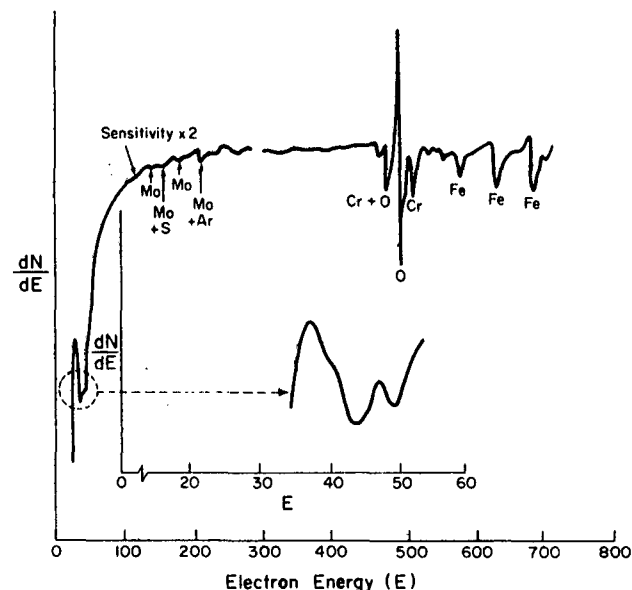


Fig. 10. Auger spectra of the passive film on Fe-25Cr-5Mo after 10 min of sputtering.

spectrum which was observed from Fe in the ferrous state. Figure 11 shows the spectra which resulted after 15 min of sputtering. The valence band spectrum for Fe at this depth is the same as that obtained for a Fe free surface although a substantial amount of oxygen remains here after the film has been sputtered for 15 min. The implication of the latter result is that oxygen is bonded to the Cr with iron being in the metallic state. The spectra obtained after 20 min of sputtering are given in Fig. 12. These spectra are essentially the same as those in Fig. 11 except that the oxygen level has substantially decreased and the Fe lines have increased in amplitude. Figure 13 summarizes the above results. This pattern was also observed for films formed by anodic polarization.

Discussion

The role of alloying elements in improving corrosion resistance properties is frequently interpreted in terms of the relative range of the thermodynamic stability,

phase or compound whose bulk properties are not known or one must consider the kinetics. The films formed at pH 14 were found to be depleted of chromium; this is consistent with the potential-pH diagram if the insoluble product is considered to be Cr_2O_3 . The vertical line representing the boundary between passivity and corrosion, i.e., $[\text{CrO}_3^{2-}] = 10^{-6}$, is located at approximately pH 12.5 for Cr_2O_3 .

The influence of potential on the chromium and iron content of the film is also predictable from thermodynamics. At 1250 mV (NHE) soluble chromate ions and insoluble Fe_2O_3 are the stable species (Fig. 7). The results obtained after cathodic polarization should be compared with those obtained in caustic solutions since the evolution of hydrogen at the electrode is accompanied by the generation of hydroxide ions. This raises the pH at the electrode surface. Both cathodic polarization in the pH 3.5 solution and anodic polarization in pH 14 solution (compare Fig. 6 and 8) resulted in a chromium depleted-iron enriched film.

Legitimate questions can be raised about the effectiveness of the Auger technique in detecting molybdenum since it seems inconceivable that an alloying addition which can increase the pitting potential over 500 mV would not be a major constituent of the film. Yet the Auger results for the relative amounts of chromium and iron in the passive films were consistent with solubility arguments. Thus, one would suspect that if the technique were altering the composition of metal ions in the film, it would be manifested in the behavior of these constituents as well as molybdenum.

A further question is whether or not the electron and ion beams are volatilizing the molybdenum oxide. Figure 15 shows the Auger spectra of a cathodically deposited molybdenum oxide film (from a molybdate solution). This film has a substantial amount of molybdenum and a small amount of iron, thus duplicating a passive film on an iron base alloy enriched in molybdenum. The spectrum remained unchanged after 5 and 15 min bombardments by the electron gun. Figure 16 shows spectra taken before and after 40 min of sputtering. Again, there were no anomalies. Although the carbon and nitrogen levels decrease substantially after 40 min of sputtering, there were only slight changes

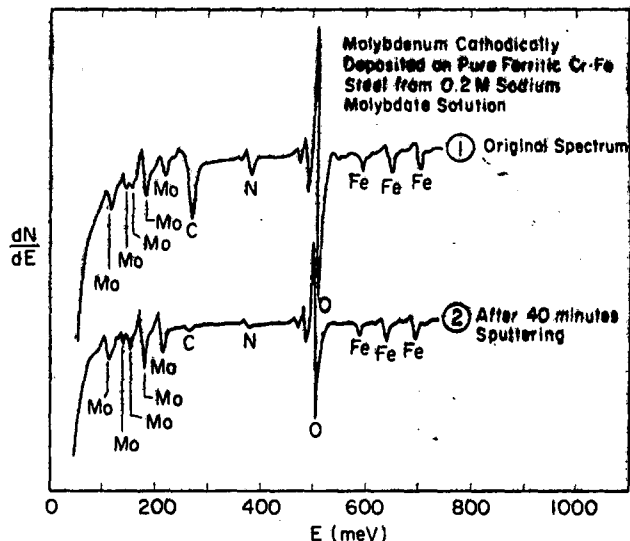


Fig. 16. Effect of sputtering on cathodically deposited molybdenum oxide film.

in the peak height ratios of the other elements. These changes could be due to the removal of adsorbed molybdate ions and water from the surface or due to an inhomogeneous film. However, the important point is that molybdenum is not preferentially removed by sputtering. Thus, these results suggest that if molybdenum is, in fact, enriched in the film, the Auger technique would detect it.

One of the inherent uncertainties in the profiling technique is the possible occurrence of differential sputtering. This arises because elemental sputtering yields are different, which results in an altered surface layer enriched in the element with the lower sputtering yield. Frankenthal and Malm (20) have concluded that films formed on iron-chromium alloys during mechanical polishing are not differentially sputtered. It is uncertain whether these results can be applied to this investigation since a different ion beam energy was used; however, when a 600 eV ion beam is used to sputter a mechanically polished surface, the Auger results are similar to the results of Frankenthal and Malm. Also, there is no evidence that large differences in the elemental sputtering rates exist. For example, if this phenomenon were causing an apparent enrichment of chromium in the films, then one would expect to observe an enrichment in those films in which chromium was depleted from the surface layers.

Carbon contamination was found on all surfaces. This was probably from hydrocarbon or carbon dioxide which was adsorbed when the specimens were transferred from the cell to the vacuum system. The varying concentrations of these overlayers cause the difference in behavior of the oxygen peak decline in Fig. 1, 2, and 7.

When the oxygen level is large relative to that of chromium, the oxygen line (510 eV) causes some distortion in the chromium line (529 eV). Coad and Cunningham (21) have analyzed iron and chromium mixed oxides using both XPS, in which there is no interference between lines, and AES. These results indicate that the errors caused by the distortion are not significant.

The Auger results for the composition of passive films differ substantially from those obtained by chemical analysis. Perhaps the high silicon and molybdenum content found by Rhodin and Nielsen (2,3) occurs because the film-stripping procedure created an altered layer. It is conceivable that such a layer would contain undissolved silicon and molybdenum from the alloy.

The Auger results eliminate from consideration the enrichment idea for explaining the improved quality

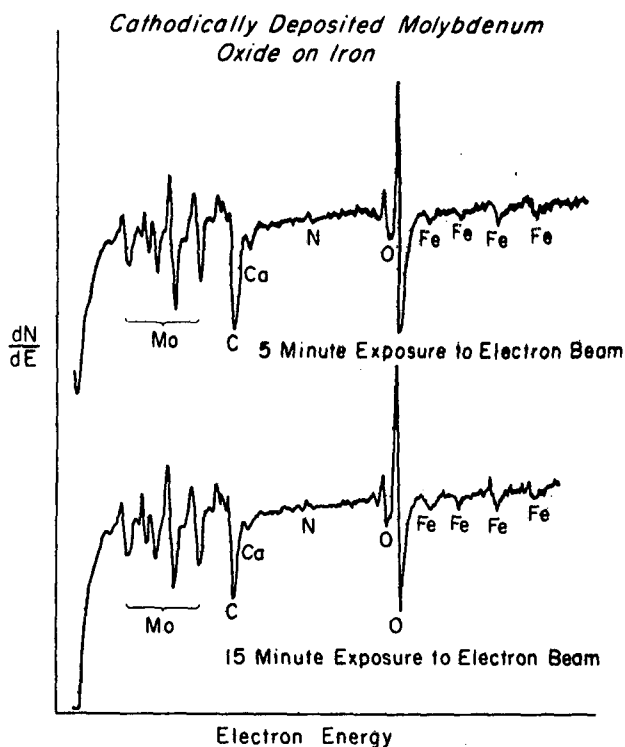


Fig. 15. Effect of electron beam on cathodically deposited molybdenum oxide film.

of the protective film derived from the presence of molybdenum in the alloy. Other possibilities for rationalizing the effects of molybdenum include an increased repassivation rate (8) or the prevention of localized acidification (19) by altering the corrosion potential or anodic dissolution kinetics. Electrochemical results indicate that indeed, both the corrosion potential and the potential necessary to maintain the high current density required to sustain pit growth increased with increased molybdenum content in the ferritic stainless steels (22).

Perhaps molybdenum exerts its beneficial effects by improving the quality of the bonding at the metal-oxide interface creating a barrier layer. There are two possible interpretations of the results shown in Fig. 9-13. One is metallic iron which is present in a chromium oxide matrix (possibly two-dimensional). The other is that there is a chromium oxide layer adjacent to the substrate. The presence of molybdenum in the layer could have a substantial influence on the quality of the bond.

Acknowledgments

The authors gratefully acknowledge support from the National Science Foundation, Grant No. DMR74-08061, and from the American Iron and Steel Institute, Grant No. 61-244.

Manuscript submitted Sept. 13, 1976; revised manuscript received Dec. 6, 1976.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1977 JOURNAL. All discussions for the December 1977 Discussion Section should be submitted by Aug. 1, 1977.

Publication costs of this article were assisted by The Ohio State University.

REFERENCES

1. M. A. Streicher, *This Journal*, **103**, 375 (1958).
2. T. N. Rhodin, *Corrosion*, **12**, 465t (1956).
3. N. A. Nielsen and T. N. Rhodin, *Z. Electrochem.*, **62**, 707 (1958).
4. E. A. Lizlovs, *Corrosion*, **22**, 297 (1966).
5. E. A. Lizlovs and A. P. Bond, *This Journal*, **116**, 574 (1969).
6. E. A. Lizlovs and A. P. Bond, *ibid.*, **119**, 22 (1971).
7. E. A. Lizlovs, ASTM STP 516, 250 (1972).
8. J. Kruger and J. R. Ambrose, NBS Report NBSIR 74-583 (September 1974).
9. H. H. Uhlig, Joint Japan-USA Seminar on Passivity and its Breakdown on Iron and Iron Base Alloys, NACE, Houston, Texas (1976).
10. J. B. Lumsden and R. W. Staehle, *Scr. Metall.*, **6**, 1205 (1972).
11. J. B. Lumsden and R. W. Staehle, ASTM SPT 596 (1976).
12. "Metals Handbook," Vol. 8, pp. 44-26, ASM, Metals Park, Ohio (1975).
13. N. D. Greene, "Experimental Electrode Kinetics," Rensselaer Polytechnic Institute, Troy, New York (1965).
14. P. W. Palmberg, G. K. Bohn, and J. C. Tracy, *Appl. Phys. Lett.*, **15**, 254 (1969).
15. P. W. Palmberg, *J. Vac. Sci. Technol.*, **9**, 160 (1972).
16. P. W. Palmberg, in "Electron Spectroscopy," D. A. Shirley, Editor, North Holland Publishing Company, Amsterdam (1972).
17. M. Seo, J. B. Lumsden, and R. W. Staehle, *Surf. Sci.*, **50**, 541 (1976).
18. J. R. Galvele, *This Journal*, **123**, 464 (1976).
19. M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions," Pergamon Press, New York (1966).
20. R. P. Frankenthal and D. L. Malm, *This Journal*, **123**, 186 (1976).
21. J. P. Coad and J. G. Cunningham, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 435 (1974).
22. J. R. Galvele and J. B. Lumsden, To be published.

Surface segregation in alloys: Equilibrium segregation of Au to the (111) surface of Ni

J. J. Burton, C. R. Helms, and R. S. Polizzotti

Exxon Research and Engineering Company, Linden, New Jersey 07036

(Received 27 August 1975; in final form 1 October 1975)

The experimental pitfalls in determining the equilibrium composition of an alloy surface are discussed. Among them are too-slow bulk diffusion, surface evaporation, and contamination. These problems are illustrated with data on alloys containing less than 1% Au in Ni. We show that in the temperature range 800°–1000°C, one can with care measure the equilibrium concentration of Au on the surface of the alloy using Auger spectroscopy. The heat of segregation of Au to the (111) surface of Ni has been obtained to be 12 ± 2 kcal/mole.

PACS numbers: 64.80.C, 82.80.L, 79.20.F

Gibbs¹ predicted a century ago (in 1875) that the equilibrium composition of the surface of a solution is not necessarily identical to its bulk composition. The solute will segregate to the surface of the solution if the surface free energy of the solution decreases with increasing solute concentration. This effect was confirmed by McBain^{2,3} in 1932 for a variety of solvents in water.

Recently many investigators have studied segregation of one component of a solid metallic alloy to its surface.^{4–23} There are major discrepancies in the results of various experimental studies intended to ascertain the equilibrium surface composition of alloys. For instance, using Auger electron spectroscopy as a probe of the surface composition, some authors^{9,10} have concluded that no surface segregation occurs in Cu-Ni alloys while others^{4,14,17,18} have reported substantial segregation of Cu to the surface of Ni. These investigations suggest the need to thoroughly examine the problems associated with attaining equilibrium surface compositions.

In this paper, we report on Auger electron spectroscopy studies of the surface composition of the (111) surface of very dilute alloys of Au in Ni. All the samples studied contained less than 1 at.% Au. This material was chosen as a model system to examine the problems associated with establishing equilibrium behavior primarily because the various theories^{24–26} of surface segregation all predict segregation of Au to the Ni surface and because Williams¹² has previously reported segregation of Au to the surface of Au-Ni alloys.

In the course of our work, we identified a number of potential pitfalls in determining the equilibrium behavior of an alloy surface. Illucidation of these difficulties will be the major task of this paper. Among the

problems identified are

(1) Contaminants can alter the surface composition. Hence, work must be carried out on very clean surfaces or the effects of contamination must be specifically studied.

(2) Surface composition measurements must be made at elevated temperatures and not after quenching to room temperature.

(3) Experiments must be performed at sufficiently high temperatures that equilibrium is attained.

(4) Experiments must be performed at sufficiently low temperatures that significant depletion of the solute from the surface by evaporation is avoided.

While the first two of these difficulties can be overcome in any careful experiment, the latter two combined imply that the equilibrium composition can be readily determined in only a very narrow temperature range in the conventional Auger experiment (described in the section on method). We discuss the problems of establishing that equilibrium is indeed seen. In dilute alloys of Au in Ni, the equilibrium behavior can be easily established in the temperature range 800°–1000°C. From the equilibrium surface composition measurements, we obtained the heat of segregation of Au to the (111) surface of Ni, 12 ± 2 kcal/mole.

EXPERIMENTAL METHODS

All of the samples used in this study were prepared by vapor depositing 99.999 at.% Au onto (111)-oriented, 0.2-mm-thick, 99.999 at.% Ni single crystals. After depositing about 1 at.% Au onto the crystal, it was annealed in vacuum at 750°C for several days; the surface was repolished; and the sample was then further annealed in vacuum at temperatures between 1000° and 1050°C for times up to a week. In this way, Au-Ni alloys were obtained containing less than 1 at.% Au

in the several-micrometer-thick surface region whose average composition was estimated with a microprobe.

Measurements of the surface composition of the alloys were made with a Physical Electronics cylindrical-mirror single-pass Auger analyzer using a beam current of 35 μA and beam energy of 2000 eV. The analyzer axis was 5° from the sample normal. All measurements, except where specifically noted, were made at pressures below 2×10^{-10} Torr (2.6×10^{-8} Pa). The sample was heated using an electron beam heater which enabled Auger measurements at elevated temperatures without any of the magnetic field effects associated with resistive heating.

OBSERVATIONS

Auger spectra

In Fig. 1 we show derivative Auger spectra of Au and Ni reference samples and of a Ni sample containing 0.5 at.% Au. Prior to taking the alloy spectrum, the sample was sputter cleaned and then annealed at 600°C for 18 h. The spectra are quite distinct. The strongest peak in Ni is at 61 eV and Au has its strongest peak at 69 eV. [The peak which we are referring as a 69-eV gold peak is actually a compound of 66- and 69-eV peaks. We were able to resolve these peaks, but shall use the compound peak in this paper.] The alloy exhibits both the 61- and 69-eV peaks, in approximately equal strengths. As the Au (69) and Ni(61) peaks are roughly equally strong in the pure metals, their near equality in the alloy indicates that the surface region (the 61- and 69-eV Auger peaks sample only a few planes into the crystal^{17,18}) contains comparable amounts of Au and Ni. Note that, unlike the 61-eV peak, the Ni Auger peaks above 600 eV are essentially undiminished in the alloy from their weights in bulk nickel. As the higher-energy Auger peaks sample more deeply into the crystal than do the low-energy peaks, it appears plausible that the large concentration of Au seen in the 69-eV peak in the alloy may be confined to the surface plane itself. This qualitative conclusion, that the segregant may be mainly limited to a surface monolayer, is in agreement with the conclusions of theoretical studies of surface segregation based on simple models,²⁵ with McDavid and Fain's experimental results for segregation of Au to the surface of Cu-Au alloys²³ and with McBain's classical studies of the surface composition of liquid solution.²⁷

In the remainder of this paper, we will be discussing primarily the ratio of the height of Au(69) Auger peak to that of the Ni(61) peak. This ratio, Au(69)/Ni(61), provides a measure of the surface composition.²⁸ For instance, if the surface plane were pure gold and the remainder of the crystal had the bulk composition, we would expect Au(69)/Ni(61) to be about 2. If the surface is 50 at.% Au, Au(69)/Ni(61) would be about 0.60; if the surface is 10 at.% Au, the ratio would be about 0.09. These numbers are only approximate and serve only to provide a qualitative guide to interpreting the

103

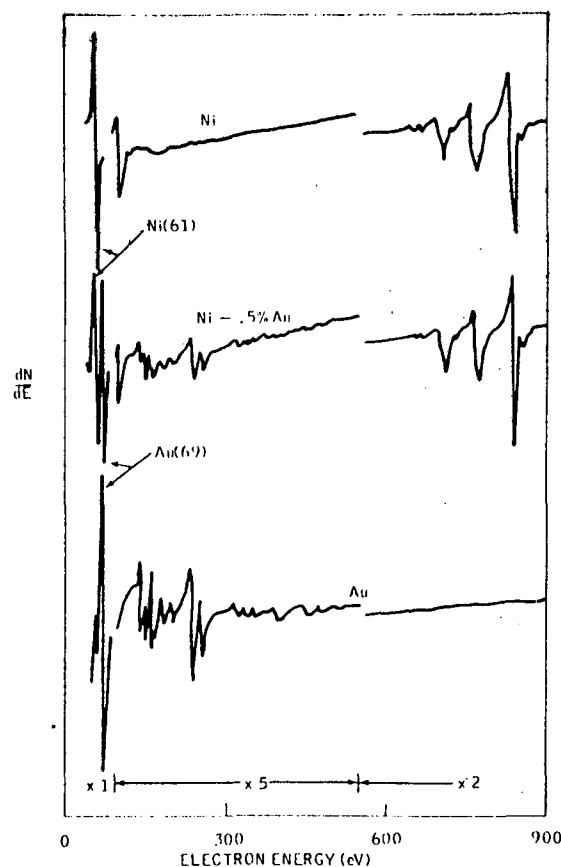


Fig. 1. Auger spectra of Au, Ni, and Ni-0.5 at.% Au. The 69-eV Au and 61-eV Ni Auger peaks which will be employed in this work are indicated. The sensitivity of the analyzer was changed at 90 and at 600 eV; the sensitivities are noted on the figure.

data in the following sections, where we will be presenting data for the Auger-peak-height ratio for various samples and sample treatments. In the discussion section of the paper, we will return to the question of the meaning of the Auger peak-height ratios.

Contamination effects

In LEED studies of solid surfaces, the importance of small amounts of surface impurity has long been appreciated. The effects of contamination on the surface composition of an alloy have been less widely commented on. We have made some observations on effects of surface impurities which we will briefly summarize here.

Some of our samples were found to contain traces of sulfur which was cleaned off by sputtering at high temperatures. In the course of this cleaning, we had the opportunity to observe the effect of the sulfur on the surface composition. We found that even small amounts of S could significantly reduce the amount of Au on the surface, even in the most dilute alloys. For one sample, with a nominal bulk concentration of about 0.5 at.% Au, Au(69)/Ni(61) was 0.27 at 1025°C when there was no sulfur noticeable on the surface. However, when the surface was covered with about 0.05 monolayer of S (as estimated very crudely from the ratio of the S(150) to Ni(102) Auger peak heights, S(150)/Ni(102) = 1.0), Au(69)/Ni(61) was reduced to 0.22. In general, we found that the Au concentration

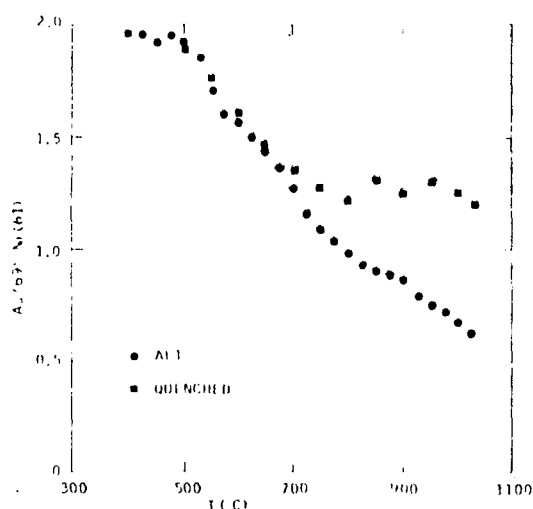


FIG. 2. Auger peak-height ratio $\text{Au}(69)/\text{Ni}(61)$ as a function of annealing temperature for a Ni crystal containing 1 at.% Au. Measurements were made both at the annealing temperature and after quenching to room temperature. Note that, at the higher temperatures, the two measurements do not agree.

decreased systematically as the sulfur increased. This phenomenon was seen at all temperatures.

Williams¹² has previously reported that exposure of Au-Ni alloys to oxygen can alter the surface composition. In order to investigate this, we heated a 0.2 at.% Au sample at 1000°C for 15 min and then quenched it to 100°C. This produced an Auger peak-height ratio of $\text{Au}(69)/\text{Ni}(61) = 0.085$. The sample was then exposed at 100°C to 1×10^{-8} Torr (1.33×10^{-6} Pa) of O_2 and the $\text{Au}(69)/\text{Ni}(61)$ ratio measured. After a 2500-s exposure (25 Langmuir), the surface had about 0.2 monolayers of O on it [assuming that the Auger oxygen signal from a heavily oxidized (200-Langmuir exposure at 100°C) Ni surface originates from a monolayer of O] and $\text{Au}(69)/\text{Ni}(61)$ was still 0.085. After 6000 s of exposure, the surface had about 0.6 monolayers of oxygen and $\text{Au}(69)/\text{Ni}(61)$ was reduced to 0.013.

These observations indicate the importance of working with clean surfaces in studies of alloy surface composition. All of the remaining data in this paper will be from surfaces with contamination below the lower limit of detectability in our system, which we estimate to be about 0.01 monolayer for C, 0.005 monolayer for O, 0.005 monolayer for P, and 0.005 monolayer for S.

Quenched samples

Many previous workers have carefully prepared their alloys by extensive annealing at high temperatures and then quenched the samples to room temperature, where they measured the surface composition, assuming that they would obtain the surface composition characteristic of the annealing temperature. In Fig. 2 we compare the surface composition ratios, $\text{Au}(69)/\text{Ni}(61)$, of a 1 at.% Au alloy made at temperature and after quenching to room temperature. In each case, the alloy was annealed for 10 min at temperature between the measurements. The quench rate was about 80°C/s. It is obvious that, at the higher temperatures, the data

measured at temperature and after quenching do not superimpose. This occurs because, during the quench, the sample surface has time to relax to a composition characteristic of a temperature lower than the annealing temperature. Therefore, in order to study the equilibrium composition of the alloy surface, it is necessary to make measurements at temperature.

ESTABLISHMENT OF EQUILIBRIUM

There are two phenomena which conspire to make difficult the measurement of the equilibrium composition of an alloy surface. These are slow diffusion and fast evaporation. If the diffusion coefficient is very low, the times required to attain equilibrium can be long compared to the time available to the experiments.²⁷ This problem can be obviated by waiting or by working at a higher temperature. At high temperatures, the vapor pressures of the alloy constituents can be significant and free evaporation from the surface can alter the surface composition.⁸ This problem can be overcome either by establishing the equilibrium metal vapor pressure in the sample chamber, which is difficult in practice, or by working at lower temperatures where significant evaporation does not occur.

Evaporation problems can be recognized in at least two ways. The most obvious is to place a cold collector near the sample and examine it for evaporants. In practice, this is sometimes inconvenient and, in addition, it only tells that evaporation is occurring, not whether it is sufficiently rapid to seriously perturb the surface composition. The second way to recognize evaporation is that it leads to a serious reduction in the concentration of segregant on the surface.⁸ From the data in Fig. 2, we would expect that were our 1 at.% Au sample heated to 1050°C, $\text{Au}(69)/\text{Ni}(61)$ should be 0.5 to 0.6. When this sample was heated to 1050°C, within 10 s $\text{Au}(69)/\text{Ni}(61)$ was 0.55, as expected. However, this ratio then began to decrease after about 10 min so that it had fallen to 0.3 within 1 h. For comparison, at 1000°C, the equilibrium ratio, 0.68, was also obtained within 10 s; however, the composition then remained constant for 3 h. In both cases, the samples reach the equilibrium composition expected from Fig. 2 within the first 10 s at temperature. We think that at 1050°C, initially, diffusion was able to replace Au which evaporated from the Ni surface and the composition retained its equilibrium value. However, subsequently, as the supply of Au in the region near the surface began to be depleted and the Au atoms had to diffuse further to reach the surface, the observed Au concentration on the surface began to fall. At 1000°C, diffusion was sufficiently rapid (relative to evaporation) that the surface retained its equilibrium composition.

Our results indicate that evaporation of Au from the surface may introduce problems at temperatures above 1050°C. Therefore, the data in the rest of this section were taken at temperatures below 1000°C.

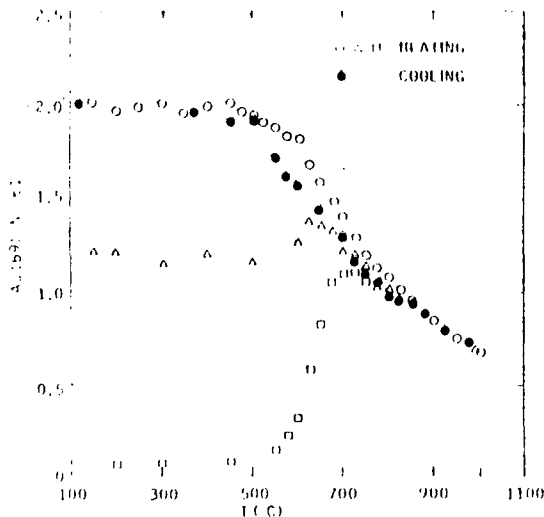


FIG. 3. Auger peak height ratio $\text{Au}(69)/\text{Ni}(61)$ of a 1 at.% Au alloy as a function of temperature for various heat treatments. Initially the sample was cooled, at a rate of $100^\circ\text{C}/\text{h}$ from 1000°C (filled circles). It was then heated, at a rate of $100^\circ\text{C}/\text{h}$ (open circles). It was then quenched from 1000°C to room temperature and heated at a rate of $100^\circ\text{C}/\text{h}$ (triangles). Finally, it was sputter cleaned at room temperature and heated at a rate of $300^\circ\text{C}/\text{h}$ (squares). Note that the various treatments give the same surface composition above 800°C , but not at low temperatures.

Slow diffusion is easily recognized. It manifests itself in hysteresis—that is, the observed surface composition of the sample will depend on its previous temperature history. This is illustrated in Fig. 3, where heating curves from well annealed, quenched, and sputter-cleaned 1 at.% Au samples are compared with a cooling curve. Note that, at temperatures above 800°C , all of the curves superimpose within experimental error. This superposition of cooling and the various heating curves is a strong test of equilibrium. The use of data from quenched or sputter-cleaned samples is particularly important as it serves as a check that the mobility is high enough that diffusion occurs at all in the time of the experiment.

HEAT OF SEGREGATION

All of the theories of surface segregation predict that the occupancy X_s of available surface sites by the segregant (Au in our case) should be related to the bulk composition X_b by an equation of the form^{24, 26}

$$X_s/(1 - X_s) = C \{X_b/(1 - X_b)\} e^{Q/RT}, \quad (1)$$

where Q is the heat of segregation; this equation is expected to describe a dilute surface layer (X_s small) well but may not be valid for concentrated alloys. We would like to obtain the heat of segregation from Auger data.

The intensity I of a particular Auger line of energy E is given, approximately, by an equation of the form²³

$$I(E) = D(E) (X_0 + e^{-d/\lambda(E)} X_1 + e^{-2d/\lambda(E)} X_2 + \dots), \quad (2)$$

where X_i is the concentration of the element giving rise to the Auger line in plane i (0 being the surface), d is the planar spacing, and $\lambda(E)$ is the penetration distance for an Auger electron with energy E .

In the very special case where the Au segregant is present in only minute quantities in the Ni bulk of the sample and all of the segregation occurs to the surface monolayer, as appears may be our case from the Auger data in Fig. 1 and as is suggested by theoretical studies^{25, 26} and by McDavid and Fain's experiments on Cu-Au alloys,²³ the gold and nickel Auger intensities, according to Eq. (2) should be related by

$$\text{Au}(69)/\text{Ni}(61) = D(69)X_0^{\text{Au}}/D(61)\{X_0^{\text{Ni}} + e^{-d/\lambda} + \dots\}. \quad (3)$$

Now if X_0^{Au} is also extremely small, i.e., $\ll 1$, X_0^{Ni} must be nearly 1. So, for the extremely dilute case,

$$\text{Au}(69)/\text{Ni}(61) = C X_0^{\text{Au}}; \quad (4)$$

comparing Eqs. (1) and (3) now we see that, for the very special case of extreme dilution where $X_s \ll 1$, the temperature dependence of Auger intensity ratio is directly related to the heat of segregation

$$\text{Au}(69)/\text{Ni}(61) = C e^{Q/RT}. \quad (5)$$

Therefore, a plot of $\text{Au}(69)/\text{Ni}(61)$ against $1/T$ for an extremely dilute alloy should give a straight line with slope Q/R .

Such an Arrhenius plot is shown in Fig. 4 for an alloy containing 0.2 at.% Au. Data are plotted only from the temperature range 800°C – 1000°C , where we have established that equilibrium is readily obtained. Note that this sample exhibits an order of magnitude less surface Au than does the sample discussed previously and so satisfies the conditions which led to Eq. (5): very dilute bulk impurity and low surface coverage. From the slope of the straight line through the data in Fig. 4, we compute the heat of segregation of Au to the Ni(111) surface to be 12 ± 2 kcal/mole.

CONCLUSIONS

In this paper we have discussed the problems involved in determining the equilibrium surface segregation behavior of an alloy. We have pointed out the need to work with very clean samples and the need to make

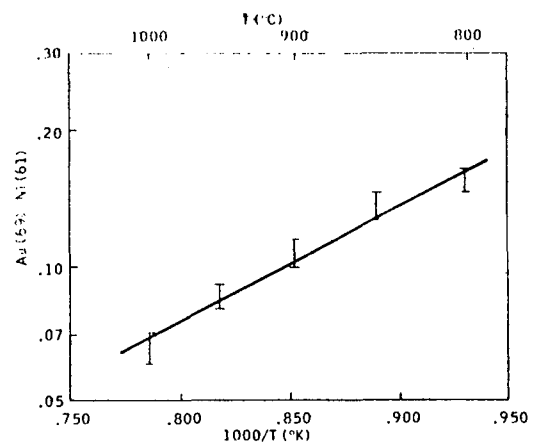


FIG. 4. Arrhenius plot of the equilibrium Auger peak-height ratio $\text{Au}(69)/\text{Ni}(61)$ for an alloy containing 0.2 at.% Au. Note that the data fall on a straight line.

measurements at elevated temperatures and not on quenched samples. We also have shown how to establish that equilibrium is attained. We noted that it is possible, on very dilute alloys, to deduce the heat of segregation from Auger data. We find that the heat of segregation of Au to the (111) surface of Ni is 12 ± 2 kcal/mole.

ACKNOWLEDGMENT

The authors wish to express their appreciation to T. Pugel for his invaluable assistance in performing these experiments.

- ¹J. W. Gibbs, *Trans. Conn. Acad. Sci.* **3**, 108 (1875/76), 343 (1877/78).
- ²J. W. McBain and C. W. Humphreys *J. Phys. Chem.* **36**, 300 (1932).
- ³J. W. McBain and R. C. Swain, *Proc. Soc. London A* **154**, 608 (1936).
- ⁴W. M. H. Sachtler and G. J. H. Dorgelo, *J. Cataly.* **4**, 654 (1965).
- ⁵R. Bouwman and W. M. H. Sachtler, *J. Cataly.* **19**, 127 (1970).
- ⁶J. Ferrante, *Acta Metall.* **19**, 743 (1971).
- ⁷H. P. Bonzel and H. B. Aaron, *Scripta Metall.* **5**, 1057 (1971).
- ⁸J. Ferrante, *Scripta Metall.* **5**, 1129 (1971).
- ⁹G. Ertl and J. Koppers, *Surf. Sci.* **24**, 104 (1971).
- ¹⁰D. Quinto, V. S. Sundaram, and W. D. Robertson, *Surf. Sci.* **28**, 504 (1971).
- ¹¹R. Bouwman and W. M. H. Sachtler, *J. Cataly.* **25**, 350 (1972).
- ¹²F. L. Williams and M. Boudart, *J. Cataly.* **30**, 438 (1973).
- ¹³R. Bouwman, L. H. Toneman, and A. A. Holscher, *Surf. Sci.* **35**, 8 (1973).
- ¹⁴Y. Takasu and H. Shimizu, *J. Cataly.* **29**, 479 (1973).
- ¹⁵S. Thomas, *Appl. Phys. Lett.* **24**, 1 (1974).
- ¹⁶S. C. Fain and J. M. McDavid, *Phys. Rev.* **B9**, 5099 (1974).
- ¹⁷C. R. Helms and K. Y. Yu, *J. Vac. Sci. Technol.* **12**, 276 (1975).
- ¹⁸C. R. Helms, *J. Cataly.* **36**, 114 (1975).
- ¹⁹G. L. Powell, R. E. Clausing, and G. E. McGuire, *Surf. Sci.* **49**, 310 (1975).
- ²⁰R. A. van Santen, L. H. Toneman, and R. Bouwman, *Surf. Sci.* **47**, 64 (1975).
- ²¹H. C. Potter and J. M. Blakely, *J. Vac. Sci. Technol.* **12**, 635 (1975).
- ²²L. C. Isett and J. M. Blakely, *J. Vac. Sci. Technol.* **12**, 237 (1975).
- ²³J. M. McDavid and S. C. Fain (unpublished).
- ²⁴D. McLean, *Grain Boundaries in Metals* (Clarendon, Oxford, UK, 1957).
- ²⁵F. L. Williams and D. Nason, *Surf. Sci.* **45**, 377 (1974).
- ²⁶J. J. Burton, E. Hyman, and D. Fedak, *J. Cataly.* **37**, 106 (1975).
- ²⁷J. J. Burton, *Phys. Rev.* **177**, 1346 (1969).
- ²⁸It is well known that the quantitative interpretation of Auger spectra is extremely difficult, if not impossible. However, our remarks here are qualitative and are intended only to provide a guide to understanding our data. All of our major conclusions will be based on changes in the Au (69)/Ni (61) peak ratio and not on the numerical value of the ratio itself. In general, we found on all of our samples that this ratio could be measured to accurately to at least 2 at. %.

EQUILIBRIUM SEGREGATION OF CARBON TO A NICKEL (111) SURFACE: A SURFACE PHASE TRANSITION

J. C. SHELTON*, H. R. PATIL** and J. M. BLAKELY

*Department of Materials Science and Engineering, and Materials Science Center, Cornell
University, Ithaca, New York 14850, U.S.A.*

Received 2 July 1973; revised manuscript received 15 November 1973

Equilibrium segregation of carbon to the (111) surface of carbon-doped nickel single crystals has been studied by Auger spectroscopy. At least three distinct equilibrium states of the surface occur, viz:

A, a high-temperature dilute carbon phase,

B, a condensed graphitic monolayer, separated from A by a sharp transition with temperature and

C, a multilayer epitaxial graphite precipitate.

State B persists in equilibrium about 100K above the observed equilibrium temperature for dissolving graphite into the nickel crystal. Our interpretation attributes this to (~ 0.05 eV) stronger binding of carbon to this monolayer phase than to bulk graphite. We believe the observed equilibrium A-B transition is the first equilibrium surface phase transition detected in segregation studies.

1. Introduction

The distribution of the components of an alloy near interfaces is of importance in a number of physical chemical and metallurgical phenomena. Accumulation of one of the components at the boundaries can have significant effects on electron emission characteristics, catalytic efficiency and fracture behavior. The theoretical problem of determining concentration profiles near free surfaces and other interfaces has been discussed extensively [Cahn and Hilliard¹), Meijering²), Murakami et al.³)] in the chemical and metallurgical literature. The problem is a complex one and quantitative predictions can be made only by using rather restrictive models for the solid solution. For example the regular solution model with nearest neighbor interactions derived from bulk properties has been used both in discrete lattice and continuum approaches to the evaluation of concentration profiles near boundaries.

* Present address: Bell Telephone Laboratories, Murray Hill, New Jersey 07974, U.S.A.

** Present address: Physical Electronics Laboratory, Hewlett-Packard Company, Palo Alto, California, U.S.A.

The term *segregation*, as applied to alloy systems, refers to an increase in the concentration of one or more of the components near lattice discontinuities. In this paper we shall be concerned with *equilibrium segregation* in a binary alloy. By this we mean compositional heterogeneity in thermal equilibrium under conditions which correspond to a one-phase field on the phase diagram. We thus distinguish equilibrium segregation from inhomogeneities which arise due to equilibrium phase separation (precipitation). *Non-equilibrium segregation* is a transient phenomenon and may occur, for example, during solidification or quenching of alloys. For example, segregation of impurities at grain boundaries in a number of systems [Aust et al.⁴), Anthony⁵), Parker⁶)] is believed to be due to the interaction of the impurities with lattice vacancies which migrate to the boundary as their sink during cooling.

In many ways impurity segregation is analogous to the phenomenon of adsorption at crystal-vapor interfaces; only the source of the adsorbate is different and the concentration of the impurity in the crystal interior is the variable which corresponds to gas pressure. The formal thermodynamic treatments of the two phenomena are essentially the same and, for example, the Gibbs' adsorption isotherm can be developed in both cases. Strictly speaking when a crystal is in equilibrium with a vapor of another component there will always be some atoms or molecules from the vapor dissolved in the crystal so that *equilibrium segregation* and *equilibrium adsorption* at a solid-vapor interface in a binary system are identical phenomena. We refer to the phenomenon as adsorption if we experimentally fix the gas pressure of one of the constituents and as segregation if we experimentally fix the concentration of the minor constituent in the solid solution.

There have been relatively few *equilibrium* studies of either adsorption or segregation at single crystal surfaces. In many of the interesting chemisorption systems the binding energy of the adsorbate to the surface is so high (several eV) that it is not possible to obtain equilibrium coverages significantly less than a monolayer over the experimentally controllable pressure range. Some equilibrium studies have however been made of gas adsorption on single crystals. Extensive studies have been made of the adsorption of sulphur on various surfaces [Bénard⁷), Domange and Oudar⁸), Kostelitz et al.⁹)] and equilibrium adsorption isotherms (as well as structural information from LEED) have clearly indicated the importance of interactions among adsorbate atoms. There have been numerous reports in the literature of impurity accumulation at free surfaces during crystal annealing and in a number of cases the impurity produces an ordered structure [see for example, Blakely et al.¹⁰)] related to that of the substrate. In a few cases the solute accumulation has been found to be reversible [Ferrante¹¹), Blakely et al.¹⁰), Bonzel and Aaron¹²)] and to be approximately of Langmuir[†] type; i.e. the tempera-

ture dependence of the occupation of surface sites may be described by a Fermi function.

In the present paper we describe equilibrium studies of the segregation of carbon to the (111) surface of a dilute Ni-C alloy. The segregation is not accounted for by the Langmuir model and in fact *three distinct equilibrium states** of the surface have been identified. At high temperatures, a state of low carbon coverage (state A) exists (possibly the lattice gas region). In a wide intermediate temperature range the carbon coverage is constant (state B), interpreted as a single segregated monolayer. This segregated state is limited at low temperatures by precipitation on the surface of multilayer graphite (state G). For the purpose of later analysis we identify the transition between B and G with normal bulk precipitation. The transition between states A and B is abrupt and is interpreted in terms of a simple Bragg-Williams condensation model for interacting atoms. A statistical thermodynamic analysis is used to obtain a value for the average binding energy of carbon in state B. An extension of this work to the study of the temperature variation of the equilibrium surface coverage of solute atoms in other systems offers a means of obtaining energies of adsorption in cases where it is too large to be accessible from measurements of coverage with varying gas pressure.

The principle technique employed in this work has been that of Auger electron spectroscopy (AES) [Harris¹⁶], Chang¹⁷], Taylor¹⁸)] using both a retarding field analyser (RFA) and a cylindrical mirror analyser (CMA) [Palmberg et al.¹⁹]] for determining the secondary electron energy distributions. Supporting experiments include low energy electron diffraction observation of the structure of the segregated layers and argon ion bombardment studies of their thickness.

2. Experimental

The Ni-C system has a number of attractive features [Graham²⁰]] as a model system for the study of solute segregation to free surfaces. Nickel surfaces have been extensively studied and techniques for producing clean surfaces have been well established. The solubility of carbon in nickel has been measured quite accurately [Lander et al.²¹], Dunn et al.²²]] and is quite large, about 0.5 at % at 1000 K, with a heat of solution of 0.49 eV. [Roughly speaking the heat of solution is the energy of a carbon atom in the Ni matrix minus its energy in a pure graphite crystal (see section 4.2, fig. 13).] The large solubility allows the use of doping levels significantly higher than those of

[†] The Langmuir isotherm is sometimes referred to as the McLean isotherm [McLean¹³]] in segregation work.

^{*} The possibility of chemical and structural transformations at interfaces has been discussed by Hart^{14,15}).

background trace impurities and gives precipitation temperatures within the readily accessible temperature range. This leads to reversible variations in surface carbon level as previously demonstrated in related work on Ni(100) [Blakely et al.¹⁰], (110) [Sickafus and Colvin^{23,24}] and polycrystalline Ni [Coad and Rivière²⁵]. On the other hand when the solubility limit is very low, as for example with C in Au or Pt, precipitation may occur over most of the normal temperature range. The diffusion coefficient of C in Ni is also quite well known [Massaro and Peterson²⁶]; this information is useful in establishing that the bulk crystal and not the vapor is the source of the carbon accumulation observed experimentally. In addition surface graphitization is of some interest in heterogeneous catalysis by the transition metals.

The (111) oriented Ni specimen was prepared by standard techniques [Shelton²⁷] of orienting, cutting, and mechanical and chemical polishing from a large nickel crystal (1.5cm diameter and 10cm long) doped with carbon nominally to $\sim 0.26\text{at}\%$. The initial nickel crystal was grown from INCO grade 270 nickel with two passes of an electron beam heated floating zone at 5×10^{-6} torr. The doping was accomplished by a third pass in CO at 4×10^{-5} torr. The crystal was then homogenized by rf heating in a quartz capsule for 100hr at 1200°C and quenched in water. Even after this treatment, considerable variation in carbon level was found for different portions of the same crystal analyzed by inert gas fusion techniques. The bulk doping level is thus not known to better than a factor of two of the nominal value; as we shall see later this has only minor consequences in interpreting the data.

The final specimen consisted of a thin sheet (14mm $\times$ 5.3mm $\times$ 0.3mm) welded between Mo supports which were wrapped with high purity Ni foil, 0.05mm thick, and mounted on a standard LEED chamber manipulator. After bakeout the surface impurities detected by Auger spectroscopy were C, O, S, Cl and N. Argon ion bombardment at 400eV, 1 μ A/cm², 10^{-4} torr decreased the Cl and N below detectability and the oxygen to less than a few percent of its initial value. The surface sulphur concentration was decreased but not eliminated by bombardment; it was reduced to an insignificant concentration by cycles of annealing (during which the sulphur accumulated at the surface) and bombarding. From the work of Perdereau et al.²⁸⁻³⁰ and of DuCharme and Gerlach³¹ we estimate that the sulphur surface concentration in these experiments was $\sim 1\text{at}\%$. In other experiments somewhat larger sulphur concentrations were found to have negligible effect; sulphur concentrations an order of magnitude larger only reduced the carbon signal in state B and produced a complex structure [which has been termed $\sqrt{39} \times \sqrt{39} R$ (16.1°) by McCarroll et al.³²] and has also been reported by Perdereau and Quidar²⁸].

The crystal was heated resistively and temperature measured with a

EQUILIBRIUM SEGREGATION OF C TO A Ni(111) SURFACE

chromel-almel thermocouple spot welded to the back face. Temperature gradients were as high as 7 K/mm* as measured optically. Temperature fluctuations were within 0.2 K and relative temperatures are accurate to about 5 K. Experiments were carried out in two different stainless steel, ion-pumped vacuum systems which housed the electron analysers used in this work. Pressures of $1-2 \times 10^{-10}$ torr were routinely obtained with maximum pressures during annealing at ~ 1200 K of less than 10^{-9} torr. With the cylindrical mirror analyser system the incident electron energy was generally about 1400 eV, the beam current typically 25 μ A, the beam width at the specimen 0.7 mm and the angle of incidence about 68° from the crystal surface normal. The signal from the electron multiplier of the analyser was detected by conventional phase sensitive detection techniques [Chang¹⁷] at 38 kHz with 12 db/oct roll-off and 0.3 sec time constant. In the retarding field analyser the typical operating characteristics were: incident electron beam energy ~ 1340 eV, beam current $\sim 2.5 \mu$ A, beam width 0.8 mm (measured using a subsidiary phosphor screen) and angle of incidence $\sim 30^\circ$ from the surface normal. The retarding field analyser was a 4 grid LEED system operated in a manner similar to that described by Palmberg³⁴). The axis of each analyser was normal to the incident electron beam and in the plane of the beam and the surface normal.

Fig. 5 is an example of the spectra obtained using the retarding field analyser. The principal features may be identified with reference to table 1, where the peak energies are given according to the normal convention as those at the minima in the derivative of the secondary electron energy distribution. The important peaks referred to in other figures are the 62 eV, 105 eV and 850 eV nickel Auger peaks and the 270 eV carbon Auger peak. The plasmon loss peaks (at multiples of 29 eV) observed with graphite covered surfaces have been discussed in some detail in another report [Patil and Blakely³⁵]). In the results presented below the heights of the various Auger peaks are given as a function of temperature and interpreted in terms of surface coverages. We have taken as the quantitative measure of peak strength the *inflection height* defined as the height from the maximum to the minimum in a derivative spectrum. No correction has been made for peak shape or background slope [Taylor¹⁸]). Shape changes with variations in surface coverage were found to be negligible except for the C Auger peak which was significantly narrower in the low coverage range (state A). The uncorrected inflection peak height of carbon thus overestimates the carbon concentration in state A since the peak strength is better represented by the product, height $\times$ (width)² from a derivative spectrum.

* By inducing large changes in the temperature gradients, thermomigration was found to be negligible in agreement with Shaw and Oates³³).

TABLE I
Identification of the main peaks observed in the secondary spectra

Peak	Energy (eV)	Material	References
Elastic	Beam energy, E_0	—	—
Loss	$(E_0 - 29)$ $(E_0 - 26)$	Graphite Nickel	Hartley and Swan ⁵⁷⁾ Heimann and Holz ⁵⁸⁾
Loss	$(E_0 - 70)$	Nickel	Heimann and Holz ⁵⁸⁾
Loss	$(E_0 - 2 \times 29)$	Graphite	Hartley and Swan ⁵⁷⁾ Scheibner and Tharp ⁵⁹⁾ Coad and Rivière ²⁵⁾
Loss	$(E_0 - 3 \times 29)$	Graphite	—
Loss	$(E - 300)$	Graphite	Bishop and Rivière ¹³⁾ Coad and Rivière ²⁵⁾
Auger $L_{23}VV$	850	Nickel	Coad and Rivière ^{25, 60)} Aksela et al. ⁶¹⁾ Yin et al. ⁶²⁾
Auger (M_1VV)	105	Nickel	—
Auger ($M_{2,3}VV$)	62	Nickel	—
Auger (KVV)	270	Carbon	Lander ⁶³⁾ Amelio and Scheibner ⁶⁴⁾ Palmberg ¹⁹⁾ Coad and Rivière ²⁵⁾ Haas et al. ⁶⁵⁾
Auger ($L_{23}M_{23}M_{23}$)	150	Sulfur	Dalmaj-Imelik et al. ⁶⁶⁾
Auger ($KL_{23}L_{23}$)	520	Oxygen	Palmberg et al. ⁶⁷⁾

The rate of change of the carbon Auger peak height with time could be used to test the assumption that the crystal interior was the source and sink for carbon. A direct demonstration that the carbon was not derived from ambient gases consisted of heating an undoped (111) nickel crystal for periods up to days (both with and without the electron beam) at temperatures between 500 K and 1000 K; the carbon Auger peak remained unchanged at much less than the saturation level. In doped samples, surface carbon could be cycled between roughly monolayer and bulk doping levels by large temperature changes in about 30 sec with pressure at $\sim 5 \times 10^{-10}$ torr.

3. Results

The variation of the peak height with temperature for a number of Auger peaks was monitored both with the cylindrical mirror analyser and with the retarding field analyser. In the CMA we relied on the well known focussing properties [Aksela³⁶]) to insure that the same area of the specimen was being examined as a function of temperature. The crystal was not moved after positioning it at the focal spot (by maximizing the elastic peak as a function of crystal and electron beam position). As magnetic fields due to the crystal heating current deflected the beam, it was repositioned on the focal spot by adjusting the deflection voltages on the gun to give a maximum elastic peak while preserving its symmetry. The observations with the RFA were made to confirm that the results in the CMA were not influenced by inhomogeneous composition along the sample. In the RFA the electron beam could be scan-

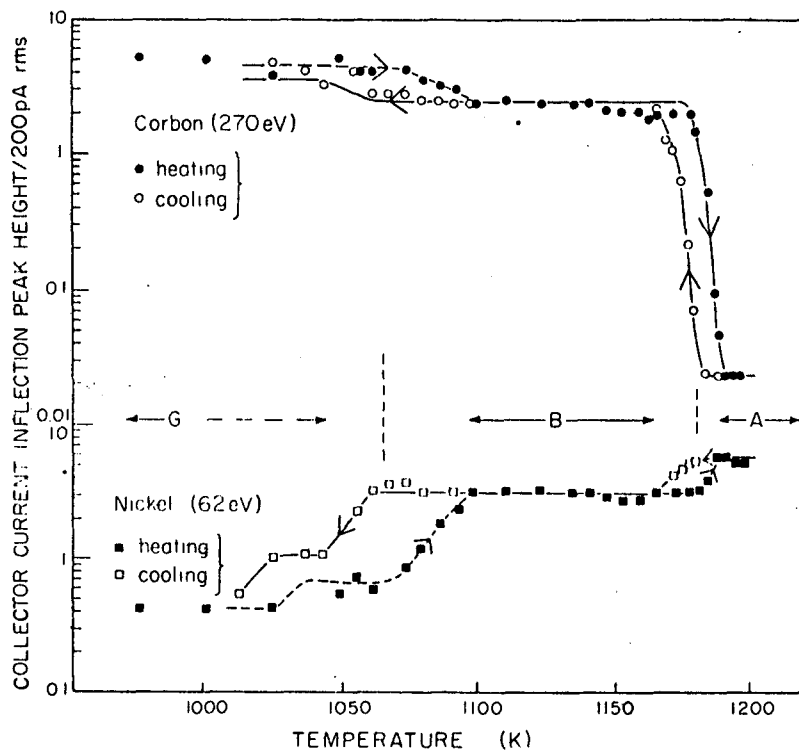


Fig. 1. Temperature dependence of the 270eV carbon and 62eV Nickel Auger peaks. Three states (A, B and G) of different carbon coverages are identified. Note the sharp decrease in carbon coverage at $\sim 1180\text{K}$. These data are for the CMA at an angle of incidence of 68° to the surface normal.

ned across the specimen without significantly affecting the line shapes and analyser collection efficiency. Electron diffraction observations gave some information on the structure of the segregated and precipitated phases. An attempt was made to probe the thickness of the surface layers by measuring Auger peak heights after various Argon ion bombardment doses in the RFA.

3.1. AUGER PEAK HEIGHTS VERSUS TEMPERATURE (CMA)

The main result is indicated in fig. 1; this shows the variation with temperature of the 62eV Ni Auger peak and the 270eV C Auger peak. The data in this figure were obtained by changing the temperature in a step-wise

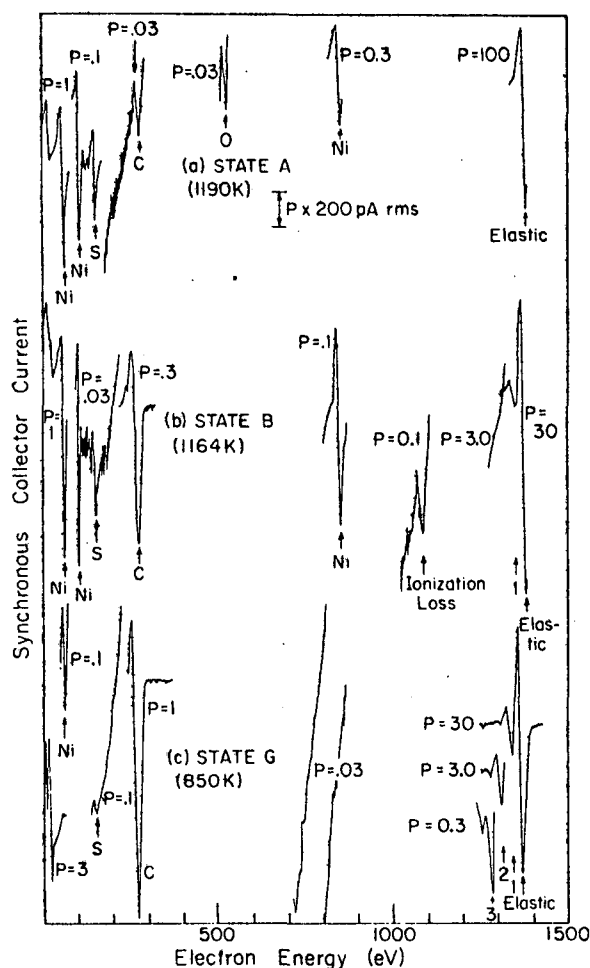


Fig. 2. Typical Auger spectra in the CMA at an angle of incidence of 68° . P gives relative full scale sensitivity of the electron multiplier and phase sensitive detector.

manner. The average heating rate was 25 K/hr to ~ 1100 K, 8 K/hr to ~ 1210 K; the cooling rate was ~ 3 K/hr from 1210 to 1010 K. The main features to note on the figure are the large and abrupt increases in the C peak heights coinciding with decreases in the Ni Auger peak and that otherwise the heights are independent of temperature. The heating and cooling rates below 1100 K were probably too high to ensure that equilibrium was attained, but above 1100 K it is believed that the system was very close to equilibrium. From this figure we identify three states* of the surface labeled A, B, and G as indicated. Typical Auger spectra for the three states are given in fig. 2. In state G (high carbon coverage), the strongest Auger peak (that due to C at 270 eV), has the shape characteristic of graphite and the nickel 62 eV peak is down to about 5% of its maximum value in state A†. The elastic peak is accompanied by three loss peaks at multiples of 29 eV; this is the same value observed during the course of this work on a graphite single crystal and agrees quite well with the plasmon loss energy in graphite observed by others in reflection experiments. These observations together with the LEED evidence presented below lead to the conclusion that state G is one in which the Ni surface is covered with several layers of graphite. In state A (the high temperature, low C coverage region) the C peak is much narrower than for graphite (~ 8 eV as compared to 20 eV) and the Ni peaks at 62 eV, 105 eV and in the 600–850 eV range, are dominant. The spectrum of state B is intermediate between that of A and G; it shows a strong 270 eV peak with the graphite shape, Ni peaks weaker than in state A with the Ni 105 eV peak most attenuated and a single 29 eV loss accompanying the elastic peak. Quantitative analysis of the peak heights in this region, as presented in section 4, together with LEED observations lead to the conclusion that state B is one in which the surface is covered with a C monolayer having the graphite basal plane structure.

In order to establish that the observed peaks were characteristic of nearly equilibrium conditions the transients in peak heights were followed after the step increments in temperature. Fig. 3 shows the variation of the carbon Auger peak height with time following typical small changes in crystal temperature. The temperature changes were accomplished within one minute. The relaxation time associated with Auger peak changes is seen to be about 1 hr in the region of the A–B transition (~ 1180 K) and this may contribute to the hysteresis observed there (fig. 1).

* It is possible that there are intermediate states between B and G as evidenced by structure in the height of the 62 eV Ni peaks in this region. In this paper we shall mainly concentrate on the upper temperature transition.

† With sufficient annealing in state G the 62 eV Ni peak could be reduced to the limit of detectability.

Fig. 4 is similar to fig. 1 but includes the temperature variation of all the main peaks of the spectrum. Note the correlation in changes of peak heights at the two transition regions. We estimate from this figure that the lower temperature limit of state B is ~ 1065 K.

Some data were also obtained from specimens of other nominal bulk carbon concentrations, ~ 0.02 and $\sim 0.5\text{at}\%$. The temperature of transition

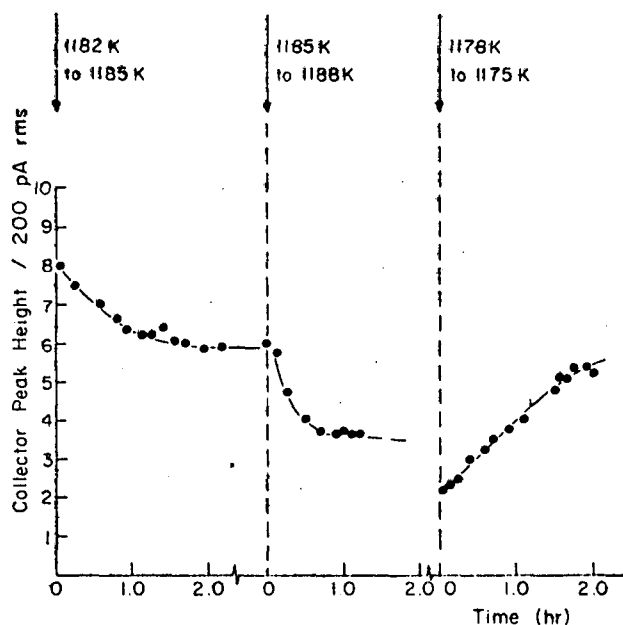


Fig. 3. Variation of carbon Auger peak height with time following small step changes in temperature. The first two sections correspond to heating increments, the last to cooling. In this temperature range the relaxation time for attainment of equilibrium near the A-B transition is ~ 1 hr. The Ni peaks, which change in the opposite direction, show a similar time dependence [Shelton²⁷].

into the high temperature phase A were respectively ~ 900 K and ~ 1115 K. Since the bulk carbon concentrations are not known to better than a factor of 2 no conclusions can be drawn from the way that the transition temperature varies with bulk carbon concentration. However the fact that it is different for crystals with different doping levels lends further support to the assertion that the crystal interior was the main source of the surface carbon.

3.2. AUGER PEAK HEIGHTS VERSUS TEMPERATURE (RFA)

The results obtained in the cylindrical mirror analyser were substantially confirmed with the retarding field analyser. However since the exciting elec-

tron beam could be scanned across the specimen without appreciably changing the sensitivity it was possible to assess the effects of temperature gradients and composition gradients on the transition between A and B. For example, compared to the results in the CMA the temperature of the A-B transition was about 15 K lower at the specimen center and about 40 K lower at the supporting ends. This is attributed to depletion of carbon from the specimen

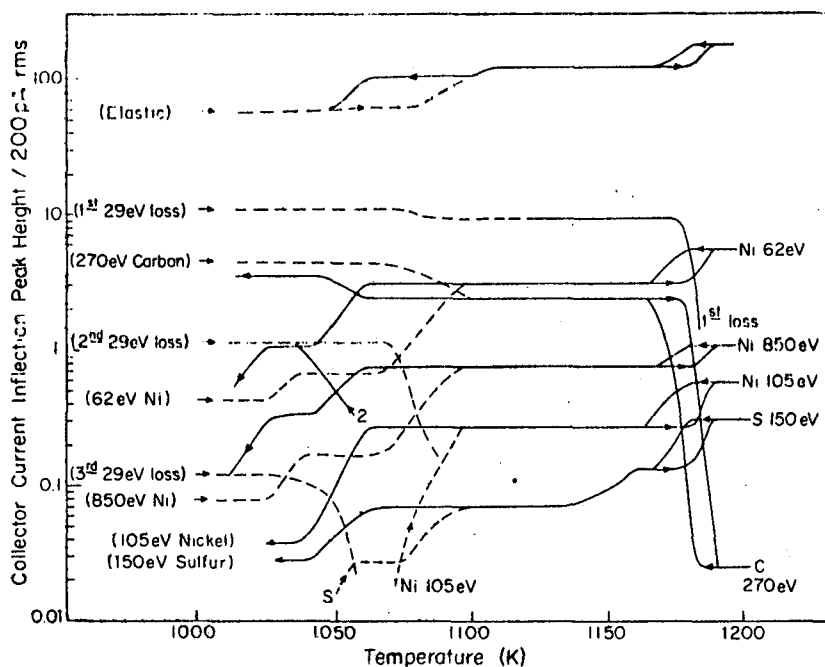


Fig. 4. Peak height versus temperature for a number of the main peaks in the CMA spectra; angle of incidence 68° to the normal. The A-B transition is estimated at ~ 1180 K and the low temperature limit of stability of state B at ~ 1065 K. For all peaks the scatter in data points is similar to the scatter shown in fig. 1.

during the anneals* resulting from intervening experiments and is evidence for the control of the equilibrium surface composition by the bulk crystal composition. Otherwise the A and B transitions displayed temperature dependence as shown in fig. 4.

Fig. 5 shows typical spectra for the three states as observed in the RFA. These are similar to those given in fig. 2 except: the sulphur level has been further reduced, the carbon peak in state A is on the limit of detectability,

* The annealing time in the CMA was sufficient for a diffusion length of ~ 0.3 cm using diffusivity data [Massaro and Peterson²⁰] on carbon in nickel.

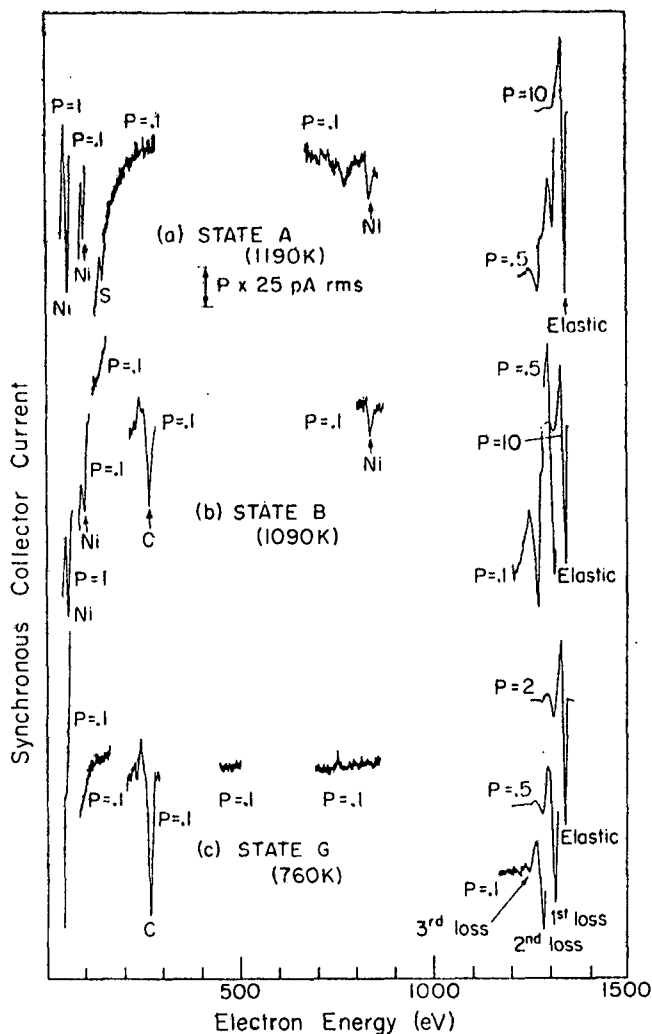


Fig. 5. Typical Auger spectra in the RFA at an angle of incidence of 30° to the crystal normal. P is the phase sensitive detector sensitivity. The absolute r.m.s. current was obtained from the measured impedance of the detector.

the loss spectra associated with the elastic peak are much better resolved, and the state G spectrum has higher carbon coverage obtained by a 15hr anneal at 760K.

For comparison with the results of model calculations (section 4), we determined the relative magnitudes of the carbon and nickel peaks in the three states using 6 spectra for state G, 10 for A and 15 for B. In state B the average peak heights of the Ni peaks relative to those for state A were:

Ni 62eV: 0.56, Ni 105eV: 0.27, Ni 850eV: 0.76. The ratio of the C 270eV peak in state B to that in state G was 0.66. The sensitivity of the RFA was insufficient to detect carbon in state A; for the CMA spectra the ratio of the C peak in state B to that in A is $\sim 10^2$.

3.3. LEED OBSERVATIONS

The low energy electron diffraction patterns from the three states were qualitatively similar. They show surface meshes consistent with both Ni(111) and graphite (0001)*. The variations with energy in the pattern from state

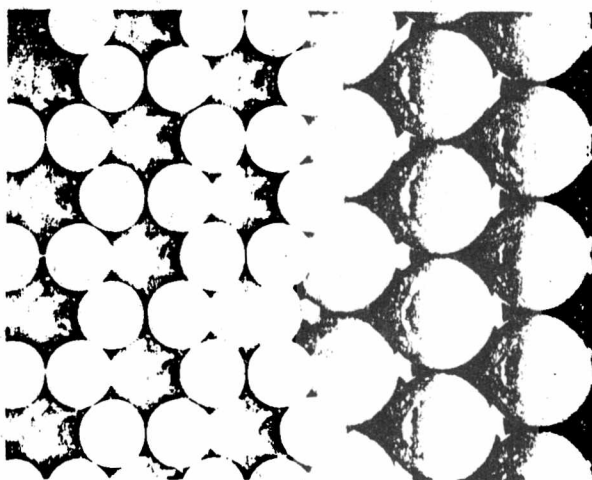


Fig. 6. Ball model of a graphite(0001) layer on the (111) surface of Ni. The left hand portion of the photographs depicts the probable arrangement in state B with (0001)graphite $\parallel$ (111)Ni; $[11\bar{2}0]$ graphite $\parallel$ $[1\bar{1}0]$ Ni. Note that the graphite layer has two atoms per unit mesh.

G show 6-fold symmetry expected of bulk graphite while those in state B and A are 3-fold symmetric. Furthermore the intensity-energy curves for the specular beam from state G at various angles of incidence agree well with the results of McRae and Caldwell³⁷⁾ on bulk single crystal graphite. Intensity data[†] has also been obtained from state B and is substantially different from that of bulk graphite and bulk nickel.

* The hexagonal lattice constant of the nickel (111) plane is 2.497 Å at 300 °C, 2.507 Å at 500 °C, 2.517 Å at 750 °C and 2.522 Å at 900 °C [Wise³⁸⁾]. By comparison, the hexagonal lattice constant of the graphite basal plane is 2.461 $\pm$ 0.0005 Å [Morgan³⁹⁾] over this range, reaching a minimum of 2.4605 Å at about 800 °C. The lattices may be compared in fig. 6.

† This is presently being analyzed and will be described in a future publication along with details of the low energy secondary spectrum in state B.

The patterns suggest that in states B and G the carbon is arranged in graphite layer(s) with the epitaxy $(0001)\text{graphite}|| (111)\text{Ni}; [1\bar{1}20]\text{graphite}|| [1\bar{1}0]\text{Ni}$ (fig. 6)*. There is some slight disorder in state G about the surface normal as evidenced by the faint diffraction ring segments in fig. 7b. Diffraction from a mesh other than $\text{Ni}(111)$ or $\text{graphite}(0001)$ was observed only when significant amounts of sulphur were present.

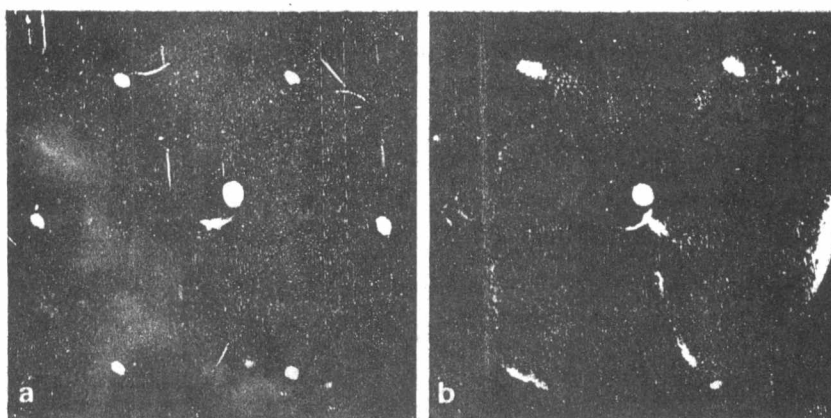


Fig. 7. LEED pattern of the graphite covered $\text{Ni}(111)$ surface (state G). (a) is at normal incidence; (b), at 22° rotation, was overexposed to show the presence of weak diffraction ring segments. The strong spots are consistent with either $\text{Ni}(111)$ or $\text{graphite}(0001)$; the ring segments indicate some rotational disorder of graphite domains.

3.4. ION BOMBARDMENT OBSERVATIONS

To assess the thickness of the surface carbon layers in states B and G and to obtain some information on the concentration profile into the crystal, measurements of Auger peak heights were made after various intervals of ion bombardment at room temperature. Two separate experiments were carried out on different (111) crystals, one prepared by quenching from state B the other with the its surface in state G. During bombardment, the crystal was biased at -200 V relative to ground and bombarded with 400 eV argon ions in an argon pressure of 10^{-4} torr^{**} . Between successive bombarding increments the chamber was evacuated and the secondary electron spectrum recorded with the RFA. The ion current density to the crystal was estimated from the measured current from the crystal to ground ($\sim 1\text{ }\mu\text{A}$) and the specimen area. This procedure will overestimate the incident ion flux since it neglects the ejected electrons. However removal rates may be

* This arrangement has earlier been suggested by Leidheiser and Gwathmey¹⁰⁾ and Speich¹¹⁾ without the advantage of supporting LEED patterns.

** The background pressure of CH_4 during bombardment was $< 3 \times 10^{-7}\text{ torr}$.

estimated using yield measurements of Laegreid and Wehner¹²⁾† since their yields are referred also to measured crystal currents.

Fig. 8 shows peak heights versus number of incident argon ions, for bombardment at normal incidence with the crystal initially in state B. With about 10^{16} ions/cm²*, the Ni Auger peaks develop rapidly and the 270 eV carbon peak shows a shape change with the peak maximum moving to higher

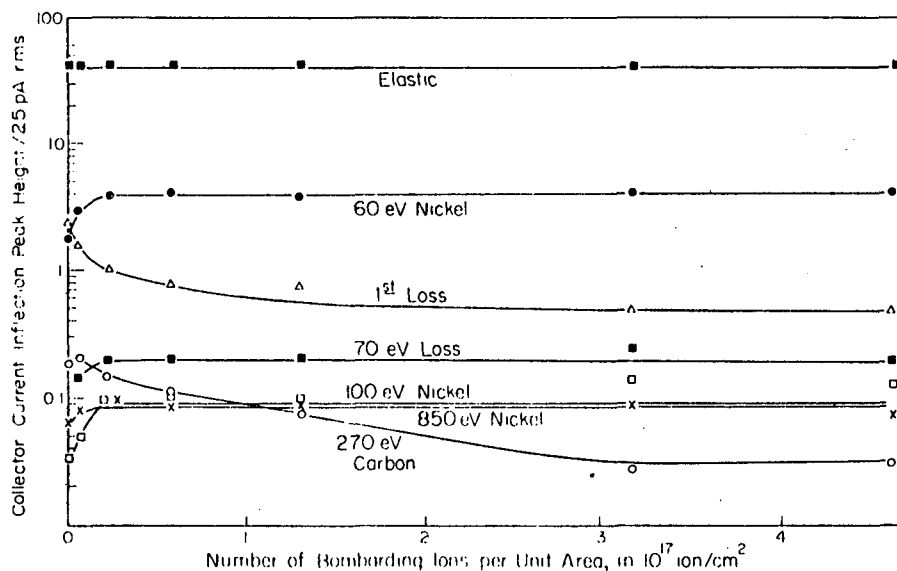


Fig. 8. Peak heights versus number of bombarding argon ions for a crystal initially in state B. The incident argon ion current was $\sim 10^{13}$ ions/cm²sec. Note the rapid increase in the Ni Auger peaks. Ion bombardment was at normal incidence, electron excitation at 30° to the normal.

energy. The width is thus reduced to about 10 eV compared to an initial value of ~ 20 eV. The carbon peak then decreases with a relaxation parameter of $\sim 10^{17}$ ions/cm² and reaches an apparent steady state value of about 0.15 of its initial height.

Fig. 9 is the corresponding result for sputtering from state G. In this case the Ni peaks undergo a rapid increase during the first 5×10^{16} ions/cm² followed by a slow approach to the apparent steady state value with a relaxation parameter of $\sim 10^{18}$ ions/cm². The carbon peak persists in the graphitic shape over the entire bombardment indicated in the figure. Using a yield of

† They report the sputtering yield by 400 eV argon for carbon from bulk graphite to be ~ 0.1 carbon atoms/incident ion and for nickel from bulk nickel, ~ 1.2 .

* For comparison, the two dimensional atom density of Ni(111) is $0.19 \cdot 10^{16}$ /cm² and for graphite (0001) it is $0.38 \cdot 10^{16}$ /cm².

about 0.1 carbon atoms per incident ion shows that the average thickness of carbon in state G is several monolayers.

The initial relaxation of the spectra are qualitatively consistent with monolayer and multilayer initial graphite coverages respectively. The persistence of the carbon Auger peaks in both cases after large bombardment intervals is probably due to the small sputtering efficiency of C relative to that of Ni. Concentration profiles near the surface cannot be measured by these techniques when the solute is sputtered less efficiently than the matrix atoms.

3.5. CHARACTERISTIC ENERGY LOSSES (RFA)

Multiple 29eV losses were observed with the surface in state G, and a single 29eV loss with state B using 10V peak to peak modulation. Reducing the peak to peak modulation amplitude from 10V to 2V allowed resolution of losses of lower energies. The width of the 29eV loss peak was 14eV at both modulation amplitudes while the elastic peak width was reduced from 10eV to 1.9eV. The loss energies, taken as the energies of the peak centers below the center of the elastic peak, were

State A: $5 \pm 0.5\text{eV}$, $10 \pm 0.5\text{eV}$, $27 \pm 1\text{eV}$;

State B: $5 \pm 1\text{eV}$, $9 \pm 1\text{eV}$, $29 \pm 1\text{eV}$;

State G: $5 \pm 0.5\text{eV}$, (multiple) $29 \pm 0.5\text{eV}$.

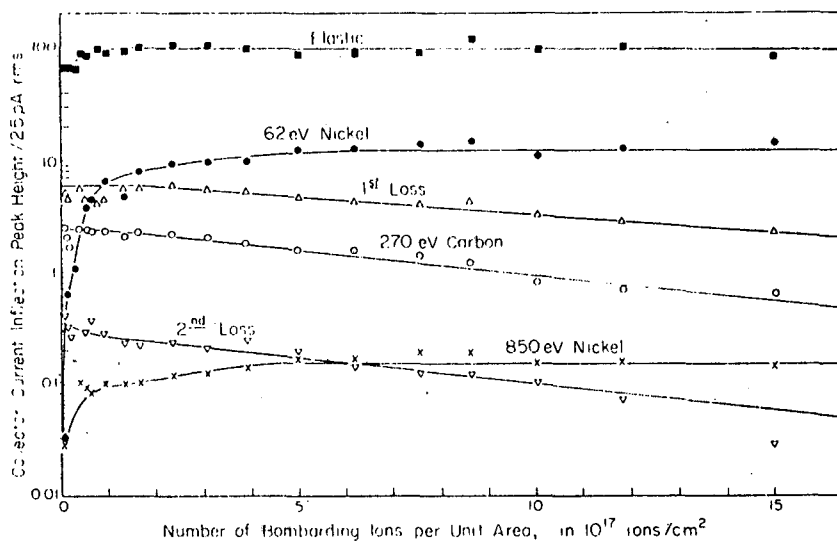


Fig. 9. Peak height versus number of bombarding argon ions for a crystal initially in state G. Ion bombardment was at 60° from the normal (to increase the sputtering yield) and electron excitation at 78° from normal. Note the slow decrease in the carbon Auger peak.

Both the peak energies and widths were insensitive to incident beam direction and energy for incident energies of 280, 900 and 1400 eV.

4. Discussion

We interpret the results presented above to indicate that under equilibrium conditions the surface in contact with the bulk solution displays one of several distinct states depending on temperature. The high temperature state, labeled A, is one of dilute carbon coverage: the extent of segregation is small with the carbon approaching a uniform distribution with depth. In the intermediate temperature region a segregated phase (state B) exists; we believe this to be a monolayer of graphite, epitaxial with the Ni(111) surface. The low temperature region is characterized by a precipitate (state G) of multilayer graphite with the same epitaxy. In this section we present the arguments which lead to these conclusions and then use a simple statistical thermodynamic model to describe the sharp transition between states A and B. From this model we obtain an estimate of the binding energy of carbon atoms in the segregated phase.

4.1. INTERPRETATION OF THE 3 REGIONS

4.1.1. State B

A quantitative estimate of the carbon concentration in state B can be made by computing the magnitude of the current in an Auger peak due to a carbon monolayer and comparing with the observed values in the RFA. We follow a procedure similar to that of Bishop and Rivière⁴³.

Assuming the X-ray fluorescence yield to be negligible for carbon (Dick and Lucas⁴⁴) the current I_A of Auger electrons (K, V, V) is given by

$$I_a = I_0 R \sigma_K N \sec \theta. \quad (1)$$

I_0 is the incident beam current, and R , a backscattering factor accounting for K-shell ionizations by electrons not in the primary beam, has been estimated as 1.1–1.3 by a number of workers [Gallon⁴⁵, Seah⁴⁶, Vrakking and Meyer⁴⁷]. σ_K is the K-shell ionization cross-section at the incident energy, N the number of C atoms per unit area and θ the angle of incidence relative to the crystal normal. Taking $R = 1.2$, $I_0 = 2.5 \mu\text{A}$, $\sigma_K = 3.3 \times 10^{-19} \text{cm}^2$ at 1440 eV [Glupe and Mehlhorn⁴⁸, Gerlach and DuCharme⁴⁹, Pessa and Newell⁵⁰, Staib⁵¹], $\theta = 30^\circ$, we obtain for state B

$$I_A = 4.37 \text{ nA}. \quad (2)$$

The inflection height H on the second harmonic spectrum may be estimated

by assuming the current I_A to be distributed as a Gaussian with half width σ and gives [Taylor⁵²]

$$H = T \frac{0.12}{\sqrt{2}} \left(\frac{V_{\text{mod}}}{2\sigma} \right)^2 I_A, \quad (3)$$

where T (~ 0.075) is a geometric factor for the analyser accounting for the limited acceptance aperture and the transmission of the grids and V_{mod} is the peak to peak modulation of the grids. Taking $\sigma \sim 10 \text{ eV}$ (half the observed peak to peak width in state B) gives $H \sim 7.0 \text{ pA}$ very close to the observed value (fig. 5). The agreement is better than can be justified by the model calculation since the carbon peak shape is clearly not Gaussian and we conclude that to within a factor of 2 or so the carbon coverage in state B is one monolayer.

Further information on the thickness of the carbon coverage in state B can be obtained from the observed attenuation of the Ni Auger peaks in the retarding field analyser. We calculate the attenuation of an Auger peak from the Ni substrate in a simple model and compare with experiment. We consider the case of coverage by a uniform C monolayer. The assumptions of the model are (a) that the spectrum emitted by the nickel substrate is unaffected in shape and strength by the overlayer, and (b) that the attenuation of the emitted Auger electrons by the carbon monolayer can be described in terms of inelastic mean free paths. The constancy of the Ni peak shapes is confirmed by comparison of the Ni spectra in states B and A. The attenuation of the incident 1400 eV beam by the overlayer is expected to be negligible for several reasons. The attenuation is believed to be due mainly to plasmon and pair excitation; from the data of Glupe and Mehlhorn⁴⁸, the mean free path for K-shell ionization is estimated to be $\sim 2600 \text{ \AA}$ at 1400 eV in graphite, while mean free paths for plasmon and pair creation are typically $\sim 30 \text{ \AA}$ at this energy (see fig. 11 below). Even if plasmon excitation in the overlayer does occur the resulting change in energy ($\sim 29 \text{ eV}$) and angle of incidence ($\sim 0.6^\circ$) should have negligible effect on the beam incident on the nickel at the incidence angle used in these experiments.

The development of the attenuation function is described elsewhere [Shelton²⁷]; it is given as a function of the angle θ between the surface normal and the analyser axis, the layer thickness x , and the electron mean free path λ by

$$A(\theta, x/\lambda) = A_0 \int_{\text{detector}} \epsilon(\Omega) \exp \left[-\frac{x}{\lambda} \sec(\Omega \cdot n) \right] d\Omega, \quad (4)$$

where Ω is the direction of emission, $\epsilon(\Omega)$ describes the angular distribution of emission from the source and n is the unit vector normal to the crystal

surface. The constant A_0 is chosen such that $A(0, 0) = 1$. The attenuation function $A(\theta, x/\lambda)$ is given in fig. 10 for the RFA at $\theta = 60^\circ$, for isotropic emission [i.e. $\epsilon(\Omega) = \text{constant}$] and for a cosine emission distribution [i.e. $\epsilon(\Omega) = \cos(\Omega \cdot n)$]. In both cases there is significant deviation from a simple exponential attenuation.

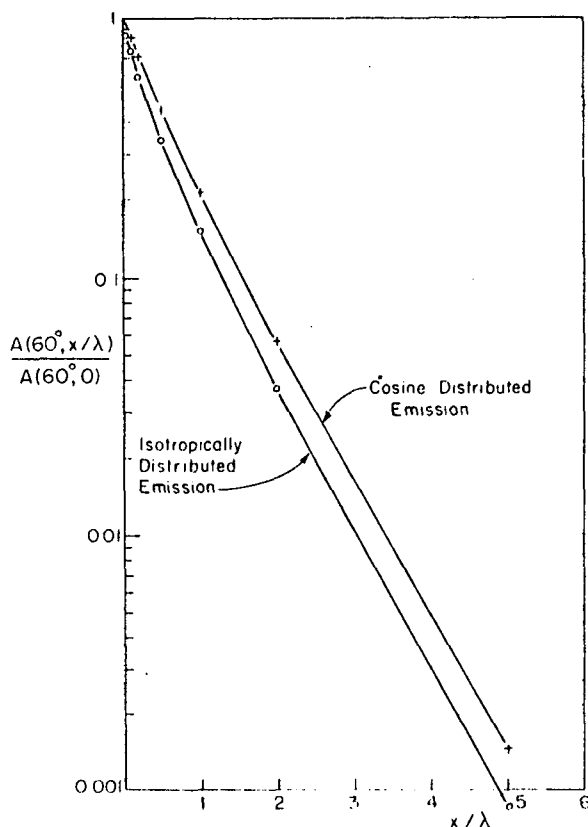


Fig. 10. Calculated thickness dependence of the overlayer attenuation function $A(\theta, x/\lambda)$. The calculations shown are for $\theta = 30^\circ$ and are normalized against zero thickness at this angle of incidence.

To compare the values predicated by eq. (4) and fig. 10 with experiment requires a knowledge of inelastic mean free paths, λ , in the carbon layer at the energies of the Ni Auger peaks. Fig. 11 displays some experimental and theoretical mean free paths in carbon as a function of primary energy. The energy for the experimental data refers to a zero at the vacuum level while that for the theoretical results is relative to an independent electron with zero kinetic energy; the experimental points should thus be moved to higher

energies by the amount of the real part of the inner potential for direct comparison. The theoretical estimates are for bulk excitation of a homogeneous electron gas; Quinn's⁵³⁾ approximation is for bulk plasmon excitation and Lundqvist's⁵¹⁾ includes both plasmon and electron-hole pair excitation. We use here the results of Lundqvist extrapolated to $r_s = 1.5$, the value appropriate to graphite considered as a free-electron system with 4 electrons per atom.

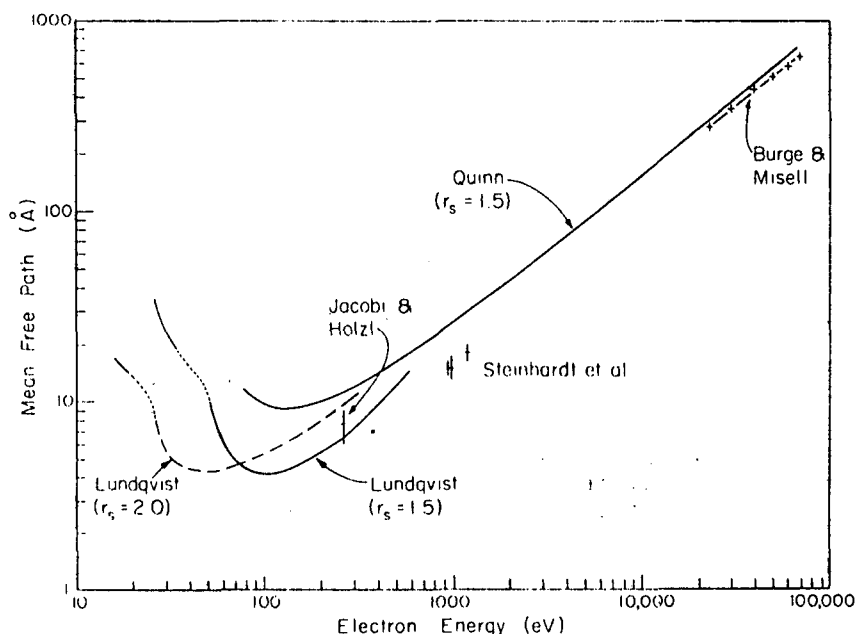


Fig. 11. Electron inelastic mean free paths in carbon. The solid curves are theoretical estimates for the average electron density of graphite.

The resulting attenuation predicted by eq. (4) for $\theta = 30^\circ$, and assuming the thickness x to be that appropriate to one layer of graphite (i.e. the interplanar spacing $3.35 \text{ \AA}$), is given in fig. 12 for the case of emission obeying a cosine distribution. Indicated also are the experimentally observed attenuations of the Ni peaks from comparison of RFA spectra from states A and B under the conditions given in section 2. The agreement is satisfactory in the light of the simplicity of the model and the absence of adjustable parameters.

The magnitude of the C peak from state B, the attenuation of the Ni peaks, the graphitic shape of the carbon Auger peak, the presence of the 29eV and ionization losses associated with graphite together with the LEED observations described above, lead us to postulate that this state is one of a monolayer of carbon with the graphite structure on the Ni(111) surface. The sput-

tering observations are qualitatively consistent with this picture. As shown later, a statistical thermodynamic analysis of the A-B transition gives a binding energy of carbon in state B approximately the same as in the basal plane in a graphite crystal.

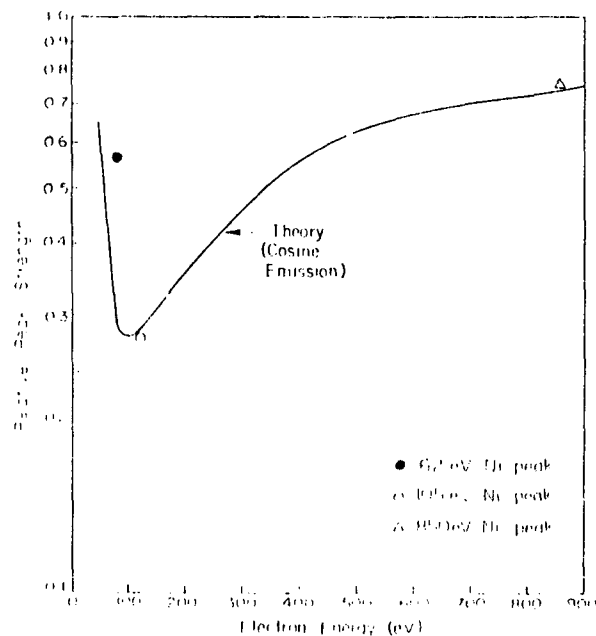


Fig. 12. The solid curve is the predicted peak height reduction as a function of energy by one monolayer of graphite from eq. (4) using a cosine emission distribution and the mean free path information of fig. 11.

4.1.2. State A

As shown in fig. 1 the carbon peak-to-peak height in this condition is $\sim 10^{-2}$ times that for state B. Taking account of the decreased width of the carbon peak in state A (i.e. $2\sigma \sim 8\text{eV}$) gives through eqs. (1) and (3) the surface density of carbon atoms $\sim 6 \times 10^{12}\text{cm}^{-2}$. This corresponds to about 0.3at%* if the state A signal were due to the top monolayer. This compares favorably with the nominal bulk carbon concentration.

4.1.3. State G

We believe that in this state the surface is covered with multilayer epitaxial graphite. The LEED pattern is that characteristic of graphite with 6-fold

* The two-dimensional atom density in the graphite (0001) plane is twice that in Ni(111).

rotational symmetry; the diffracted intensity-energy curves and multiple loss characteristics are very similar to those from a bulk graphite crystal and the Ni Auger peaks are attenuated by amounts consistent with a thick overlayer (of the order of 4 layers). The fact that the C peak retains its graphitic shape even after long sputtering intervals further supports our conclusion. We also note that the reduction in surface carbon concentration as the crystal is heated beyond state G is evidence that the crystal is then unsaturated with respect to graphite precipitation.

4.2. STATISTICAL THERMODYNAMICS OF THE A-B TRANSITION

As mentioned above we believe that the data presented in fig. 1 closely approximates the equilibrium situation in the region of the A-B transition but less closely near the low temperature limit of stability of state B. The most striking feature of the A-B transition is its sharpness, the width of the transition being less than 15 K. To interpret this sharpness on a Langmuir model for segregation from the crystal interior to noninteracting surface sites would require an energy of segregation per carbon atom of ~ 60 eV! However such a sharp transition can be explained by recognizing interactions among the carbon atoms. We first deduce a value for the binding energy of C in the state B by a general thermodynamic argument and then illustrate the origin of the condensation of state B with a simple Bragg-Williams model.

4.2.1. Heat of segregation

From fig. 4 we take the temperature of the A-B transition, T_{AB} , to be ~ 1180 K while the low temperature limit of stability of B, T_{BG} , is estimated at 1065 K. If we identify this lower temperature as that of precipitation, i.e. that at which bulk graphite is in equilibrium with the nickel-carbon solid solution, the heat of segregation to state B can be found as follows.

The chemical potential μ of carbon in its reservoir, the bulk solution, taking pure graphite as the reference state is given in the usual way for a dilute solution as

$$\mu = F_{\text{sol}}(T) + kT \ln \chi, \quad (5)$$

where $F_{\text{sol}}(T)$ is the excess partial atomic free energy of solution and χ the fractional occupancy of the interstitial octahedral sites in Ni by carbon atoms. From Dunn et al.²², $F_{\text{sol}}(T) \approx (0.49 \text{ eV} - 0.2kT)$. If we assume that the state B is a homogeneous complete monolayer of carbon, as discussed above, the chemical potential in this phase is the free energy per atom F_B . At T_{AB} , F_B is equal to the chemical potential of carbon in solution so that

$$F_B(T_{AB}) = F_{\text{sol}}(T_{AB}) + kT_{AB} \ln \chi. \quad (6)$$

Similarly when precipitation occurs at T_{BG} the free energy per atom F_G in the precipitate phase is equal to the chemical potential in solution so that

$$F_G(T_{BG}) = F_{sol}(T_{BG}) + kT_{BG} \ln \chi. \quad (7)$$

Setting $F_G=0$ as the reference state, expanding the free energies into their energy (E) and entropy (S) parts gives on combining (6) and (7)

$$\frac{E_B - \bar{E}_{sol}}{\bar{E}_{sol}} = \frac{-T_{AB}(\bar{S}_{sol} - k \ln \chi - S_B)}{T_{BG}(\bar{S}_{sol} - k \ln \chi)} \quad (8)$$

If we neglect S_B , the entropy per atom of the segregated state relative to that in bulk graphite, eq. (8) gives on defining $(E_B - \bar{E}_{sol})$ as $\Delta \bar{E}_{seg}$, the energy of segregation per atom

$$\frac{\Delta \bar{E}_{seg}}{\bar{E}_{sol}} = - \frac{T_{AB}}{T_{BG}}, \quad (9)$$

and inserting numerical values

$$\Delta \bar{E}_{seg} \approx -1.11 \bar{E}_{sol} \approx -0.55 \text{ eV}.$$

In other words the binding of carbon in state B is slightly greater ($\sim 0.05 \text{ eV}$) than in graphite. The relative partial atomic energies of carbon in the various states are collected on the energy level diagram of fig. 13. This shows for example that the energy of adsorption of C on Ni in the form of a graphite monolayer is $\sim 7.5 \text{ eV}$.

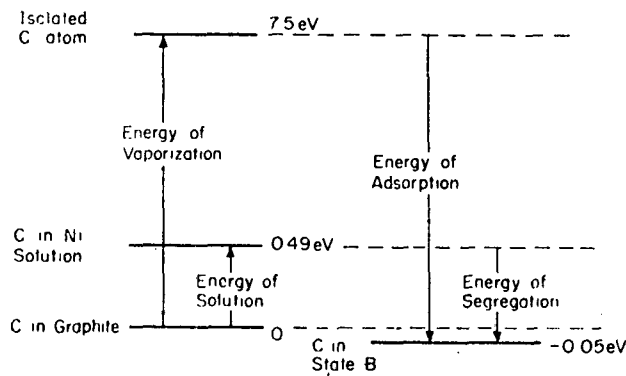


Fig. 13. Partial atomic energies of carbon in various states. This should be regarded as an effective "one atom" energy level diagram. The level labeled "C in State B" is from the present study; this result can be used to predict the energy of adsorption into this state from carbon vapor as indicated. The vaporization data for graphite are reviewed by Reynolds⁽⁸⁾ and Honig and Kramer⁽⁹⁾.

4.3. BRAGG-WILLIAMS MODEL OF THE A-B TRANSITION

This is the simplest model which shows a sharp transition between phases such as A and B and allows an identification of the energy of segregation in terms of the binding of the carbon atoms. It has been used to describe adsorption of interacting adsorbates and to give a qualitative explanation of condensation phenomena [Fowler and Guggenheim⁵⁵]. We consider the equilibrium of two phases; viz, the Ni-C solid solution and the surface C layer considered as a separate phase.

Within the Bragg-Williams formulation the segregated atoms are assumed to be randomly distributed among equivalent adsorption (or segregation) sites, which may be considered to be surface sites. This leads to an expression for the chemical potential of carbon in the surface phase in terms of θ , its fractional coverage ($\theta=1$ for a monolayer) [Clark⁵⁶]

$$\mu_s(T, \theta) = kT \ln \left(\frac{\theta}{1-\theta} \frac{1}{q} \exp \frac{c\omega\theta}{kT} \right), \quad (10)$$

where q is the partition function of a single C atom in an isolated surface site, c is the coordination number in the complete layer ($=3$ for a graphite layer) and ω is the interaction energy between pairs of nearest neighbors ($\omega = -5\text{eV}$ for graphite); longer range interactions are ignored. Setting

$$kT \ln(1/q) = E_0 - TS_0,$$

where E_0 and S_0 are respectively the energy and entropy of an isolated atom at a particular site, gives

$$\mu_s(T, \theta) = E_0 + \omega c\theta + kT \ln \left(\frac{\theta}{1-\theta} \right) - TS_0. \quad (11)$$

The equilibrium value of θ is determined by equating this chemical potential to that in the reservoir. In our case the reservoir is the bulk solid solution with carbon chemical potential given by eq. (5). The variation of θ with T is then described by the equation

$$F_{\text{sol}} + kT \ln \chi = E_0 + \omega c\theta + kT \ln \left(\frac{\theta}{1-\theta} \right) - TS_0. \quad (12)$$

For sufficiently high temperature ($T > T_c \equiv -\omega c/4k$, the critical temperature), eq. (12) has a single solution for θ for each T , and θ increases smoothly as T decreases. For $T < T_c$, θ is a multivalued function of μ_s . This is indicated in fig. 14a where we have sketched the quantity $1/T[\mu_s(T, \theta) - \mu_s(T, \frac{1}{2})]$ versus θ . The model chemical potential is odd about $\theta = \frac{1}{2}$ and a Helmholtz

equal area theorem [Fowler and Guggenheim⁵⁵] shows that when the surface phase separation occurs the chemical potential is given by $\mu_s(T, \frac{1}{2})$. Inspection of fig. 14a shows that only very low coverage or very high coverage phases occur at equilibrium with T appreciably below T_c ; for example in the 1000 K temperature range, a value of $\omega c \approx 1\text{eV}$ is sufficient to limit the

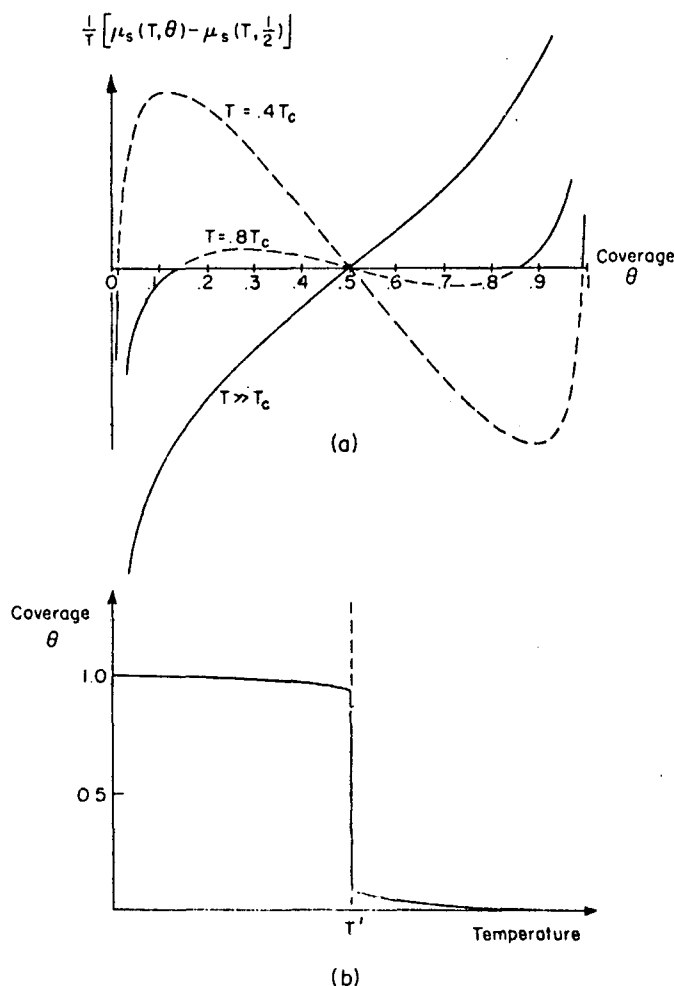


Fig. 14. (a) Chemical potential versus coverage for interacting segregated atoms in the Bragg-Williams model. The homogeneous phase is unstable with respect to phase separation below the critical temperature T_c ($\omega c/4k$) in the range of coverage indicated by dashed lines. The temperature of the phase transition between low and high coverages is determined by the chemical potential of the solute in the crystal. (b) Schematic coverage temperature plot deduced from the model for fixed crystal doping. A surface phase transition of the type indicated at T' is believed to be the reason for the sharp coverage decrease at $\sim 1180\text{K}$ in fig. 1.

possible values of θ to the regions 0 to ~ 0.01 and ~ 0.99 to 1. This is indicated in the schematic coverage versus temperature curve of fig. 14b.

If we identify the temperature of the surface phase transition T' with our observed temperature T_{AB} we obtain from (12) with $\theta = \frac{1}{2}$

$$(E_0 + \frac{1}{2}\omega c) - T_{AB}S_0 = F_{sol} + kT_{AB} \ln \chi. \quad (13)$$

This may then be compared to eqs. (6) and (8) to give a microscopic identification of the contribution to the energy of segregation, i.e.

$$\Delta \bar{E}_{sep} \approx (E_0 + \frac{1}{2}\omega c) - \bar{E}_{sol}. \quad (14)$$

The Bragg-William model is too simple to describe the real situation. One would expect clustering to occur so that in practice the average coverage would increase smoothly over a range of temperatures. However the interaction energy between pairs of neighbors in a graphite layer is so large that at the temperature range used the transition should still be very sharp.

5. Summary

We have studied the segregation of carbon to the (111) surface of nickel containing ~ 0.3 at% carbon in solution. Distinct states of the surface occur as the temperature is varied with transitions between the states occurring over narrow temperature ranges.

At low temperatures (< 1065 K) the surface is covered with multilayer graphite epitaxially precipitated on the Ni substrate.

In the intermediate temperature range (~ 1065 – 1180 K) the surface coverage is constant at a value which we believe to be one monolayer. This surface layer is identified as an *equilibrium segregated phase*. It has the graphite basal plane arrangement and is oriented epitaxially on the nickel substrate.

A reversible sharp transition occurs (at about 1180 K) between the intermediate state to one of low coverage; the surface carbon concentration in the low coverage state is of the same order as the bulk atomic fraction.

We believe that this is the first observation of a phase transition in segregation studies. By analogy with phase transitions in layers produced by adsorption from the vapor we have described the transition by a model involving interacting segregated atoms. Interpretation of the experimental transition temperatures shows that the binding of carbon in the segregated monolayer is slightly greater than in bulk graphite.

It is shown that the energy of *adsorption* may be obtained from these experiments; the same technique may be possible in other cases where equilibrium with the vapor is not feasible.

Acknowledgment

We would like to acknowledge the contributions from the Central Facilities of the Materials Science Center at Cornell. In particular the assistance of B. F. Addis in crystal growing has been invaluable. This work was supported by the National Science Foundation, Grant #GH-33233X and through the Materials Science Center at Cornell University.

References

- 1) J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28** (1958) 258.
- 2) J. L. Meijering, *Acta Met.* **14** (1966) 251.
- 3) T. Murakami, S. Ono, M. Tamura and M. Kurata, *J. Phys. Soc. Japan* **6** (1951) 309.
- 4) K. T. Aust, R. E. Hanneman, I. Niessen and J. M. Westbrook, *Acta Met.* **16** (1968) 291.
- 5) T. R. Anthony, *Acta Met.* **17** (1969) 603.
- 6) R. L. Parker, *Solid State Phys.* **25** (1970) 151.
- 7) J. Bénard, *Catalysis Rev.* **3** (1969) 93.
- 8) J. L. Domange and J. Oudar, *Surface Sci.* **11** (1968) 126.
- 9) M. Kostelitz, J. L. Domange and J. Oudar, *Surface Sci.* **34** (1973) 431.
- 10) J. M. Blakely, J. S. Kim and H. C. Potter, *J. Appl. Phys.* **41** (1970) 2693.
- 11) J. Ferrante, *Scripta Met.* **5** (1971) 1129.
- 12) H. P. Bonzel and H. B. Aaron, *Scripta Met.* **5** (1971) 1057.
- 13) D. McLean, *Grain Boundaries in Metals* (Oxford, 1957).
- 14) E. W. Hart, *Scripta Met.* **2** (1968) 179.
- 15) E. W. Hart, in: *The Nature and Behavior of Grain Boundaries*, Ed. Hsun Hu (Plenum, New York, 1972).
- 16) L. A. Harris, *J. Appl. Phys.* **39** (1968) 1419.
- 17) C. C. Chang, *Surface Sci.* **25** (1971) 53.
- 18) N. J. Taylor, in: *Techniques of Metals Research*, Vol. 7, Ed. R. F. Bunshah (Wiley-Interscience, New York, 1971).
- 19) P. W. Palmberg, G. K. Bohn and J. C. Tracy, *Appl. Phys. Letters* **15** (1969) 254.
- 20) C. D. Graham, Jr., *Met. Progr.* **71** (1957) 75.
- 21) J. J. Lander, H. E. Kern and A. L. Beach, *J. Appl. Phys.* **23** (1952) 1305.
- 22) W. W. Dunn, R. B. McLellan and W. A. Oates, *Trans. Met. Soc. AIME* **242** (1968) 2129.
- 23) E. N. Sickafus, *Surface Sci.* **19** (1970) 181.
- 24) E. N. Sickafus and A. D. Colvin, *Rev. Sci. Instr.* **41** (1970) 1349.
- 25) J. P. Coad and J. C. Rivière, *Surface Sci.* **25** (1971) 609.
- 26) T. A. Massaro and E. E. Peterson, *J. Appl. Phys.* **42** (1971) 5534.
- 27) J. C. Shelton, Ph. D. Thesis, Cornell Univ., Materials Science Center Report # 1959 (1973).
- 28) M. Perdereau and J. Oudar, *Surface Sci.* **20** (1970) 80.
- 29) M. Perdereau, *Surface Sci.* **24** (1971) 239.
- 30) M. Perdereau, *Compt. Rend. (Paris) C* **274** (1972) 448.
- 31) A. R. DuCharme and R. L. Gerlach, *J. Vacuum Sci. Technol.* **10** (1973) 188.
- 32) J. J. McCarroll, T. Edmonds and R. C. Pitkethley, *Nature* **223** (1969) 1260.
- 33) J. G. Shaw and W. A. Oates, *Met. Trans.* **2** (1971) 2127.
- 34) P. W. Palmberg, *Appl. Phys. Letters* **13** (1968) 183.
- 35) H. R. Patil and J. M. Blakely, *Electron Energy Losses in Thin Graphite Layers on the (111) Face of Nickel*, Materials Science Center Report # 1965, Cornell Univ. (1973).

- 36) S. Aksela, *Rev. Sci. Instr.* **43** (1972) 1350.
- 37) E. G. McRae and C. W. Caldwell, *Surface Sci.* **7** (1967) 41.
- 38) E. M. Wise, in: *Metals Handbook*, Vol. 1, 8th ed. (American Society for Metals, 1961) p. 1217.
- 39) W. C. Morgan, *Carbon* **10** (1972) 73.
- 40) H. Leidheiser, Jr. and A. H. Gwathmey, *J. Am. Chem. Soc.* **70** (1948) 1205.
- 41) G. R. Speich, *Trans. AIME* **221** (1961) 417.
- 42) N. Laegreid and G. K. Wehner, *J. Appl. Phys.* **32** (1961) 365.
- 43) H. E. Bishop and J. C. Rivière, *J. Appl. Phys.* **40** (1969) 1740;
H. E. Bishop and J. C. Rivière, *Appl. Phys. Letters* **16** (1970) 21.
- 44) C. E. Dick and A. C. Lucas, *Phys. Rev. A* **2** (1970) 580.
- 45) T. E. Gallon, *J. Phys. D* **5** (1972) 822.
- 46) M. P. Seah, *Surface Sci.* **32** (1972) 703.
- 47) J. J. Vrakking and F. Meyer, *Surface Sci.* **35** (1973) 34.
- 48) G. Glupe and W. Mehlhorn, *Phys. Letters* **25A** (1967) 274.
- 49) R. L. Gerlach and A. R. DuCharme, *Surface Sci.* **32** (1971) 329.
- 50) V. M. Pessa and W. R. Newell, *Phys. Scripta* **3** (1971) 165.
- 51) P. Staib, *Phys. Letters* **41A** (1971) 3.
- 52) N. Taylor, *Rev. Sci. Instr.* **40** (1969) 792.
- 53) J. J. Quinn, *Phys. Rev.* **126** (1962) 1453.
- 54) B. I. Lundqvist, *Phys. Status Solidi* **32** (1969) 273.
- 55) R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Oxford, 1939).
- 56) A. Clark, *The Theory of Adsorption and Catalysis* (Academic Press, 1970).
- 57) B. M. Hartley and J. B. Swan, *Australian J. Phys.* **23** (1970) 655.
- 58) B. Heimann and J. Holz, *Z. Naturforsch.* **27a** (1972) 408.
- 59) E. J. Scheibner and L. N. Tharp, *Surface Sci.* **8** (1967) 247.
- 60) J. P. Coad and J. C. Rivière, *Z. Physik* **244** (1971) 19.
- 61) S. Aksela, M. Pessa and M. Karras, *Z. Physik* **237** (1970) 381.
- 62) L. I. Yin, E. Yellin and I. Adler, *J. Appl. Phys.* **42** (1971) 3595.
- 63) J. J. Lander, *Phys. Rev.* **91** (1953) 1382.
- 64) G. F. Amelio and E. J. Scheibner, *Surface Sci.* **11** (1968) 242.
- 65) T. W. Haas, J. F. Grant and G. J. Dooley III, *J. Appl. Phys.* **43** (1972) 1853;
T. W. Haas, G. J. Dooley III, J. T. Grant, A. G. Jackson and M. P. Hooker, *Progr. Surface Sci.* **2** (1972) 155.
- 66) G. Dalmay-Imelik, J. C. Bertolini and J. Rousseau, *Surface Sci.* **27** (1971) 379.
- 67) P. W. Palmberg, G. E. Riach, R. E. Weber and N. C. MacDonald, *Handbook of Auger Electron Spectroscopy* (Physical Electronics Industries, Inc., 1972).
- 68) W. N. Reynolds, *Physical Properties of Graphite* (Elsevier, Amsterdam, 1968).
- 69) R. E. Honig and D. A. Kramer, *RCA Rev.* **30** (1969) 285.

SEGREGATION ISOTHERES FOR CARBON AT THE (100) SURFACE OF NICKEL

L.C. ISETT* and J.M. BLAKELY

*Department of Materials Science and Engineering and Materials Science Center,
Cornell University, Ithaca, New York 14853, USA*

Received 21 October 1975; manuscript received in final form 27 February 1976

Measurements of segregation isotheres are reported for C to Ni(100). The model independent isosteric heat of segregation is found to be in agreement with the value derived from coverage versus temperature data using the Langmuir model. Results for other nickel surfaces are summarized and compared with predictions using the empirical bond energy bond order scheme. The relative success of this scheme supports the suggestion that the carbon-surface bonding is to be regarded as arising from localized interactions.

1. Introduction

The industrial importance of heterogeneous catalysis provides much of the motivation for current experimental and theoretical work on transition metal surfaces. In this paper we will discuss experimental observations of surface phases and binding energies of carbon atoms on single crystal surfaces of nickel. The determination of binding energies provides input into useful empirical and semi-empirical theories of atom-surface interactions such as the CFEO-BEBO approach [1]. In addition, the presence of ordered carbonaceous deposits is believed to be an important factor in some gas-surface interactions [2,3]. For these reasons, our observations of surface phases on nickel surfaces may be of value.

The segregation of carbon to single crystal nickel surfaces has been the subject of previous papers. The results obtained on Ni(111) [4], Ni(100) [5] and Ni(S)[7(100) × (133)] (a stepped surface) [6] have been published. The purpose of this paper is to present additional experimental work on Ni(100) which is extremely important for the correct understanding of the segregation of carbon to this surface. In addition we will describe a preliminary study of the segregation of carbon to the Ni(110) surface. Finally, we will discuss the understanding of the interactions of carbon atoms with nickel surfaces which is emerging.

The elementary theoretical concepts relevant to the segregation experiment have

* Present address: Kodak Research Laboratories, Rochester, New York 14650, USA.

been discussed in detail elsewhere [7]. We wish to remind the reader of the relation between adsorption and segregation experiments. In the adsorption case the chemical potential of the adsorbate is fixed by the temperature and vapor pressure. In segregation experiments the chemical potential of the segregate is fixed by the bulk doping level and the temperature. In each case one can derive an equation analogous to the Clausius-Clapeyron equation which defines an isosteric heat of segregation or adsorption. For the segregation case this is [7]

$$(\partial \log X_b / \partial (1/T))_\theta = \Delta \bar{H}_{\text{seg}}, \quad (1)$$

where X_b is the bulk concentration of the segregating component and the derivative is evaluated at constant surface coverage θ . We emphasize that $\Delta \bar{H}_{\text{seg}}$ obtained from (1) is independent of any model assumptions. The measurement of adsorption isosteres has previously been used to determine heats of adsorption for single crystal surfaces in a few cases; see for example the work of Tracy [8] and of Christman and Ertl [9].

An important aspect of our work has been the application of eq. (1) to the segregation of carbon to Ni(100). This yields a heat of segregation which is model independent and provides a sensitive test of the validity of statistical mechanical models of the segregation system. The simplest model is the Langmuir model involving localized, non-interacting atoms restricted to a monolayer*. This model predicts that the fractional surface coverage θ varies with temperature so that

$$\log \frac{\theta}{1-\theta} = \frac{\Delta \bar{H}_{\text{seg}}}{KT} + \frac{\Delta S_{\text{seg}}}{K}, \quad (2)$$

where ΔS_{seg} is the partial molar excess entropy of segregation [7]. If this is in fact a reasonable model for the segregation then the enthalpy of segregation obtained via (2) should equal the value obtained from (1).

2. Experimental

Experiments were performed in a standard Varian UHV LEED/Auger system. Auger spectroscopy was performed using the 4-grid LEED optics as a retarding field analyzer. Detailed descriptions of the experimental apparatus may be found in refs. [4] and [13]. Typical system pressure after bakeout was $\sim 2 \times 10^{-10}$ Torr.

Oriented single crystal nickel samples doped with various amounts of carbon were prepared from high purity nickel crystals grown from 6 pass zone refined

* Strictly speaking the monolayer model can satisfy the Gibb's Adsorption Isotherm only in the ideal solution limit [10] so that the composition will reach its bulk value in any real system only after a number of atomic planes. However, these composition profiles are not generally experimentally accessible, especially in the nickel-carbon system. Therefore, we appeal to model calculations [11] and experimental measurements of profiles [12] to justify our treatment of segregation as being restricted to the outer monolayer.

nickel. Sample dimensions were typically 1.5 cm X 0.3 cm X 0.06 cm. The crystals were oxidized by heating in air and carburized by heating to 1100 K for periods of about 1 h at 1 atm CO. Oxidizing the surfaces of the samples apparently produced a more uniform carbon uptake, but control of the carbon doping level to better than a factor of 2 was not achieved. Homogenization was achieved by encapsulating the samples in quartz and heating to about 1473 K for approximately 100 h. The samples were subsequently spark-cut in half resulting in final dimensions of 1.5 cm X 0.3 cm X 0.03 cm. One of the halves was analyzed for carbon content (Ledoux Inc., using the LECO commercial technique). The other half was mechanically and chemically polished to remove the oxidized portion and to obtain a smooth surface.

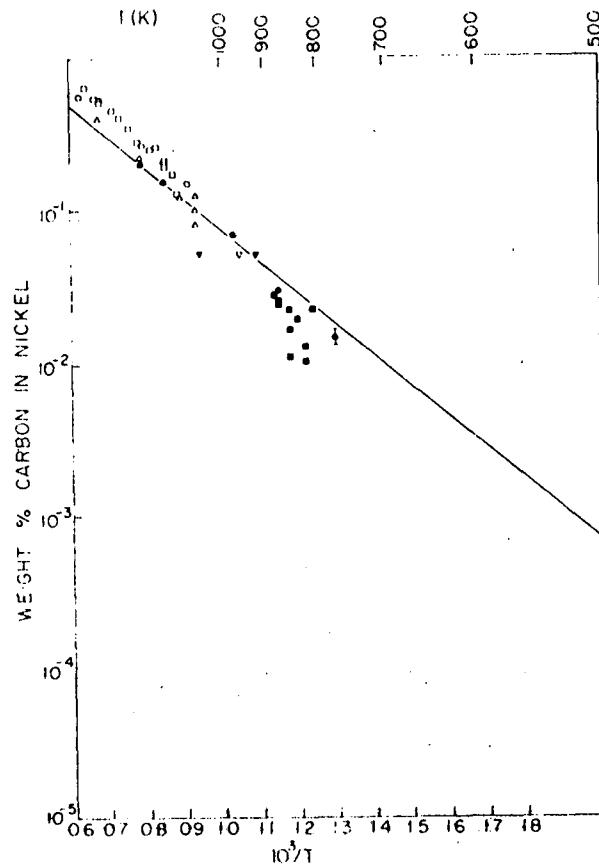


Fig. 1. Solubility data for carbon in nickel. Data shown are (●) Natesan and Kassner [14]; (■) Alcock and Stavropoulos [44]; (○) Dunn et al. [45]; (△) Lander et al. [15]; (×) Wada et al. [46]. The line represents the values used in this study, as explained in the text.

The application of eq. (1) requires accurate measurements of the bulk carbon concentration A_b . In these experiments, the carbon bulk doping was determined in situ by observing the temperature at which precipitation occurred and using available solubility data. The curve which we have used to represent the solubility dependence on temperature is shown in fig. 1. It represents an absolute value of carbon solubility at the high temperature end as given by Natesan and Kassner [14] and a heat of solution given by the average of the result of Natesan and Kassner and of Lander et al. [15], i.e., 10.0 kcal/mole.

Precipitation temperatures were obtained from a combination of LEED and Auger measurements. LEED information on precipitation was provided from the appearance of "rings", characteristic of graphite, in the diffraction pattern. Auger spectra showed a change in carbon Auger peak size and shape when graphite precipitated on the surface. The uncertainty in the precipitation temperature obtained in this manner is about 25 K, due in part to hysteresis in the phase transition and in part to the inaccuracy of the (chromel-almel) thermocouple temperature measurements with respect to an absolute scale. This results in approximately a 25% uncertainty in determining the absolute carbon doping level, and about a 10% uncertainty in relative doping levels.

The analysis we have used to interpret the segregation data is dependent upon the assumption that the bulk crystal provides a carbon reservoir which is essentially unperturbed by the segregation to the nickel surface. In table 1 we indicate that this assumption is reasonably well justified even for the sample with the lowest bulk doping (45 ppm). The table shows by how much the bulk level is perturbed by the segregation of various amounts of carbon to the surface.

Carbon atoms will also segregate to other defects in the bulk, such as impurities or dislocations and this effect will lower the free carbon atom concentration. Typical dislocation densities (10^8 cm/cm^3) would be expected to trap about 1 ppm carbon while transition metal impurities in the original nickel stock are found at the $1-10$ ppm concentration levels [16]. However, in the analysis of our experimental results the carbon concentration determined in situ by precipitation measurements has been used and since this method measures the free carbon doping level in the crystal, we may ignore segregation to other defects.

In table 2 we list the carbon doping levels of the crystals studied with (100)

TABLE 1

Amount of carbon from solution required to produce various surface structures

Structure	Amount of carbon from solution (wppm)
Graphite (monolayer)	0.75
$\text{p}(2 \times 2)$ (1 carbon/4 nickel)	0.075
$\text{c}(2 \times 2)$ (1 carbon/2 nickel)	0.15

TABLE 2

Carbon content of crystals studied

Crystal	Carbon wppm	
	LECO analysis	In situ
No. 1	138	45
No. 2	266	75
No. 3	510	600
No. 4	1238	1300

surface orientation. Crystal No. 3 was initially of (110) orientation but recrystallized to (100) as determined by both LEED and X-ray observations. Preliminary observations of the segregation of carbon to Ni(110) were made on this crystal. Sample No. 4 was processed through several different doping levels in situ by sputtering with 400 eV argon ions at temperatures which resulted in graphite precipitation *. Data points at doping levels of 1050 wppm carbon and 850 wppm carbon were obtained by this technique. All the data presented below were obtained on surfaces containing, according to Auger spectra, less than 0.5% of a monolayer of sulfur or phosphorus, and are believed to be characteristic of clean surfaces.

Auger spectroscopy was used in these experiments to monitor how the surface carbon concentration varied with temperature. Conventional measurements from Auger spectra use the peak-to-peak height of the appropriate signal in the derivative spectrum. However, as discussed by a number of authors [18], for iVV type transitions, the line shape is dependent upon the chemical bonding environment of the adsorbate. Thus, changes in the line shape with coverage may complicate measurements of surface coverage.

Solutions to these problems have been described by Houston and Park [19] and by Houston [20] who show that areas under Auger peaks ($\int N(E)dE$) provide a better measure of adsorbate concentration and are undistorted by potential modulation in the detection system. These concepts have been implemented by Grant, Haas and Houston [21], and by Staib and Kirschner [22]. The analogue techniques which we have employed to compute areas under Auger peaks have been described in a recent paper [23].

An important aspect of our work is the quantitative calibration of the integrated Auger signal for carbon. This is based on the equation [23,24]

$$V_{\text{out}} = \frac{g}{(RC)^2(dE/dt)^2} \frac{e_0^2 ZT}{4\sqrt{2}} o(E_p) (1 - \omega) i_p \csc \phi_p \Omega N r. \quad (3)$$

* The sputtering yields of nickel and carbon at this energy are in the ratio 10 : 1 [17], so that sputtering times become quite long.

Here $\sigma(E_p)$ is the ionization cross-section of the appropriate atomic level at E_p , the primary electron energy; i_p is the current in the primary electron beam; $(1 - \omega)$ is the probability that an Auger process occurs; ϕ_p is the angle between the primary beam and the crystal surface; Ω is the fraction of solid sphere centered on the crystal which is subtended by the detector; r is the backscattering factor, N the number of atoms in the surface monolayer, e_0 the potential modulation amplitude; (RC) is the integrator time constant, dE/dt the analyzer voltage sweep rate, Z the detector impedance, T the transmission of the grids, and g the gain of the lock-in amplifier.

We have used the following procedure to normalize our Auger measurements of carbon concentration. In the initial stages of studying Ni(100) doped at about 1300 wppm carbon (sample No. 4) it was possible to precipitate large amounts of graphite on the surface. From measurements of the attenuation of the nickel Auger peaks at different energies and the use of overlayer attenuation functions and inelastic mean free paths determined by Shelton [25,26] for jellium, with $r_s = 1.5$ for graphite, it was possible to estimate the thickness of the graphite layer and the fraction of the surface covered. This procedure was followed for two different amounts of graphite and integrated Auger signal * measurements made in each case. In our other experiments, the integrated carbon Auger signal strengths corresponding to saturated $c(2 \times 2)$ and $p(2 \times 2)$ structures on Ni(100) were estimated from data on the dependence of coverage on temperature extrapolated to saturation and from LEED patterns. The backscattering factor was determined experimentally using the technique of Gerlach and Ducharme [27]; $r = 1.25$ was obtained.

Eq. (3) may be written in the form

$$V_{\text{out}} = KN\sigma(E_p). \quad (4)$$

where all the known parameters are lumped in the constant K . For the $p(2 \times 2)$ and $c(2 \times 2)$ structures N is assumed to correspond to one quarter and one half monolayer respectively. To interpret the thick graphite case we use the experimental results of Shelton et al. [4]. They observed that the ratio of the carbon Auger signal from one monolayer of graphite on Ni(111) to that from thick graphite precipitated on Ni(111) was 1 : 1.52. This ratio accounts both for the attenuated contributions from the bulk crystal and the changes in backscattering factor from nickel to graphite. Thus in each case we could obtain an experimental estimate of σ . The results are listed in table 3.

* In general, as recently discussed by Houston [29], Auger features on $N(E)$ spectra, with the secondary electron background removed, appear as step like features with non-zero values of $N(E)$ extending to lower energies. This is attributed to inelastic scattering of Auger electrons, due for example, to plasmon excitation. In our measurements of $\int N(E)dE$ from graphite covered surfaces, we adjusted the background compensation so that $N(230 \text{ eV}) = N(290 \text{ eV}) = 0$. A rough calculation indicates that the area measured in this way is within $\sim 10\%$ of the true Auger current with no inelastic interactions. $N(E)$ curves measured here for the carbon Auger peak with the carbide form show no low energy tail, suggesting that in these cases the system is described reasonably well by a monolayer model.

Table 3
K-shell ionization cross section for carbon, at $E_p/E_i = 4.8$

Structure	$\sigma (\times 10^{-19} \text{ cm}^2)$
p(2 × 2)	3.39
Graphite $f = 0.74$	3.40
Graphite $f = 0.88$	3.39
Quasi-c(2 × 2)	3.28
Average	3.36

f = fraction of the surface covered with graphite as determined by method described in text.

The values we obtain are in good agreement with the results of other workers [22,24,27,28]. It should also be noted from table 3 that the values obtained under different, reasonably well defined conditions are in good agreement.

3. Results

3.1. Ni(100)

Preliminary results obtained on Ni(100) have been the subject of an earlier publication [5]. To obtain isosteric heats of segregation through application of eq. (1) we have obtained data at 5 different carbon doping levels. In fig. 2 we present isosteres for three different values of carbon coverage. The carbon coverage was determined from integrated Auger signals using eq. (3) with values of the parameters determined as described above. The values of fractional coverage, θ , are based on the convention that $\theta = 1$ for a p(2 × 2) structure (1 carbon per 4 nickel atoms).

From fig. 2 the isosteric heat of segregation is -10.8 kcal/mole at $\theta = 0.70$. The values of the isosteric heat of segregation at the other two coverages ($\Delta H_{\text{seg}} = -12.0$ kcal/mole at $\theta = 0.59$ and $\Delta H_{\text{seg}} = -10.4$ kcal/mole at $\theta = 0.78$), suggest that ΔH_{seg} decreases with increasing θ , but the differences are smaller than the expected experimental uncertainty. The LEED pattern for all the data of fig. 2 was p(1 × 1).

From fig. 2, it is seen that a wide range of surface coverages can be obtained at reasonable temperatures only with a crystal possessing a rather low doping level, such as the crystal designated No. 1. The results for the variation with temperature of the carbon coverage on this sample surface have been described previously [5]. As reported, we find that an analysis of the coverage-temperature data using eq. (2) (i.e., the Langmuir model) can describe the data for coverages less than 1 carbon per 4 nickel atoms with $\Delta H_{\text{seg}} = -10.8$ kcal/mole K, in remarkably good agreement with the isosteric value; the excess entropy of segregation is found to be 3.4 cal/mole K. At $T = 652$ K and $\theta \approx 0.86$ (based on 1 carbon per 4 nickel atoms) a phase transition was observed resulting in a LEED pattern which we have

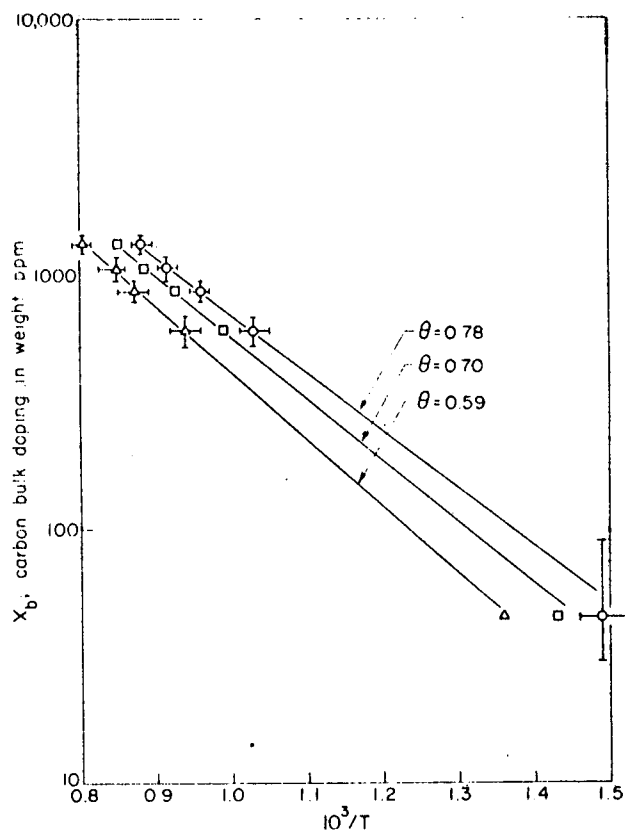


Fig. 2. Isosteres of carbon on Ni(100) for surface coverages of 0.78, 0.70, 0.59; these are based on $\theta = 1$ for $p(2 \times 2)$.

previously called a quasi- $c(2 \times 2)$. With decreasing temperature the carbon Auger signal slowly increases and saturates at 1 carbon per 2 nickel atoms. In fig. 3 we present a Langmuir plot* ($\log \theta/(1 - \theta)$ versus $1/T$) for the data from sample No. 1.

To obtain the heat of segregation in the quasi- $c(2 \times 2)$ phase we have used thermodynamic arguments [5]. At 652 K, the phase transition temperature, two phases are in equilibrium: the disordered phase and the ordered quasi- $c(2 \times 2)$ phase. At 615 K, the precipitation temperature, graphite and the quasi- $c(2 \times 2)$ phase are in equilibrium. Equating chemical potentials of the surface carbon at the two temperatures to the values in the bulk solution and using the heat of solution of carbon in nickel one finds $\Delta H_{\text{seg}}(\text{quasi-}c(2 \times 2)) \approx -4.6 \text{ kcal/mole}$ [5].

* A detailed discussion of kinetic evidence to substantiate our claim that all data are equilibrium data is available elsewhere [13].

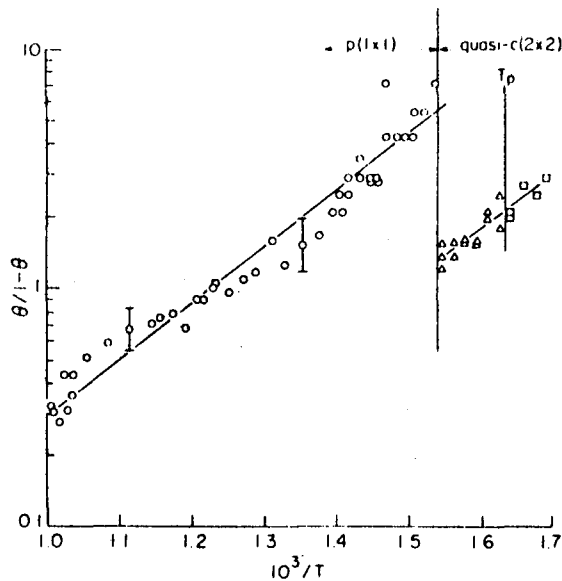


Fig. 3. Langmuir plot of data from a nickel sample containing ~ 45 ppm by weight; the data are normalized to $\theta = 1$ at $p(2 \times 2)$. The slope indicated for the high temperature region corresponds to a heat of segregation of -10.8 kcal/mole. T_p is the temperature at which precipitation was observed.

3.2. Ni(110)

The sample containing ~ 600 ppm by weight of carbon was initially of (110) orientation, but partially recrystallized to expose half (100) and half (110) surfaces, as verified by X-ray back reflection measurements and LEED. We have briefly studied segregation to Ni(110) on this crystal. We found no carbon on the surface, within our signal to noise limitations, except when graphite was precipitated on the surface as the temperature was lowered and the solubility limit exceeded. This could be interpreted as implying that the heat of segregation to this surface is positive, i.e., that carbon is more strongly bound in the bulk than on Ni(110). However, we were never able to obtain a sharp (110) LEED pattern from this surface, and therefore we suspect that some unknown structural defects may be present. The LEED pattern from the (100) half of the sample was of excellent quality. The carbon-Ni(110) system therefore requires some additional study to test our preliminary observation that no significant surface segregation occurs.

3.3. Ni(S) [7(100) $\times$ (133)]

Our observations of segregation of carbon to a stepped nickel surface have also been discussed previously [6], and some speculative attempts at interpretation were

presented. Here we will review only the most important results of this work. On this surface, as contrasted with Ni(100), a dependence of Auger peak shape on coverage was observed. We noted that this appears to require a coverage dependent binding energy and that the binding energy decreases with increasing θ . Further we found that the segregation to this surface could not be well described by a simple Langmuir model. Finally the quasi- $c(2 \times 2)$ structure did not form on this surface, and the carbon coverage appeared to saturate at the coverage of a $p(2 \times 2)$ structure. We were, in fact, able to form $p(2 \times 2)$ LEED patterns on the stepped surface in contrast to Ni(100) where this structure was not observed.

4. Discussion

We have demonstrated that the segregation of carbon to Ni(100) can be well described by a Langmuir model; i.e., of non-interacting localized segregated carbon atoms. Saturation of the surface phase described by the Langmuir model occurs at 1 carbon per 4 nickel atoms. This result is interesting for several reasons. The Langmuir dependence is observed to high coverages ($\theta \sim 0.86$), so that the interactions between carbon atoms must be very weak. Furthermore, an ordered structure corresponding to 1 carbon per 4 nickel atoms was never observed on Ni(100), which is again consistent with weak carbon-carbon attractive interactions. Saturation at 1 carbon per 4 nickel atoms may be due to strong nearest neighbor and next neighbor repulsions. All these observations are consistent with a nickel-carbon bonding interaction which is highly local. The reader is reminded that although the heat of segregation to (100) is $-10.8 \text{ kcal/mole} \pm 1.8 \text{ kcal/mole}$ the total binding energy of a carbon atom at this surface is $\sim 170 \text{ kcal/mole}$, and thus the variation of this binding energy with coverage for $0.3 < \theta < 0.68$ is less than $\sim 2\%$. The Ni-C system should therefore be a good candidate for theoretical studies of chemisorption in the surface molecule limit [30].

The formation on Ni(S)(7(100) $\times$ (133)) of $p(2 \times 2)$ structures as shown by LEED suggests that the surface steps may provide sites for easy nucleation of this ordered phase. Even in this case, however, ordered structures did not form until a coverage $\theta \sim 0.9$ was reached, so that the influence of the stepped surface is rather small. The presence of surface steps does increase the heat of segregation at low coverages to -18.9 kcal/mole (and prevents the formation of the quasi- $c(2 \times 2)$ phase [6]) again suggesting that local interactions are the most important.

CFO- BEBO calculations

Since the nickel-carbon interaction is believed to be primarily due to local interactions, with carbon-carbon interactions on (100) being negligible for the observed structures even at very high coverages, a theoretical treatment emphasizing local interactions may be successful. We have applied the crudest such theory which has

given reasonable results in other situations, the CFSSO-BEBO (Crystal Field Surface Orbital Bond Energy Bond Order) method developed by Weinberg and Merrill [1].

The BEBO concept is based upon the observation that the bonding energy generally may be described by the relation

$$E = E_s n^p \quad (5)$$

for homonuclear bonds between elements in the first row of the periodic table. Here n is the so-called bond order, E_s the energy of the single order bond, and p an empirical constant usually near unity. To apply the BEBO concept, one requires the value of E_s for all bonds being formed and broken and a relation describing how the various bond orders vary [31].

Consider, for example, the case of hydrogen chemisorption on nickel, illustrated in fig. 4. The hydrogen molecule can interact with the dangling surface orbital, forming a nickel-hydrogen bond. As the nickel-hydrogen bond order increases, the hydrogen-hydrogen bond order must decrease, so that

$$n_{\text{Ni-H}} + n_{\text{H-H}} = 1$$

Furthermore, the bond order between the surface nickel atom and the rest of the solid, n' , can remain constant only if $n_{\text{Ni-H}}$ does not exceed some value $n_{\text{Ni-H}}^{\text{max}}$. When this value is exceeded, the bond order between the surface nickel atom and the rest of the solid, n' , must decrease. This is the situation referred to as *spin unpairing* by Weinberg and Merrill [1] and requires the weakening of Ni-Ni bonds.

Weinberg and Merrill [1] proposed that the surface orbitals in the chemisorption bond be determined by crystal field symmetry, following the work of Bond [32] (1966). The electronic configuration of nickel in the bulk, as given by Brewer [33], is $(3d)^7(4sp^2)$, so that, following ref. [11], 0.6 d holes are available per d-orbital for bonding and 0.67 p-electrons are available per p-orbital for bonding. These would be the values of $n_{\text{Ni-H}}^{\text{max}}$ of the previous discussion. The orbitals are divided into the $e_g(d_{z^2}, d_{x^2-y^2})$ and $t_{2g}(d_{xy}, d_{yz}, d_{zx})$ types.

In the discussion that follows, a departure is made from the procedure described by Weinberg and Merrill [1]. We will neglect the p-electron contribution to binding.

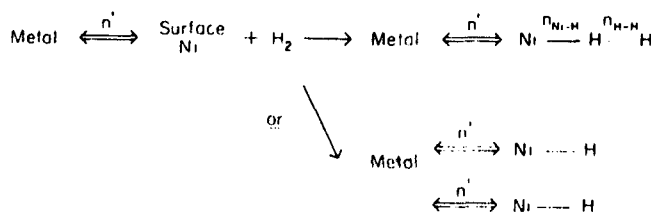


Fig. 4. Schematic representation of the bonding of dissociated hydrogen atoms to surface nickel atoms. n' is the bond order associated with the bonding of the surface nickel to the rest of the metal, and $n_{\text{Ni-H}}$, $n_{\text{H-H}}$ the bond orders of the nickel-hydrogen and hydrogen-hydrogen bonds respectively.

This simplification is consistent with the work of Doyen and Ertl [34] in which the Anderson model was successfully employed to calculate CO adsorption on nickel. They worked only with d-orbitals, and described the density of states in nickel by a delta function at the Fermi level. Thus we feel that d-orbital contributions may dominate in the cases to be discussed here. In particular, so long as the value of $E_{\text{Ni}-\text{C},s}$ is determined in a manner consistent with the number of (Ni) electrons available for bonding, the results will depend only very weakly on the number of Ni bonding electrons assumed.

To apply the BEBO formalism, we require a value of the nickel-carbon single order bond ($E_{\text{Ni}-\text{C},s}$) and the nickel-nickel spin unpairing energy ($E_{\text{Ni}-\text{Ni},s}$). The latter quantity was determined from data of ref. [33] (see appendix), to be 34 kcal/mole. Additional input to our calculation may be obtained from observations of bond lengths. From studies of $\text{Ni}(\text{CO})_4$, the nickel-carbon bond order, calculated from IR data, was found to be 1.33 [35] and the Ni-C distance, R , in this compound is known to be 1.82 Å [36]. Using the Pauling relation [37],

$$R = R_s - 0.26 \ln n, \quad (6)$$

where R_s is the single Ni-C bond distance, one finds $R_s = 1.89$ Å.

The most important quantity in our analysis is the nickel-carbon single bond order bond energy ($E_{\text{Ni}-\text{C},s}$). We have obtained this quantity from several empirical approaches and the results are listed in table 4. We adopt an average value of ~56 kcal/mole. Details of these calculations are described in the appendix.

The experimental heat of segregation of carbon to Ni(100) (-10.8 kcal/mole) may be used to obtain the enthalpy of bonding of carbon on Ni(100). Using the relation between the heat of solution, the heat of segregation, and the heat of adsorption [7], i.e.,

$$q_{\text{sol}} - q_{\text{segregation}} + q_{\text{adsorption}} - q_{\text{sublimation}} = 0, \quad (7)$$

and available data for the heat of solution of carbon in nickel, 10.0 kcal/mole, and the heat of sublimation of graphite, 169.9 kcal/mole [38], the binding enthalpy of carbon on Ni(100) is found to be 170.7 kcal/mole. To obtain a theoretical value with which to compare this quantity we have neglected the difference between

Table 4
Nickel carbon single order bond binding energies

$E_{\text{Ni}-\text{C},s}$ (kcal/mol)	Method
55	Mixing rule without electronegativity term
55.7	Mixing rule with screened ionic (electronegativity) term in bulk
56.4-59.2	Mixing rule with screened ionic term at surface
55.3	Heat of solution data

enthalpy and energy. (Since we are dealing with enthalpy differences, the distinction between enthalpy and energy will be partially cancelled.) The BEBO formalism yields for the binding energy E of a carbon atom to Ni(100)

$$E = 4n_{\text{Ni-C}(1)}E_{\text{Ni-C},s} - 34(n_{\text{Ni-C}(1)} - 0.6)4 + n_{\text{Ni-C}(2)}E_{\text{Ni-C},s} \text{ kcal/mole.} \quad (8)$$

where * the bond types 1 and 2 are shown in fig. 5. We have assumed that the carbon atom sits in the centered site on Ni(100). At the surface, we assume nickel to have a covalent radius of 1.15 Å, and carbon to have a covalent radius of 0.77 Å [37]. This fixes the adsorption geometry and using the Pauling relation [37] (eq. (6)) for bond lengths, one finds $n_1 = 0.89$ and $n_2 = 0.2$. From eq. (8) we then obtain $E = 171.4$ kcal/mole which is certainly in reasonable agreement with the experimental value.

In the BEBO model, carbon-carbon interactions arise from the depletion of nickel surface orbitals in the neighborhood of the carbon atom. For nearest neighbors on Ni(100), the repulsion energy would be given by $(0.89)(2)(E_{\text{Ni-Ni},s})$, i.e., 60.5 kcal/mole since, for nearest neighbors, the 0.89 bond order must be supplied to two orbitals by breaking Ni-Ni bonds. For the case of next nearest neighbors, the repulsion would be 30.2 kcal/mole. This simple calculation therefore gives an explanation of why in segregation of carbon to Ni(100), the coverage saturates at 1 carbon per 4 nickel atoms.

In a similar manner we have calculated binding energies of single carbon atoms to Ni(110) and Ni(111). The site geometries considered are shown in fig. 6 and the binding energies at these sites listed in table 5. Our results are consistent with the

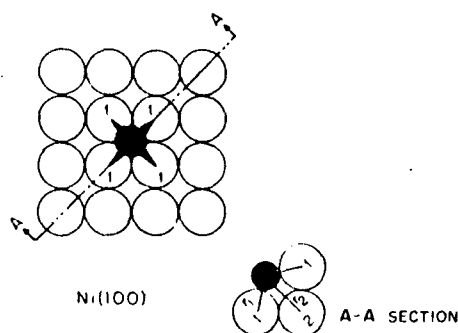


Fig. 5. Assumed carbon atom binding to Ni(100) at the centered site as described in the text. Bond types 1 and 2 are indicated.

* The second term is the spin unpairing contribution, arising from the breaking of Ni-Ni bonds as required to allow $n_{\text{Ni-C},s}$ to exceed 0.6.

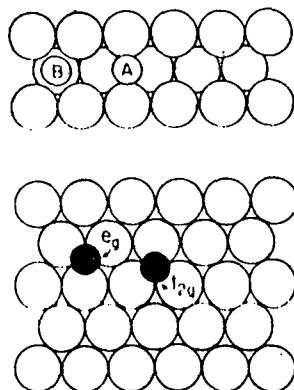


Fig. 6. Possible binding geometries for carbon at Ni(110) and Ni(111). On Ni(110) there are two sites A and B with nearly the same binding energy, as explained in the text. On Ni(111) there are two distinct sites e_g and t_{2g} . The next plane of nickel atoms would occupy the t_{2g} sites.

experimental observation that single atom segregation of carbon does not occur on Ni(110) and Ni(111). It is interesting to note that the differences in the calculated binding energies of carbon to these surfaces is primarily due to co-ordination effects: on (100) a hard sphere carbon atom may contact 4 nickel atoms, while this number is reduced to 3 on Ni(111) and 2 on Ni(110).

The increased binding energy for small carbon coverage on Ni(S)[(100) $\times$ ($\bar{1}$ 33)] may also be explained by the BEBO model. A hard sphere model of this surface is shown in fig. 7. We consider segregation of carbon to sites of the type A and B at the steps. At site A, the broken Ni-Ni bond provides an additional 0.15 d-electron before spin unpairing, thus increasing the binding energy by ~ 5.1 kcal/mole. At site

Table 5
Binding energy of C on various Ni surfaces

Site	Binding energy (kcal/mole)	
	Calculated	Experiment
Ni(100)	171.4	169.5
$\theta < 1$ carbon/4 nickels		
Ni (S) (7(100) $\times$ (133))	181	178.8
($\theta < 1/3$ p(2 $\times$ 2))		
Ni(111) t_{2g}	123.0	ΔH_{sep} may be positive; i.e., $E < 159.9$
e_g	152.9	
Ni(110) A	100.7	
B	90.7	

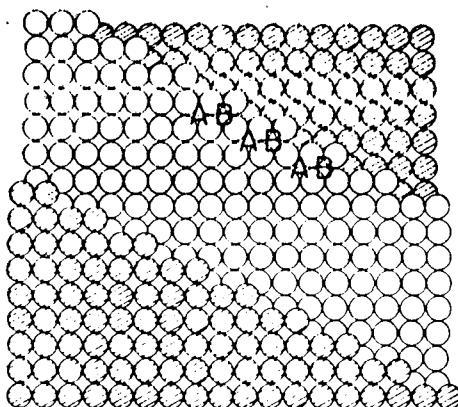


Fig. 7. Average atomic arrangement at the stepped surface $\text{Ni(S)}[7(100) \times (133)]$. For carbon atoms at sites A and B the nearest neighbor Ni atoms have some of their nearest neighbors missing.

B, the contribution is three times as great i.e., ~ 15.3 kcal/mole. Assuming that no order exists, so that the 2 types of site have equal occupation, the average increase would be ~ 10 kcal/mole, giving the low coverage binding energy on the stepped surface as ~ 181 kcal/mole. The agreement with the experimental result (shown in table 5), is again reasonable.

5. Conclusions

The agreement between the isosteric heat of segregation of carbon to $\text{Ni}(100)$ for $0.56 < \theta < 0.78$ ($\theta = 1$ at 1 carbon per 4-nickel atoms) with the heat of segregation obtained using the Langmuir model for data in the range $0.3 < \theta < 0.86$ provides strong support for the Langmuir model. It is particularly interesting that normalization to $\theta = 1$ at 1 carbon per 4 nickel atoms is required, as no ordered structures corresponding to this coverage are observed on $\text{Ni}(100)$. This additional observation supports our picture of weak carbon-carbon attractive interactions and strong nearest neighbor repulsive interactions on $\text{Ni}(100)$. We have applied the Bond Energy-Bond Order formalism to the bonding of carbon on nickel surfaces. The success of this simple approach further suggests that the nickel-carbon bond involves mainly local interactions, with the binding energy determined largely by co-ordination effects.

The differences observed between the nickel surfaces examined is particularly interesting. On $\text{Ni}(111)$, where there is an excellent fit between the basal plane of graphite and $\text{Ni}(111)$, the carbon-carbon interactions appear to dominate, and a stable segregated monolayer phase of carbon on $\text{Ni}(111)$ has been observed [4]. Tentative results on $\text{Ni}(110)$ show no detectable surface segregation of carbon.

It is instructive to inquire as to the possible relevance of these studies to the problems of catalysis on transition metal surfaces. The first comment is that the particular states and structures which we have observed are probably not directly involved in any surface reaction since the binding energies (~ 170 kcal) are so large. However, the importance of carbonaceous deposits has been discussed by Somorjai and co-workers [2]. The well defined structures which we have studied offer excellent systems for the quantitative study of the effect of carbon layers on reaction rates; these are currently being pursued using molecular beam techniques.

Acknowledgments

This work was supported by the National Science Foundation and by ARPA through the Materials Science Center of Cornell University. The authors are grateful to B.F. Addis for crystal preparation and to W.N. Unertl for useful discussions.

Appendix

The methods used to determine $E_{\text{Ni-C},s}$ are described here. The reader is reminded that BEBO is an empirical theory and that we have attempted to determine the necessary parameters in as self-consistent a manner as possible.

Pauling [39] proposed a series of empirical mixing rules for the determination of bond energies. One of the forms which he proposed is

$$E_{\text{A-B},s} = (E_{\text{A-A},s} E_{\text{B-B},s})^{1/2} + 30(X_{\text{A}} - X_{\text{B}})^2, \quad (6.1)$$

where $E_{\text{A-A},s}$ and $E_{\text{B-B},s}$ are the experimental single bond energies available from heats of sublimation or energies of dissociation. X_{A} and X_{B} are the standard electro-negativities; the second term represents the ionic contribution to the binding energy. In a metallic solid, or at its surface, the ionic term will be small due to screening by the free-electron gas. Weinberg [40] dropped the second term completely in his work. An alternative intuitive approach is to write

$$E_{\text{A-B},s} \approx (E_{\text{A-A},s} E_{\text{B-B},s})^{1/2} + 30(X_{\text{A}} - X_{\text{B}})^2 \exp(-r_{\text{AB}}/\lambda), \quad (6.2)$$

where r_{AB} is the A-B bond distance and λ the screening length. For nickel, we have determined λ from the Thomas-Fermi formula using a local density of free electrons, n , of 0.54/atom [41] in the bulk. At the surface, this density changes, and we have used the computations of Lang [42] to obtain the local free-electron density at the surface. We have estimated λ ($\propto n^{1/3}$) at the site of the carbon atom at a distance of 0.76 Å from the centers of the last plane of Ni. This position was obtained by locating the carbon atom in the four-fold centered site (fig. 5) and determining its position from the Pauling covalent radii for carbon and nickel. The resulting values of $E_{\text{Ni-C},s}$ from eq. (6.2) are given in table 4. Note that the screening is very

effective, even at the surface and that the electronegativity term may reasonably be neglected altogether.

The solubility of carbon in nickel has been studied by a number of workers, as noted earlier. Using an experimental heat of solution of 10.0 kcal/mole (see fig. 1) and the heat of sublimation of graphite, 170 kcal/mole [38,43], the experimental binding energy in solution E_{sol} is 160 kcal/mole. In the bond energy bond order formalism we may write

$$E_{\text{sol}} = n_{\text{Ni-C,s}} E_{\text{Ni-C,s}} - W, \quad (6.3)$$

where W is the strain energy involved. To calculate $E_{\text{Ni-C,s}}$ from the measured binding energy in solution E_{sol} we assume $n_{\text{Ni-C,s}} = 0.6$ the maximum available at the octahedral interstitial site without spin unpairing and that W can be calculated from the isotropic elasticity formula; $W = \frac{2}{3} \mu (\Delta V/V) \Delta V$, where μ is the shear modulus of nickel, V the volume of the undistorted interstitial hole, and ΔV the excess volume of the atom occupying the hole. The radius of the undistorted hole is 0.52 Å and if we assume the radius of carbon to be 0.77 Å we obtain $W \approx 39$ kcal/mole. We then obtain $E_{\text{Ni-C,s}} \approx 55.3$ kcal/mole in reasonable agreement with the value from the simple mixing rule.

The value of $E_{\text{Ni-Ni,s}}$ was obtained using the work of Brewer [33] who proposes that Ni bonds in the scheme $((3d)^7(4sp^2))$, i.e., 3 electron pairs are involved in the binding of each Ni atom. Using the experimental value of the sublimation energy of nickel, 102 kcal/mole [43], the value of the bonding energy per electron pair is therefore 34 kcal/mole.

References

- [1] W.H. Weinberg and R.P. Merrill, *Surface Sci.* 33 (1972) 493; 39 (1973) 206.
- [2] G.A. Somorjai, R.W. Joyner and B. Lang, *Proc. Roy. Soc. (London)* A331 (1972) 335.
- [3] S.L. Bernasek and G.A. Somorjai, *Surface Sci.* 48 (1975) 204.
- [4] J.C. Shelton, H.R. Patil and J.M. Blakely, *Surface Sci.* 43 (1974) 493.
- [5] L.C. Isett and J.M. Blakely, *Surface Sci.* 47 (1975) 645.
- [6] L.C. Isett and J.M. Blakely, *J. Vacuum Sci. Technol.* 12 (1975) 237.
- [7] J.M. Blakely and J.C. Shelton, *Equilibrium Adsorption and Segregation*, in: *Surface Physics of Materials*, Ed. J.M. Blakely (Academic Press, 1975).
- [8] J.C. Tracy, *J. Chem. Phys.* 56 (1972) 2736, 2748.
- [9] K. Christmann and G. Ertl, *Surface Sci.* 33 (1972) 254.
- [10] T. Murakami, S. Onno, M. Tamura and M. Kurata, *J. Phys. Soc. Japan* 6 (1951) 309.
- [11] S. Ono, *Mem. Fac. Engng., Kyushu Univ.* 12 (1950) 1.
- [12] H.L. Marcus and P.W. Palmberg, *Trans. AIME* 245 (1969) 1664.
- [13] L.C. Isett, Ph.D. Thesis, Cornell Univ. (1975), Materials Science Center Report No. 2540.
- [14] K. Natesan and T.F. Kassner, *Met Trans.* 4 (1973) 2557.
- [15] J.J. Lander, H.S. Kern and A.L. Beach, *J. Appl. Phys.* 23 (1952) 1305.
- [16] J.C. Shelton, Ph.D. Thesis, Cornell Univ. (1973), Materials Science Center Report No. 1959.

- [17] N. Laegrid and G.K. Wehner, *J. Appl. Phys.* 32 (1961) 365.
- [18] E.N. Siefkus, *Surface Sci.* 36 (1973) 472.
- [19] J.E. Houston and R.L. Park, *Rev. Sci. Instr.* 43 (1972) 1437.
- [20] J.E. Houston, *Surface Sci.* 38 (1973) 283.
- [21] J.T. Grant, T.W. Haas and J.E. Houston, *Surface Sci.* 42 (1974) 1.
- [22] P. Staib and J. Kirschner, *Appl. Phys.* 3 (1974) 421.
- [23] L.C. Isett and J.M. Blakely, *Rev. Sci. Instr.* 45 (1974) 1382.
- [24] F. Meyer and J.J. Vrakking, *Surface Sci.* 33 (1972) 27.
- [25] J.C. Shelton, *J. Electron Spectroscopy* 4 (1974) 143.
- [26] J.C. Shelton, *Surface Sci.* 44 (1974) 305.
- [27] R.L. Gerlach and A.R. DuCharme, *Surface Sci.* 32 (1972) 329.
- [28] G. Glupe and W. Mehlhorn, *Phys. Letters* 25A (1967) 274.
- [29] J.E. Houston, *Appl. Phys.* 6 (1975) 281.
- [30] J.W. Gadzuk, *Interaction of Atoms and Molecules with Surfaces*, in: *Surface Physics of Materials*, Ed. J.M. Blakely (Academic Press, 1975).
- [31] H.S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald Press, New York, 1966).
- [33] L. Brewer, *Viewpoints of Stability of Metallic Structures*, in: *Phase Stability in Metals Alloys*, Eds. Rudman, Stringer and Jaffee (1966).
- [34] G. Doyen and G. Frtl, *Surface Sci.* 43 (1974) 197.
- [35] H. Stannreich, K. Kawai, O. Sala and P. Krumholz, *J. Chem. Phys.* 35 (1961) 2168.
- [36] L.E. Sutton, *Spec. Publ. Chem. Soc.* 11 (1958).
- [37] L. Pauling, *J. Am. Chem. Soc.* 69 (1947) 542.
- [38] H.B. Palmer and M. Shelef, in: *Chemistry and Physics of Carbon*, Vol. 4 (1969) p. 85.
- [39] L. Pauling, *The Nature of the Chemical Bond* (Cornell Press, Ithaca, N.Y., 1960).
- [40] W.H. Weinberg, Ph.D. Thesis, Univ. of California, Berkeley (1971).
- [41] C. Kittel, *Introduction to Solid State Physics* (Wiley, 1971).
- [42] N.D. Lang, *Solid State Phys.* 28 (1973) 225.
- [43] O. Kubaschewski, E.L. Evans and C.B. Alcock (Metallurgical Thermochemistry, 1967).
- [44] C.B. Alcock and G.P. Sravapoulos, *Trans AIME* C77 (1968) 232.
- [45] W.W. Dunn, R.B. McLellan and W.A. Oates, *Trans. AIME* 242 (1968) 2129.
- [46] T. Wada, H. Wada, J. Elliott and J. Chipman, *Met. Trans.* 2 (1971) 2199.

Section 3

TASK 1.0 METALLURGICAL STUDIES

GENERAL OBJECTIVE

Many of the failures which have been observed in stress corrosion cracking, corrosion fatigue, and intergranular corrosion are directly related to special but not as yet fully understood compositional features of grain boundaries. The general objective of this task is to develop a comprehensive understanding of solute segregation at grain boundaries in Fe-Ni-Cr alloys. This understanding coupled with a rationalization of the electrochemical activity of grain boundary regions can ultimately reduce intergranular attack in stress corrosion and corrosion fatigue through control of compositional or processing variables.

CURRENT GOALS

The four major goals under Task 1 of this reporting period were as follows:

- o To complete the work on the surface segregation of sulfur in nickel single crystals. This work on surface segregation provides insight to the more difficult experimental task of evaluating segregation to grain boundaries.
- o To conduct a limited investigation of the effect of sulfur segregation on the electrochemical kinetics of nickel surfaces.
- o To begin an investigation of grain boundary solute segregation in polycrystalline nickel along with Inconel 600 and 304 stainless steel via Auger spectroscopy of in situ intergranular fractures.
- o To start studying the use of alloying elements to prevent the segregation of minor impurities such as sulfur, dilute binary nickel alloys will be studied.

Subsequent sections describe the work performed toward the attainment of these goals.

PREVIOUS WORK

Previous work using Auger analysis has shown that vacuum heating of single crystals and polycrystals of nickel can cause minor constituents to diffuse to the surface producing layers rich in impurities. Earlier experimental results suggest that the impurity segregation to the surface arises only from the alloy and not from the experimental chambers. Depth-composition profiles

of the impurity-segregated surface have been obtained by Auger spectroscopy after inert ion sputtering (Ar^+) as a function of time. The segregated layer has been estimated to be localized to a monolayer.

Vacuum heating of 304 stainless steels and Inconel alloy 600 also has been found to produce surface layers rich in sulfur and phosphorus. Each of these impurity elements may affect the rate and extent of segregation of the other.

CURRENT PROGRESS

Current progress under Task 1.0 is described in the following sections. The sections are organized according to the previous description of goals for this reporting period. That is:

- o Surface segregation of sulfur in nickel.
- o Electrochemical behavior of sulfur segregated nickel.
- o Grain boundary segregation.
- o Alloying effects on solute segregation.

Surface Segregation of Sulfur on Nickel

The following paragraphs present experimental and analytical results of the surface segregation on sulfur on nickel single crystal surfaces. This work provides a fundamental understanding of the nature of sulfur segregation on nickel and allows insights to the phenomena of solute segregation in commercial alloys. The study of segregation to the easily accessible metal surface will serve as a guide in studying the more difficult problem of grain boundary segregation. Much of the work on sulfur segregation on nickel single crystals has been already reported. This report provides an analysis of earlier results.

Experimental Details. The details of specimen preparation and the Auger electron spectroscopy technique have been reported earlier. The only pertinent modifications to earlier techniques and facilities is the addition of a scanning attachment to the Auger unit along with a device to permit fracturing of specimens in situ.

Effects of Temperature. A plot of the normalized Auger peak heights of segregated sulfur on a cleaned nickel (001) surface versus temperature is shown in Figure 3.1.

The Auger analyses were carried out after the specimens had completely cooled to room temperature. They had been heated previously for 30 minutes at selected temperatures. The Auger normalized peak heights reflect the relative quantities of the segregated-sulfur on the surface. A sulfur-induced structure on the nickel (001) surface seemed to initiate below 450°C. The signal of the sulfur peak, however, was too small to be detected. The amount of segregated-sulfur accumulated slowly for temperatures below 600°C. However, the segregated sulfur built up quickly in the temperature range of 600°C and 700°C. As temperature rose to 850°C, the Auger normalized peak height of S(150)/Ni(61) approached a value of 0.66 ± 0.05 . Two other isochronous segregation curves, 2 hr and 10 hr of heating, are also plotted in Figure 3.1. For temperatures below 550°C, it was difficult to reach the saturated value even for times longer than 10 hours. This was due to carbon segregation below 550°C. The site-competition between sulfur and carbon made interpretation of the segregation more complex. However, reheating or step-cooling specimens with a saturated sulfur surface built up at higher temperatures did not change the surface composition.

It is interesting to note that the degree of segregation decreased after the specimen had been heated and sputtered. Figure 3.2 shows a variation of the amount of segregation as a function of heating and sputtering for a nickel single crystal with a (001) face at 850°C. The results shown in this figure were obtained by a series of 10 minute periods of heating and subsequent ion sputtering. A clean specimen was first heated to 850°C for 10 minutes and then followed by a 10 minute sputtering to remove the segregated sulfur. The identical procedure was serially repeated. The S(150)/Ni(61) value was nearly 0.66 ± 0.05 at the first heating, and decreased to about 0.18 by the fifth heating. The decrease of segregation amount could be explained by the depletion of sulfur near the surface. Subsequently, when the specimen was heated for 30 minutes, the S(150)/Ni(61) value increased to 0.3. The segregated-sulfur which accumulated on the surface later in the experiment diffused from the deeper bulk material.

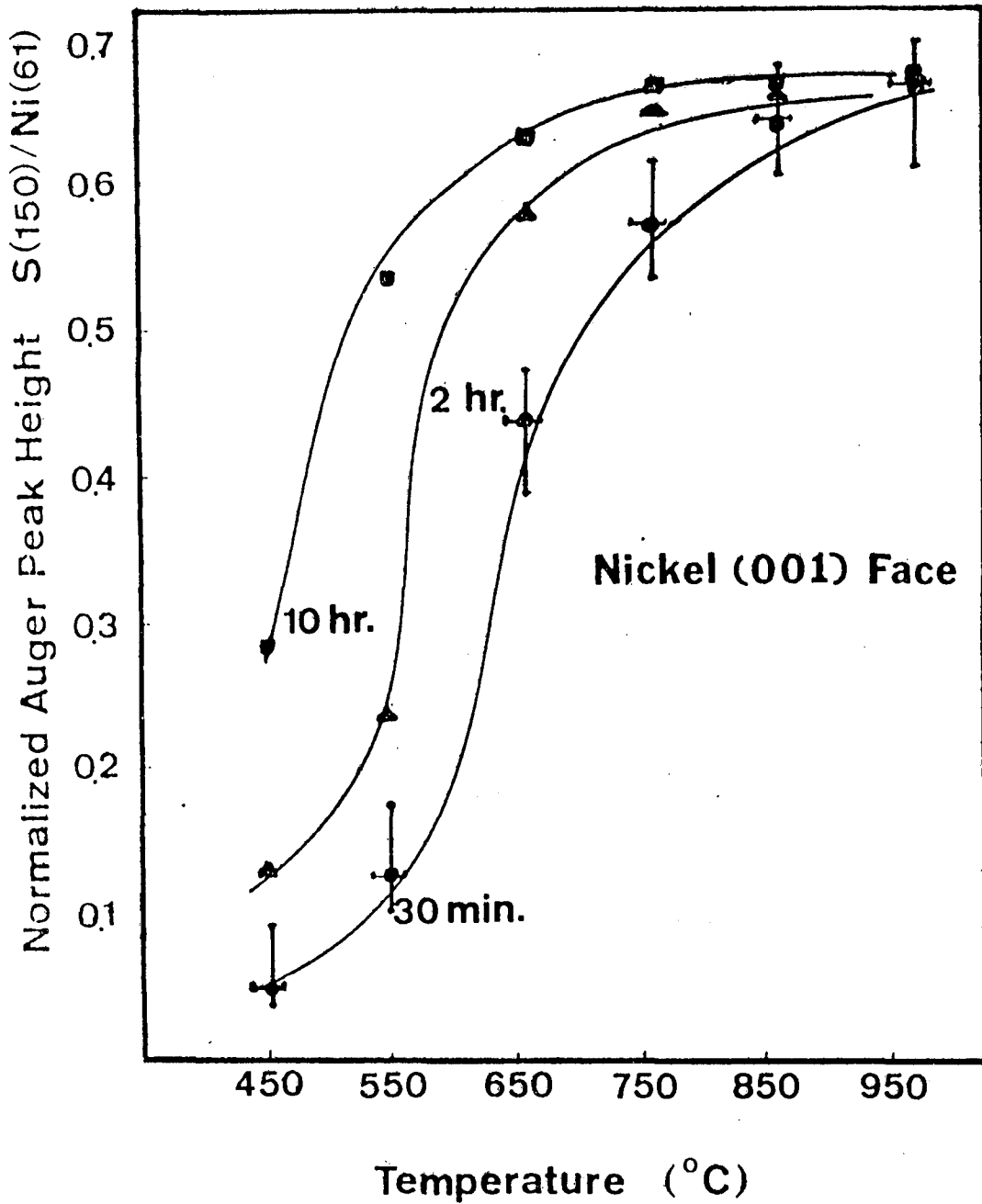


Figure 3.1 The iso-chronous surface segregation curves for sulfur to the (001) face of a nickel single crystal.

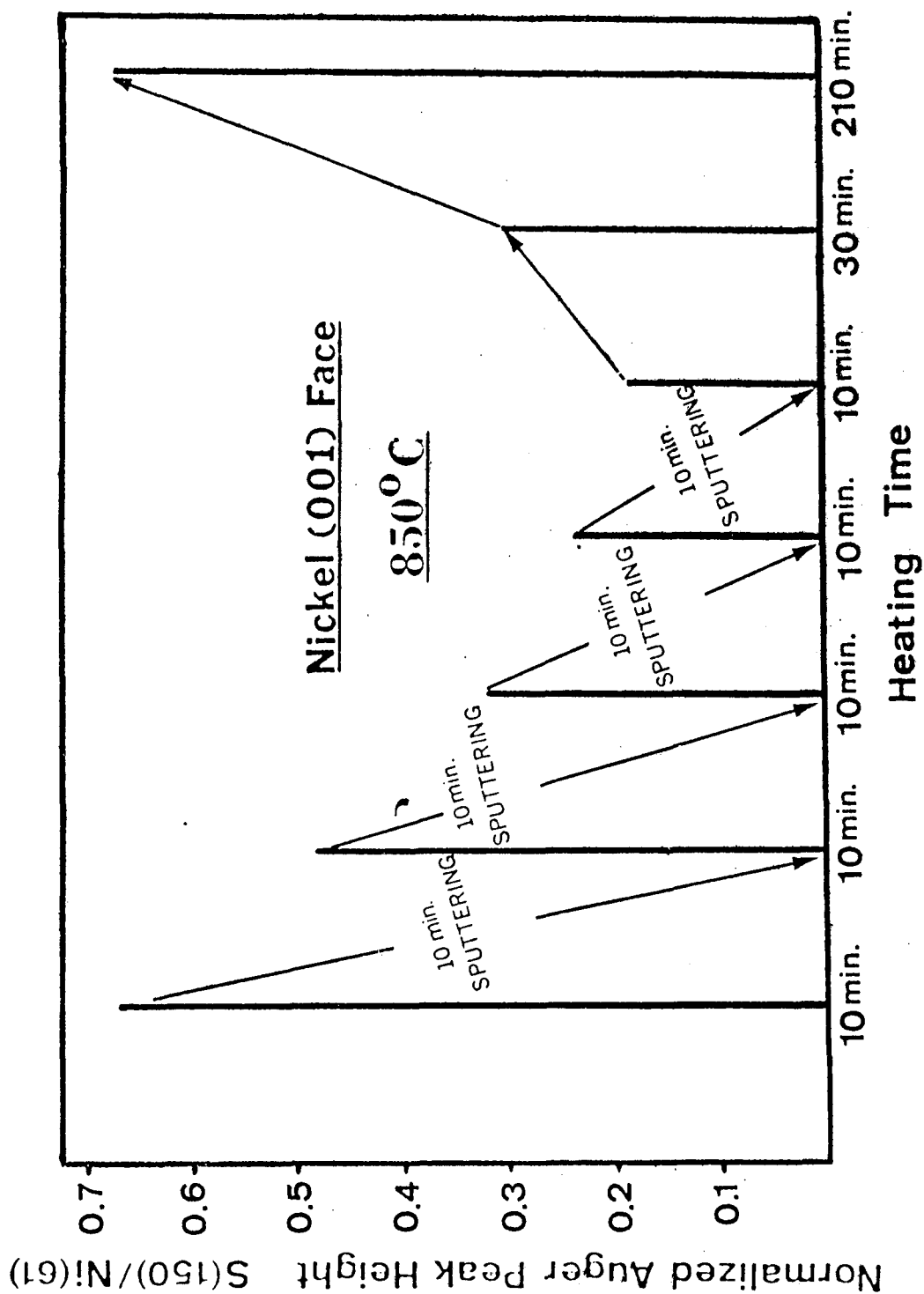


Figure 3.2 Variation of the Auger normalized peak height as a function of heat and sputtering.

Dynamic Segregated Measurements. A better approach in studying the segregation process is the plotting of isothermal segregation curves. This approach was used after simultaneous ion bombardment and pre-heating, hence the term dynamic. After the selected temperature stabilized, ion bombardment was stopped, and the Auger analysis was carried out as a function of time. Ion bombardment during pre-heating sputtered away segregated sulfur which formed during the course of pre-heating. Thus, the Auger analysis was started from a sulfur-free surface at the selected temperature.

This is demonstrated for (001) nickel in Figure 3.3. Each curve of this figure represents the data for a selected temperature and shows the amount of segregation as a function of time. As can be seen from this figure, sulfur diffused onto the surface at a constant rate during the early stages at all temperatures. The Auger sulfur peak was too small to be determined for 5×10^3 seconds at temperatures of less than 650°C . However, segregated sulfur slowly saturated when the specimens were heated for long periods of time. Figure 3.4 illustrates this behavior. Normalized Auger peak heights, $S(150)/Ni(61)$, are plotted as a function of logarithm of time. It is evident that the $S(150)/Ni(61)$ saturation values were independent of temperature. For lower temperatures saturation of segregated sulfur might well occur for longer times. It should be noted that the Auger analyses during heating were calibrated to offset temperature and magnetic field effects.

Thickness of the Surface Segregation Zone. Bombardment by argon ions for less than two or three minutes almost completely removed the segregated-sulfur which had built up during heating. Figure 3.5 shows a depth-composition profile of a typical region of the sulfur-segregated surface. These are plots of the normalized Auger peak heights of the selected peak $S(150)/Ni(61)$ as a function of sputtering time. Since the sputtering rate was approximately 1 to 2 $\text{\AA}/\text{min}$, it seems that the segregated-sulfur is localized within 5 $\text{\AA}$ of the surface.

Effect of Sulfur Content. A set of nickel single crystals (001) faces having different sulfur levels in the range of 5 ppm was examined. The saturation of sulfur segregation as a function of sulfur content is shown in Figure 3.6. Saturated segregated-sulfur was built up at 850°C . The Auger analyses were carried out at room temperature. The results showed no significant difference in the amount of segregated-sulfur after heat-treatment. The deviation of

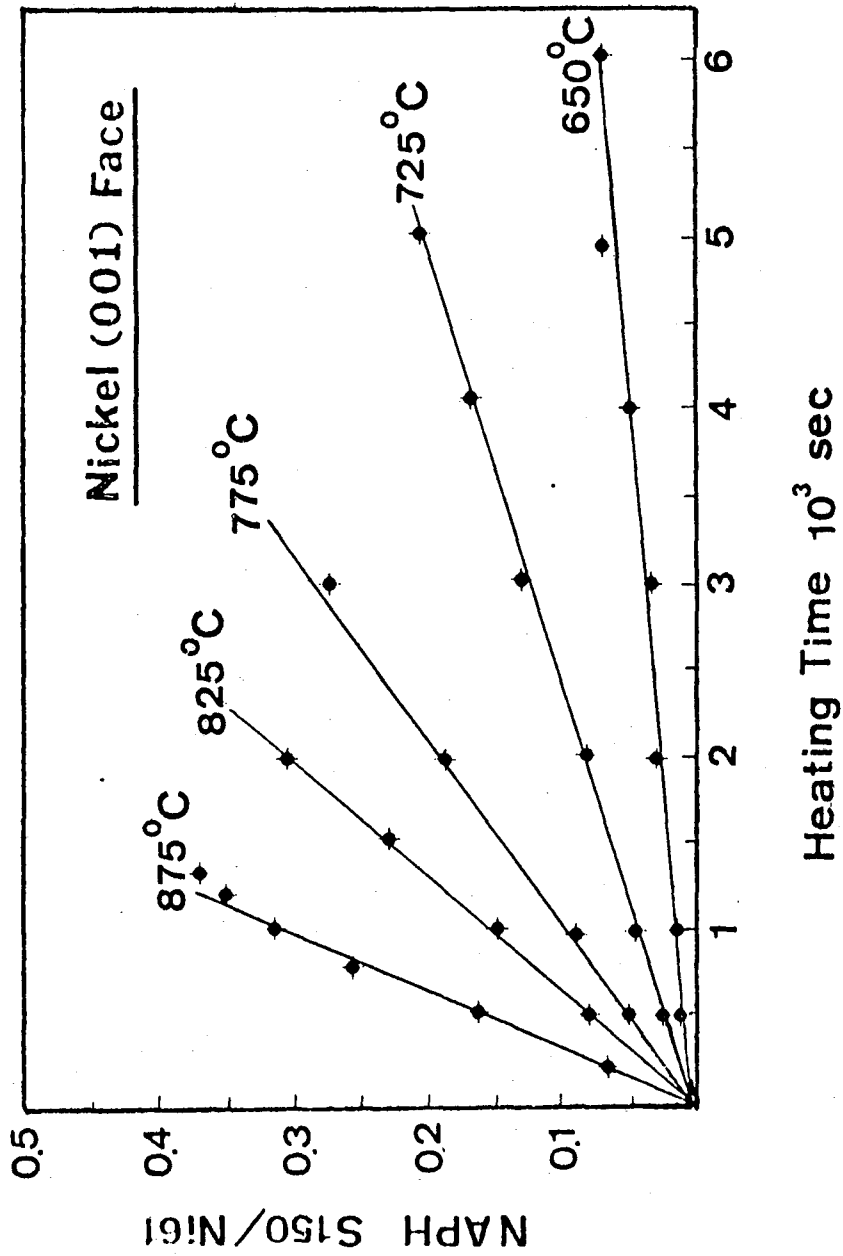


Figure 3.3 Auger normalized peak height as a function of time and temperature.

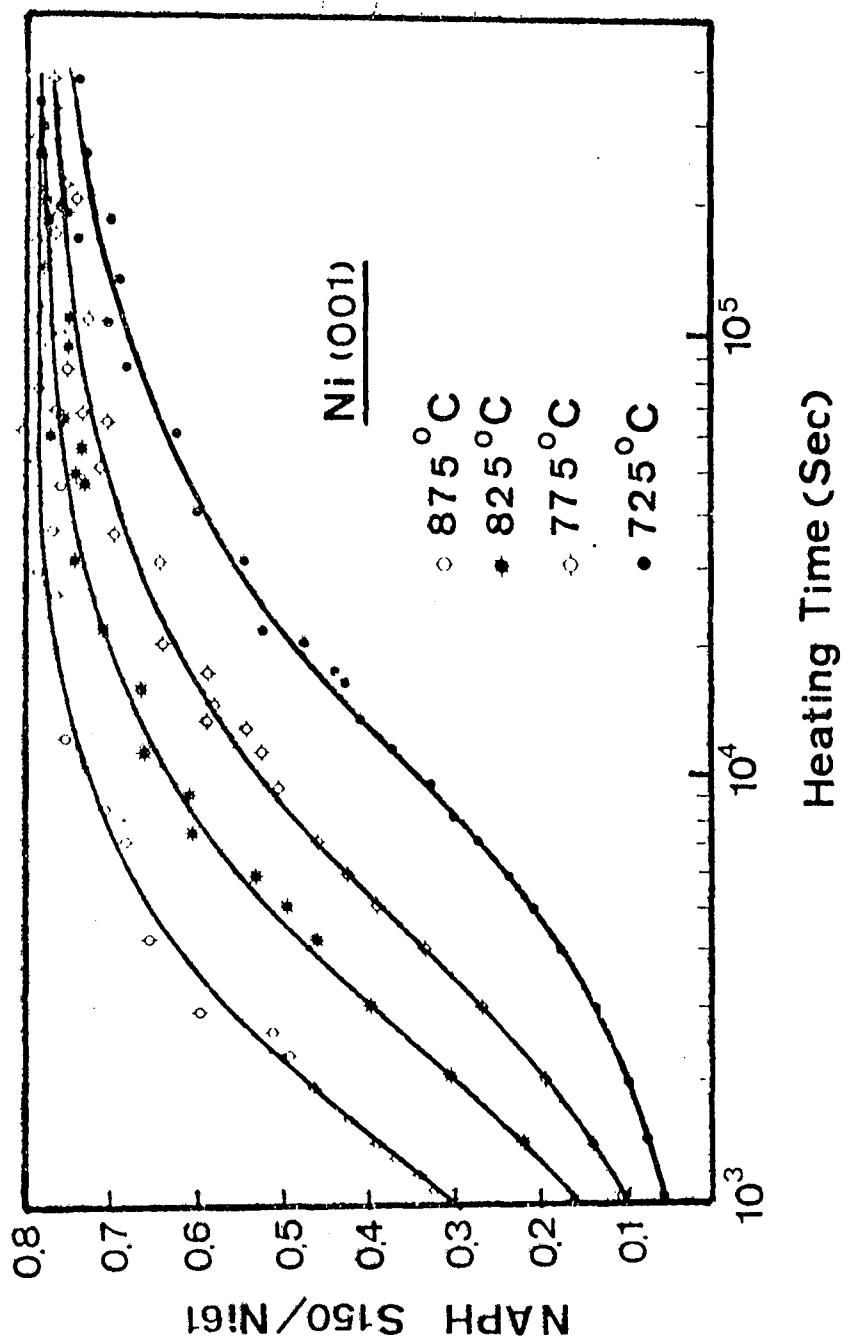


Figure 3.4 Normalized Auger peak height as a function of time and temperature.

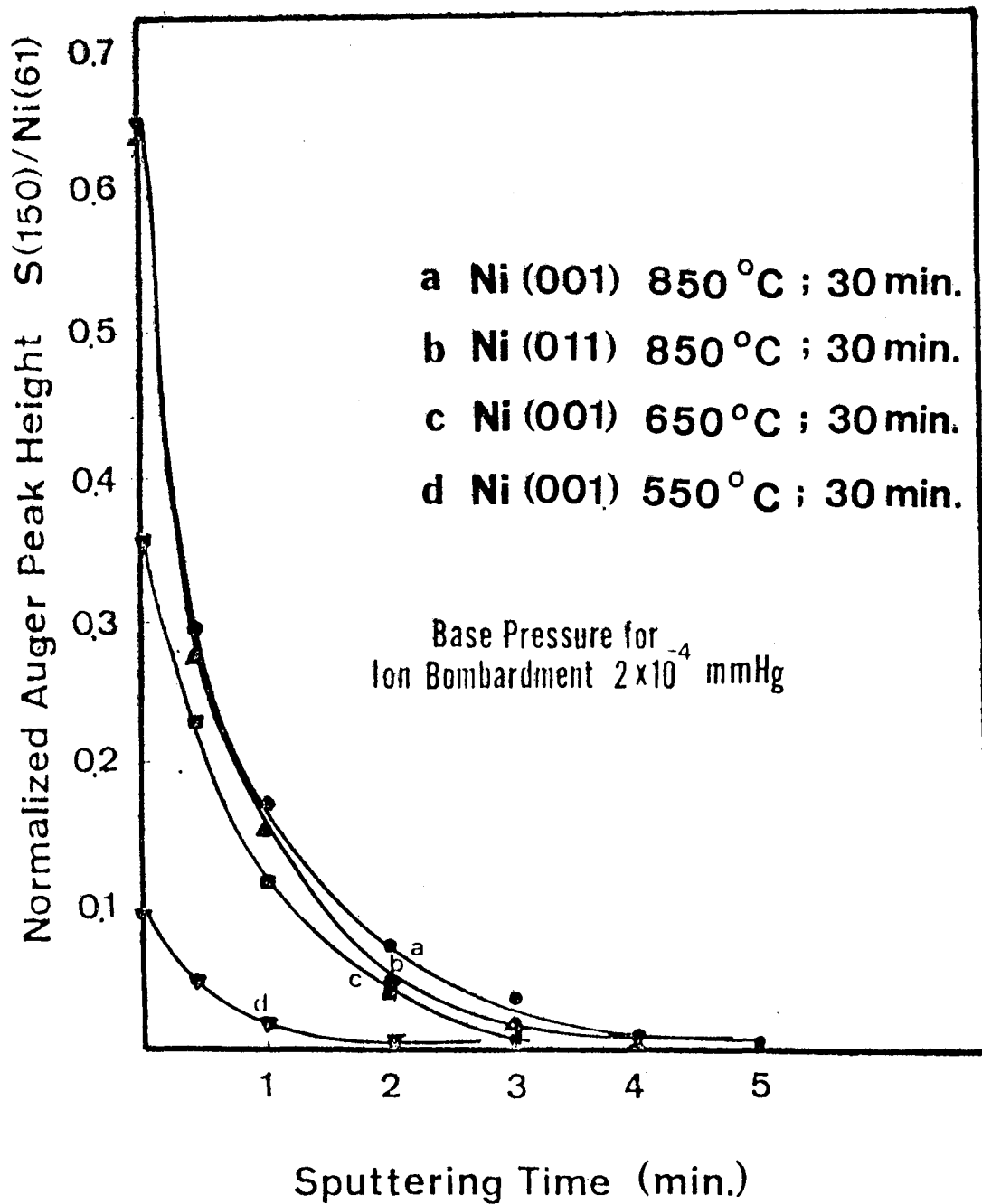


Figure 3.5 Depth-composition profiles of various systems.

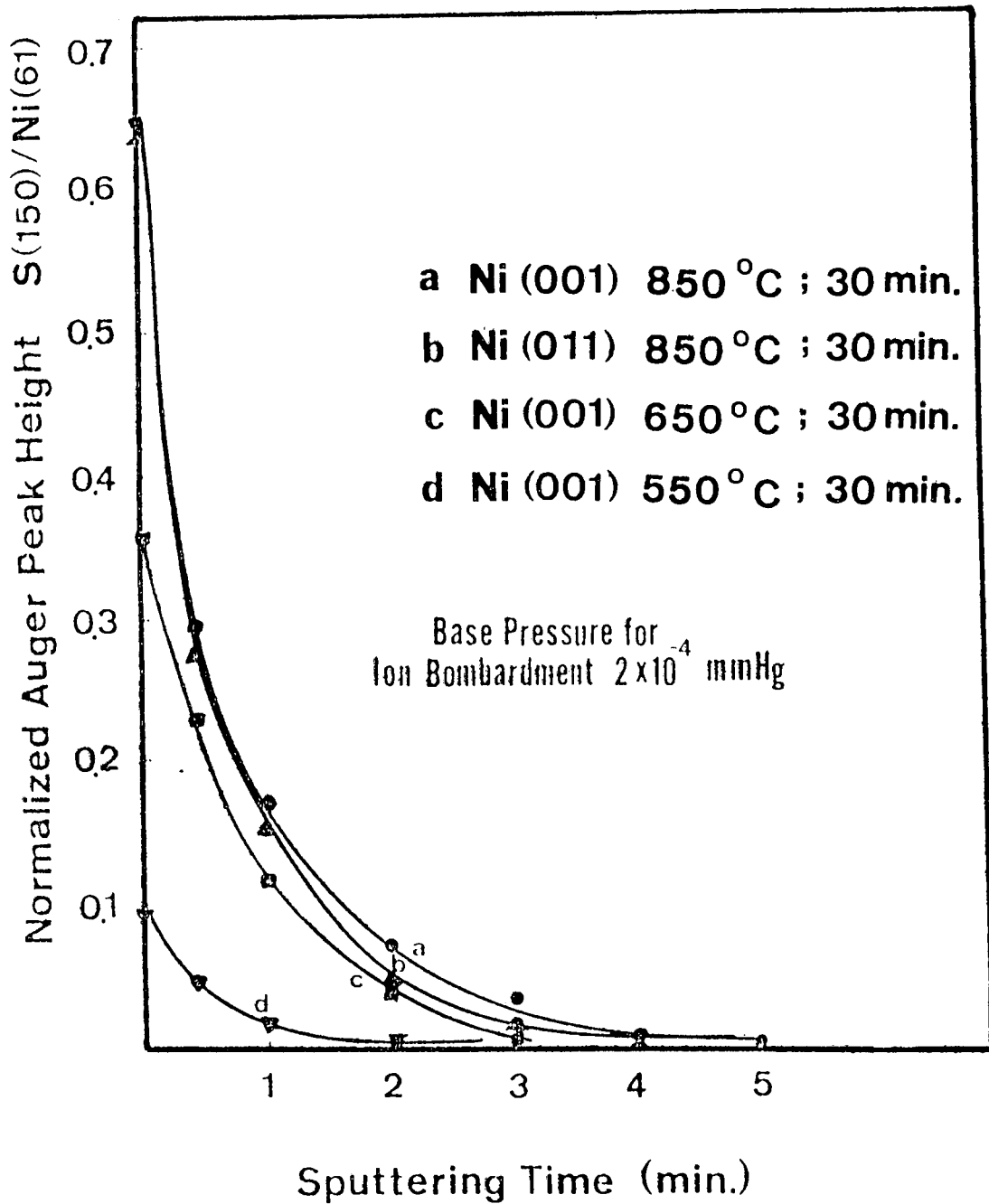


Figure 3.5 Depth-composition profiles of various systems.

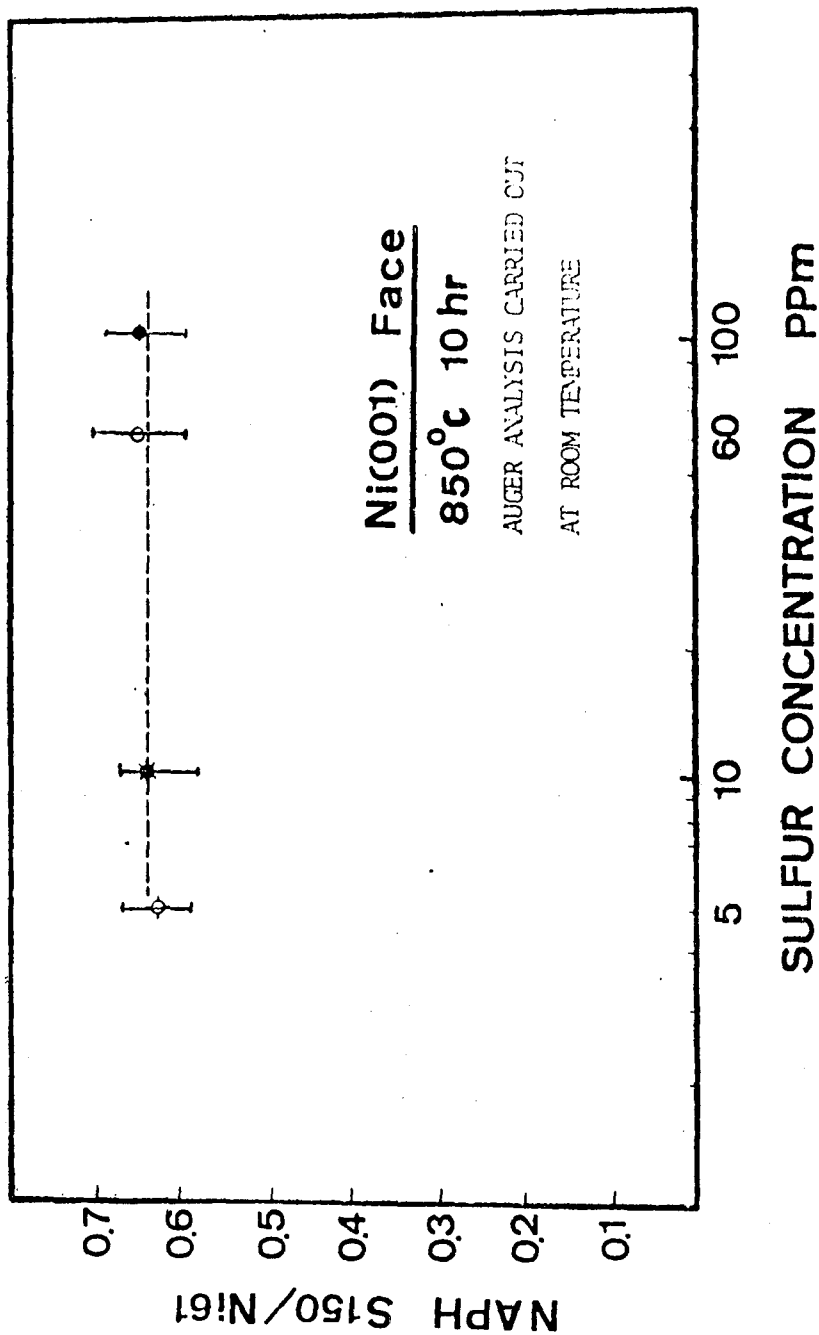


Figure 3.6 Saturation of sulfur segregation as a function of sulfur concentration in the nickel specimens. Tested specimens have been treated at 850°C for 10 hours and were Auger analyzed at room temperature.

Auger measurements was ± 0.05 of NAPH for S(150)/Ni(61) which was due to the instrument conditions, operation errors, specimen roughness, and other sources of uncertainty. However, the saturation of segregated sulfur was 0.66 ± 0.05 .

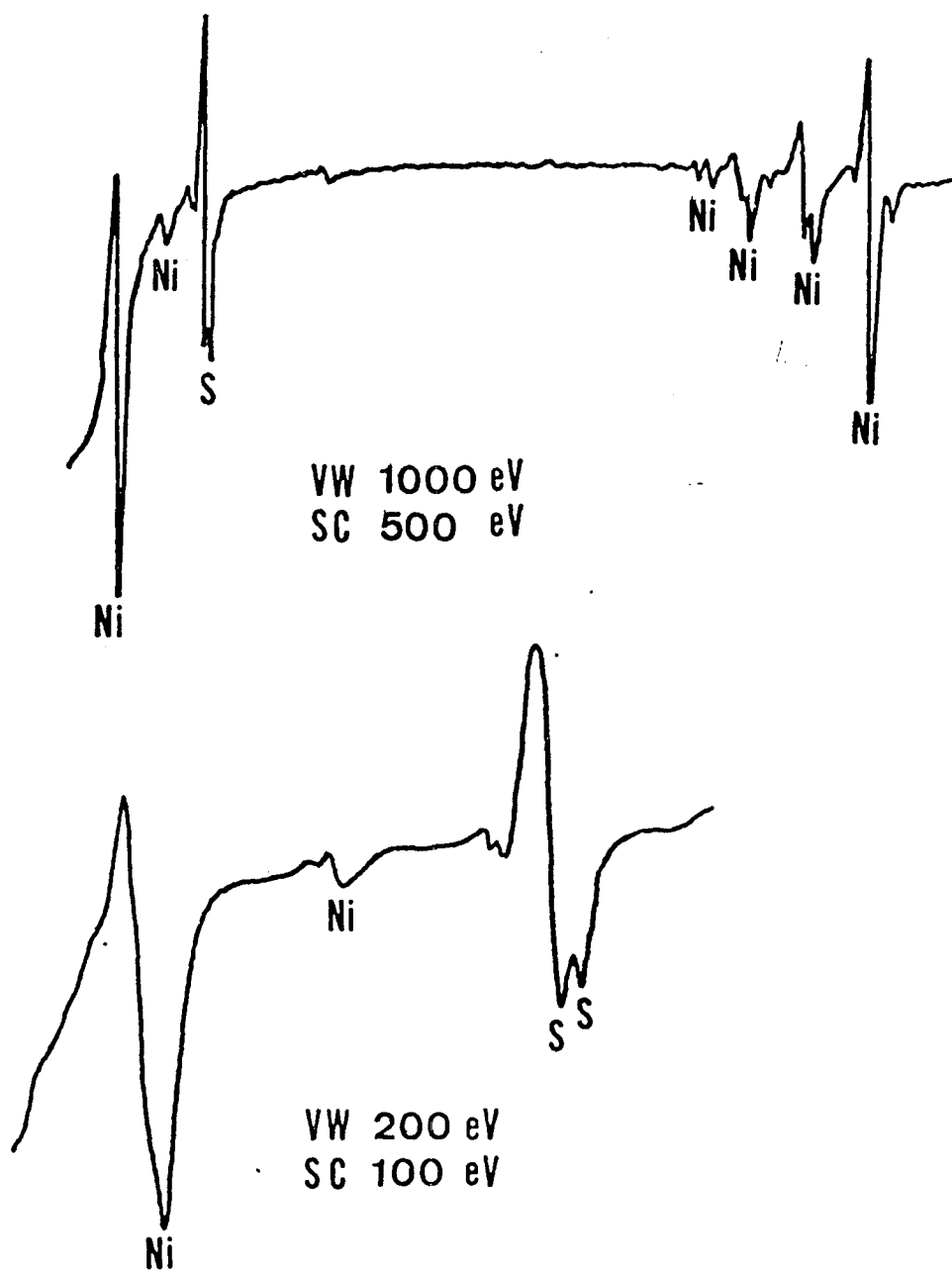
Structure of Segregated Sulfur. In this experiment, the fine structures of Auger peaks were examined with an expanded energy scale. Auger spectra taken after heating nickel with an (001) face to 850°C are shown in Figure 3.7. This figure contains two Auger spectra. One is the regular Auger spectrum and other one shows the lower energy Auger peaks of nickel and sulfur with an expanded energy scale. The center of the spectrum was set at 100 eV on a full scale of 200 eV. Upon segregation, two Auger peaks of sulfur were observed. These dissociated peaks are attributed to the formation of chemisorbed sulfur.

In order to verify the chemical shift of sulfur on a segregated surface, the Auger spectra of pure sulfur and standard nickel sulfides (Ni_3S_2 and NiS) were examined. The representative AES- expanded structures for S, Ni_3S_2 , and NiS are shown in Figure 3.8. As can be seen from this figure, the AES-expanded structure of nickel sulfide also has two dissociated peaks.

Discussion

Driving Force of Sulfur Segregation. Thermodynamic considerations (3-1, 3-2, 3-3) predict that equilibrium segregation of impurities to the surface (or other lattice imperfections) should be associated with a reduction in free energy. The Gibbs adsorption isotherm (3-1, 3-2) predicts that the solute elements (or impurities) which decrease the surface tension will concentrate at the surface, and those which increase the surface tension will deplete. Unfortunately, the dependence of sulfur concentration on the surface tension of nickel has not been reported in the literature. As mentioned by McLean (3-3) the elastic strain energy may be the driving force for the equilibrium segregation process--the segregation of impurity (or solute) atoms is attributed to the presence of external surface (or other lattice imperfections) where the strained atoms best fit. During heating, the strained impurity atoms situated under the surface jump onto the surface when they receive the necessary thermal energy to overcome the activation barrier. Consequently, the free energy of the system is reduced. Sulfur sits on a substitutional site in the nickel matrix. The misfit of a sulfur atom in the regular nickel

165



Nickel (001) Face 850°C

Figure 3.7 Representative AES spectra from nickel (001) face after heating to 850°C in regular energy scale (VW = eV) and expanded energy scale (VW = 300 eV).

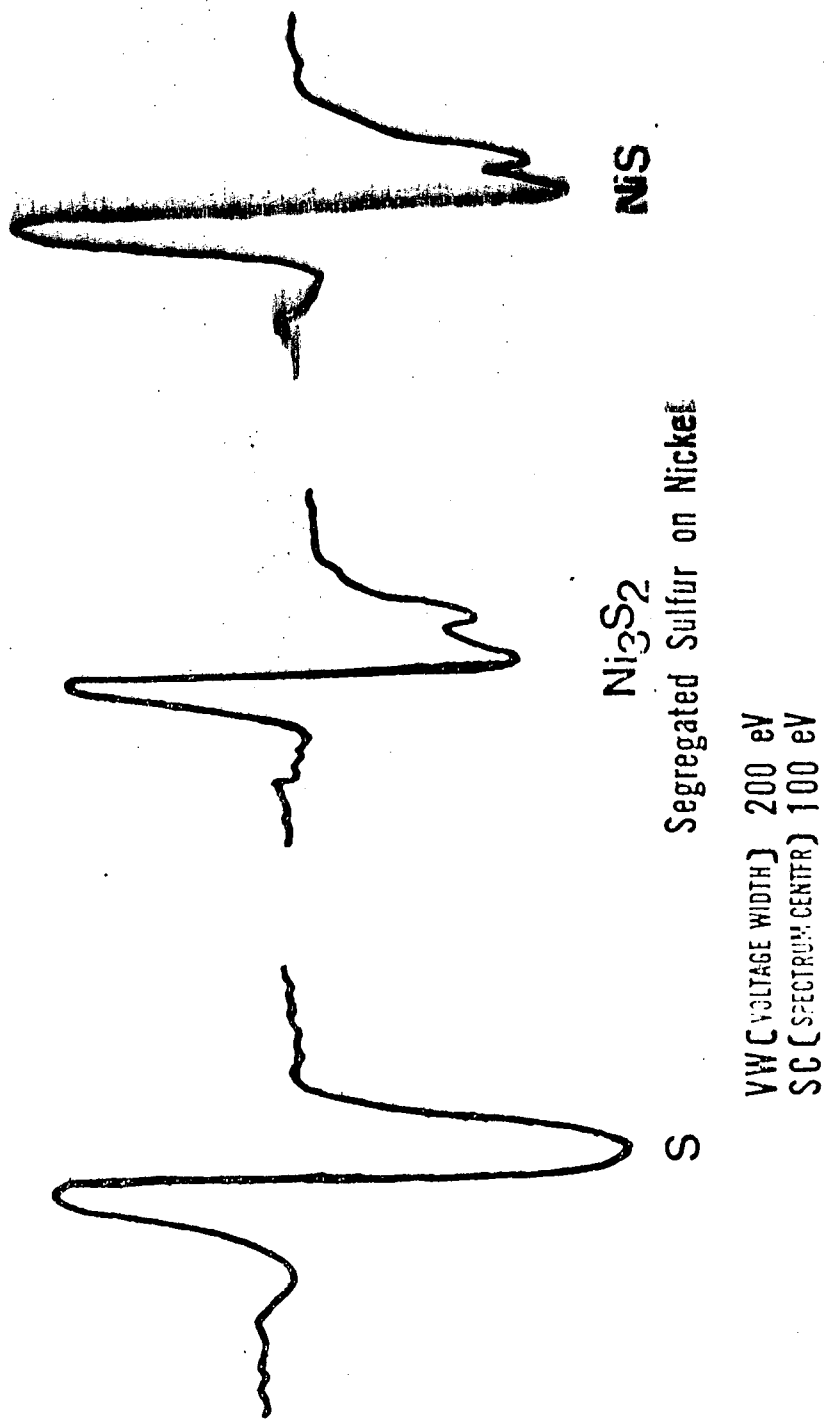
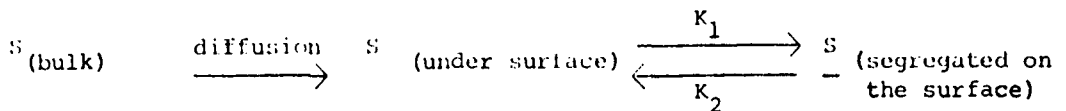


Figure 3.6 Representative Auger expanded spectra for S, Ni₃S₂, and NiS.

lattice is about -0.40 eV . Therefore, sulfur would tend to segregate onto the nickel surface in order to lower the strain energy.

Sulfur Segregation Isotherms. Sulfur segregation can be thought of as a chemisorption process. It may be expressed as



where k_1 is the rate constant for sulfur inside the nickel bulk jumping to the chemisorbed site on the nickel surface; k_2 is the rate constant for desorption of chemisorbed sulfur back to the bulk.

Thus, the rate equations can be described as

$$\frac{dC_s}{dt} = k_1 M_s (1 - \theta) C_s \quad (1)$$

$$\frac{dC_s}{dt} = k_2 M_s \theta \quad (2)$$

Where

C_s is the concentration of sulfur at layer just under surface;

C_s is the concentration of segregated-sulfur on the surface;

θ is the coverage of segregated-sulfur, i.e.; $\frac{M}{M_s}$;

M is the number of sites which have been occupied by the segregated sulfur; and

M_s is the number of available sites for sulfur segregation.

At equilibrium,

$$\frac{dC_s}{dt} = \frac{dC_s}{dt} \quad (3)$$

Hence

$$k_1 M_s (1 - \theta) C_s = k_2 M_s \theta$$

or

$$\frac{\theta}{1 - \theta} = \frac{k_1 C_s}{k_2} \quad (4)$$

Using the equilibrium criterion, the thermodynamic equilibrium constant, K is

$$K = \frac{k_1}{k_2} = \exp \left(- \frac{\Delta F^0}{RT} \right) \quad (5)$$

where ΔF° is defined as the sum of the relaxation energy for the strained sulfur atoms to jump to the surface and the free energy of chemisorption and ΔF° is a function of temperature only.

Equation (6) can be rearranged as

$$\theta = \frac{C_s \exp \left(-\frac{\Delta F^\circ}{RT} \right)}{1 + C_s \exp \left(-\frac{\Delta F^\circ}{RT} \right)} \quad (6)$$

This segregation isotherm shows Langmuir-type behavior and has the same form of McLean's equation (3) which was derived from a statistical thermodynamics approach.

Unfortunately, the value of ΔF° for sulfur segregation on a nickel surface is not known at this time. However, nickel which contains a very small amount of sulfur (< 10 ppm in this study) segregates a considerable amount of sulfur on the surface; a high value of ΔF° is likely to exist in such a case. For instance, a saturated value of sulfur segregation at 650°C, 750°C, and 850°C will be reached when ΔF° is about -27500 cal/mole, -30000 cal/mole, and -35,000 cal/mole respectively (as $S < 10$ ppm). The results shown in Figure 3.6 indicate that sulfur segregation does not follow the isotherm. It may be that the concentration of sulfur in the nickel specimens is higher than the critical value to obtain an isotherm. This implies that if one can purify nickel to a very low content of sulfur (e.g. much less than ppm range) that sulfur segregation isotherm may be followed.

Extent of Sulfur Segregation. The extent of sulfur segregation in the experimental results is expressed by the "normalized Auger peak height" which provides only a relative measurement. The major drawback of AES is the fact that the heights of the Auger peaks, measured as the first derivatives of the energy distribution, cannot be correlated directly with a surface coverage.

In the present quantitative study a theoretical formula described by Bishop and Riviere (3-4) has been used as follows. The number, n , of Auger electrons emitted per incident electrons is given by

$$n = Nr \cos \phi (1 - \omega) \phi(u) \quad (7)$$

Where N is the number of atoms in the detected volume, r is the correction for additional ionization by back-scattered electrons, ϕ is the angle of

incidence of the primary beam, ω is the probability of photon emission, and $\phi(U)$ is the cross section for ionization of an atom by electrons (3-4).

As the Auger current is roughly proportional to n , one can determine the number of atoms in the detected volume from the Auger current (3-5). That is the concentration ratio of sulfur to nickel on the surface is taken as

$$X_{S/Ni} = \frac{N_S}{N_{Ni}} = \frac{I_S r_{Ni} CSC\phi_{Ni} (1 - \omega)_{Ni} \phi(U)_{Ni}}{I_{Ni} r_S CSC\phi_S (1 - \omega)_S \phi(U)_S} \quad (8)$$

The value of r_{Ni} can be assumed to be equal to r_S according to the higher incident electron energy (3-4), and ϕ_{Ni} is equal to ϕ_S . $(1 - \omega)_{Ni}$ is approximately equal to 0.6 (3-6) and $(1 - \omega)_S$ is about 1 (3-6). $\phi(U)_{Ni}$ and by the aid of the equations in Reference 14, are 13.5 and 4.66 respectively. I_S/I_{Ni} (i.e. S(150)/Ni(61) for saturated sulfur segregation is 0.66 ± 0.05 . Therefore, $X_{S/Ni} = 1.17$. This value is about twice as high as the value obtained from a standard calibration which is described as follows.

A simple procedure may be used for calibrating Auger signals to obtain a quantitative analysis; the accuracy is on the order of the achieved in electron microprobe analysis (3-7). The extent of sulfur segregation in this study has been calibrated by the normalized Auger signal from the sample with respect to a standard concentration of Ni_3S_2 . In this approximation, the atomic concentration of sulfur on the segregated surface is:

$$C_{S, Ni} = \frac{H_{S, Ni}}{H_{S, Ni_3S_2}} \times C_{S, Ni_3S_2} \quad (9)$$

where $H_{S, Ni}$ and H_{S, Ni_3S_2} are the normalized Auger peak heights of the sample and the standard, respectively. C_{S, Ni_3S_2} is the atomic concentration of sulfur in the Ni_3S_2 standard.

The normalized Auger peak height of S(150)/Ni(61) in Ni_3S_2 standard is 0.8 ± 0.05 . Therefore, the atomic concentration of segregated sulfur on the nickel surface (i.e. 0.66 ± 0.05) is approximately 33 at % ($\frac{0.66}{0.8} \times 0.4 = 0.33$, where 0.4 is the stoichiometric factor of S in Ni_3S_2). This value is about half of that estimated from Bishop and Riviere's formula (3-4). In view of the complexities involved in the Auger process and specimen surface conditions (surface roughness and surface defects), no confidence has been placed on the accuracy of these two values. However, one can realize that the concentration

of sulfur has been enhanced relative to the matrix concentration at least by a factor 10^3 to 10^4 .

Since the original concentration of sulfur in the zone-refined nickel is less than 10 ppm, the concentration on the surface may be enhanced relative to the matrix concentration by a factor of 10^3 to 3×10^4 depending on the annealing temperature and time (based on Ni_3S_2 standard calibration) as shown in Figure 9.

The difference in the amount of segregated sulfur on the three most close packed faces of nickel (as shown in Figure 9) may be attributed to the different surface atom densities. With regard to the crystallographic geometry, the surface atom densities (number of surface atoms/cm²) of the three most packed faces of FCC structure, the (111), the (001), and the (011) are 1.8×10^{15} , 1.6×10^{15} and 1.1×10^{15} , respectively. Atoms on these surfaces have 9, 8, and 7 nearest neighbors respectively, instead of 12 for atoms in the bulk lattice of a FCC material. Consequently, the (111) face has more available sites for sulfur to segregate, whereas the (011) has the least number of sites.

Thickness of the Equilibrium Sulfur Segregation Zone. The depth-composition profiles of the segregated surface region as shown in Figure 3.5 demonstrate that the sulfur segregation layer is localized within $5 \text{ \AA}$ of the surface (according to a sputtering rate of $1 - 2 \text{ \AA/min}$). It is reasonable to assume that segregated-sulfur is localized within a monolayer. This localization to a monolayer could be explained by the concept of chemisorption proposed by Langmuir (3-8). However, it has been reported recently (3-6) that strong exothermic surface reactions (such as oxygen on nickel) can rearrange the substrate structure to form so-called reconstructed surface structures. This reconstruction may be followed by further chemical reactions as the surface species diffuse into the bulk. Fortunately, the possibility of forming a three-dimensional structure need not be considered in our case.

It has been assumed that sulfur segregation exhibits the behavior of chemisorption rather than physical adsorption. In support of this view the following arguments are made:

(a) It is well known that the forces of interaction between adsorbent and adsorbate are predominantly van der Waals forces in physical adsorption and

valence forces in chemisorption. This implies that chemisorption involves a transfer of electrons. In this work, the fine structures associated with the sulfur Auger peak on the nickel surface with an expanded energy scale have been examined. After heating, additional peaks in the Auger derivative spectrum of sulfur were observed, as shown in Figure 3.7 and 3.8. Coad and Riviere (3-9) have used the ion scattering results of Becker and Hagstrum (3-10) on sulfur-and-oxygen-covered low-index faces of nickel to identify the additional sulfur Auger peak. They (3-9) concluded that this additional sulfur peak (high energy side) arises from the surface molecular orbitals formed by electrons in chemisorption bonds between sulfur and the outermost nickel atoms.

The chemisorbed sulfur is not necessarily a stoichiometric sulfide. The conclusions concerning the segregated-sulfur (chemisorbed sulfur) structure presented in the literature (3-11) lead one to expect that the determination of the detailed structure of segregated-sulfur may be complicated by the occurrence of surface lattice distortions, electron structures, and the impossibility of considering all conceivable structures. Demuth, et. al. (3-11) found that Ni-S bond length in the surface-sulfur structure was $2.8 \pm 0.06 \text{ \AA}$ which was slightly smaller than the bulk compound bond length of 2.28, 2.38, and 2.34 $\text{\AA}$, respectively for Ni_3S_2 , NiS and NiS_2 .

(b) Generally, physical adsorption tends to occur below the boiling point of the adsorbate, whereas chemisorption takes place at high temperature. Segregated-sulfur has been found to be stable at very high temperature (e.g. 850°C). There is no thermodynamic reason why physically adsorbed sulfur (with a boiling point at 445°C) is stable on the nickel surface around 850°C. The possibility of evaporation of segregated-sulfur in a vacuum of 2×10^{-9} mm Hg has been checked. This was done by a residual gas analysis (RGA) using a quadrupole system in a 3M mass spectrometer unit. No sulfur or sulfur compound vapor was detected during heating (350° ~ 850°C) or after heating in RGA experiments.

(c) The adsorption isotherm in chemisorption indicates monolayer adsorption; physical adsorption may be monolayer or multilayer. The width of the segregated-sulfur zone has been studied by Ar^+ ion bombardment. It has been shown that segregated-sulfur seems to localize within a monolayer.

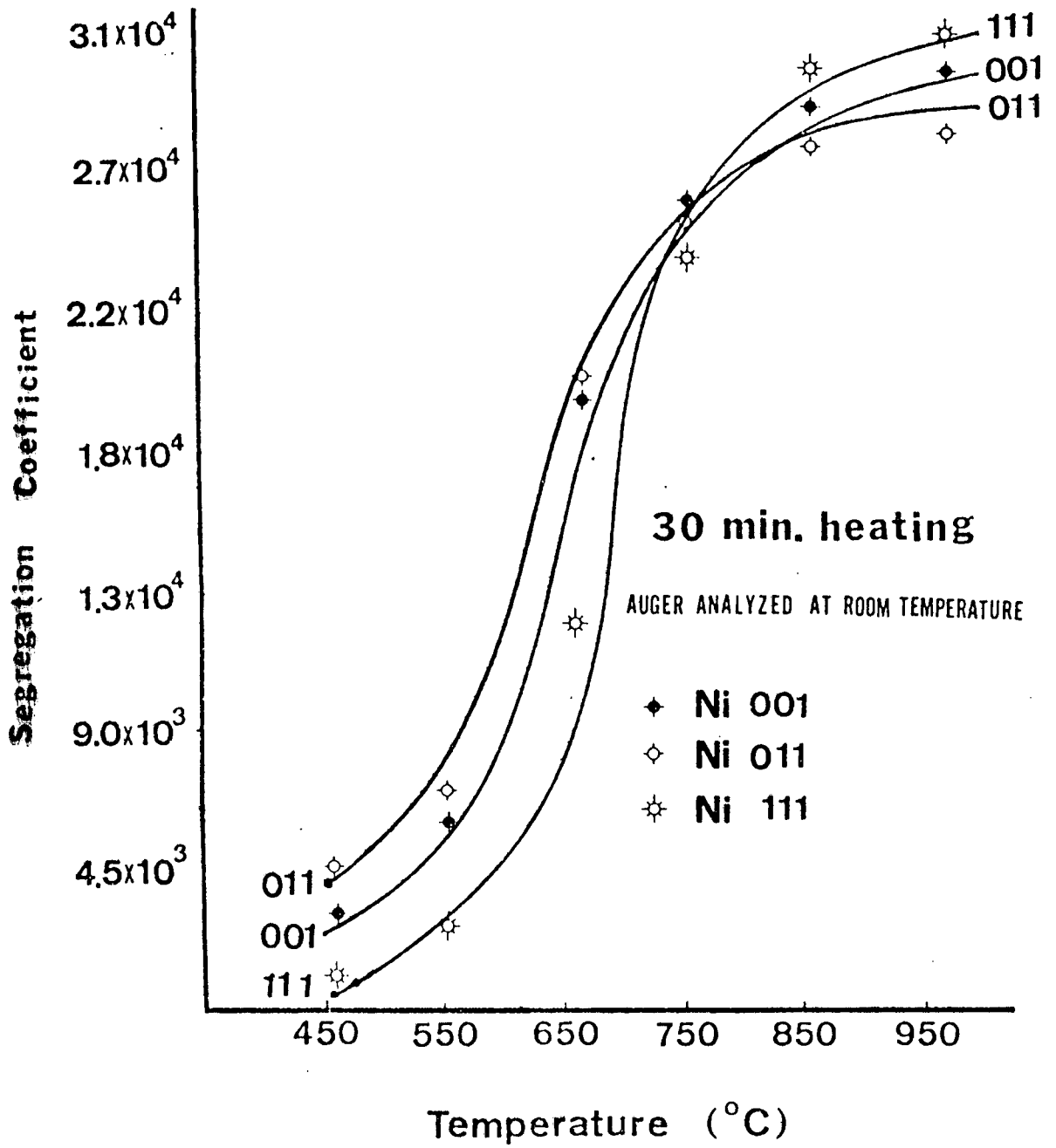


Figure 3.9 The plot of sulfur segregation coefficient as a function of temperature and crystal orientation.

Therefore, it is reasonable to propose that segregated-sulfur is chemisorbed on the nickel surface.

Role of Sulfur Diffusion. It has already been recognized that the strain energy misfit solute atoms associated with the solvent lattice can be relieved by the segregation process. A high concentration of segregated species will subsequently build up on the surface if a metal is heated to a temperature at which diffusion can occur; otherwise segregation will cease because of depletion of segregated species under the surface. Thus, it is also recognized that diffusion plays an important role in the segregation process.

Figure 3.5 shows that the amount of sulfur on the surface of a nickel single crystal increases linearly with time in the initial stage of the segregation process; this implies that sulfur diffuses from the bulk of nickel at a constant rate. The diffusivity of sulfur involved in the segregation process may be estimated by a simple diffusion model.

An one-dimensional model was used with the following conditions imposed:

(a) a specified initial homogenous bulk concentration of sulfur in nickel, $C_{(s)}^0$, (b) sulfur is assumed to diffuse out of both sides of a slab (for supplying the further segregation process) with a thickness of h (0.3 cm in this study), and (c) the concentration of sulfur has built up within the bulk crystal during segregation (as shown in Figure 3.10) and has a zero concentration at the layer ($x = 0$ and $x = h$) just under the surface from there sulfur will jump to the surface. Therefore, the initial and boundary conditions have been assumed to be:

$$\begin{aligned} C_{(s)} &= C_{(s)}^0 & \text{for } 0 < x < h & \quad \text{at } t = 0, \\ C_{(s)} &= 0 & \text{for } x = 0 \text{ and } x = h & \quad \text{at } t > 0 \end{aligned}$$

The solution of the $\frac{dc(x,t)}{dt} = D \frac{d^2c(x,t)}{dx^2}$ is given by the well-known Fourier summation (3-12):

$$C_{(s)}(x,t) = \frac{4C_{(s)}^0}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j+1} \sin \frac{(2j+1)\pi x}{h} \exp \left[-\left(\frac{(2j+1)\pi}{h} \right)^2 Dt \right] \quad (10)$$

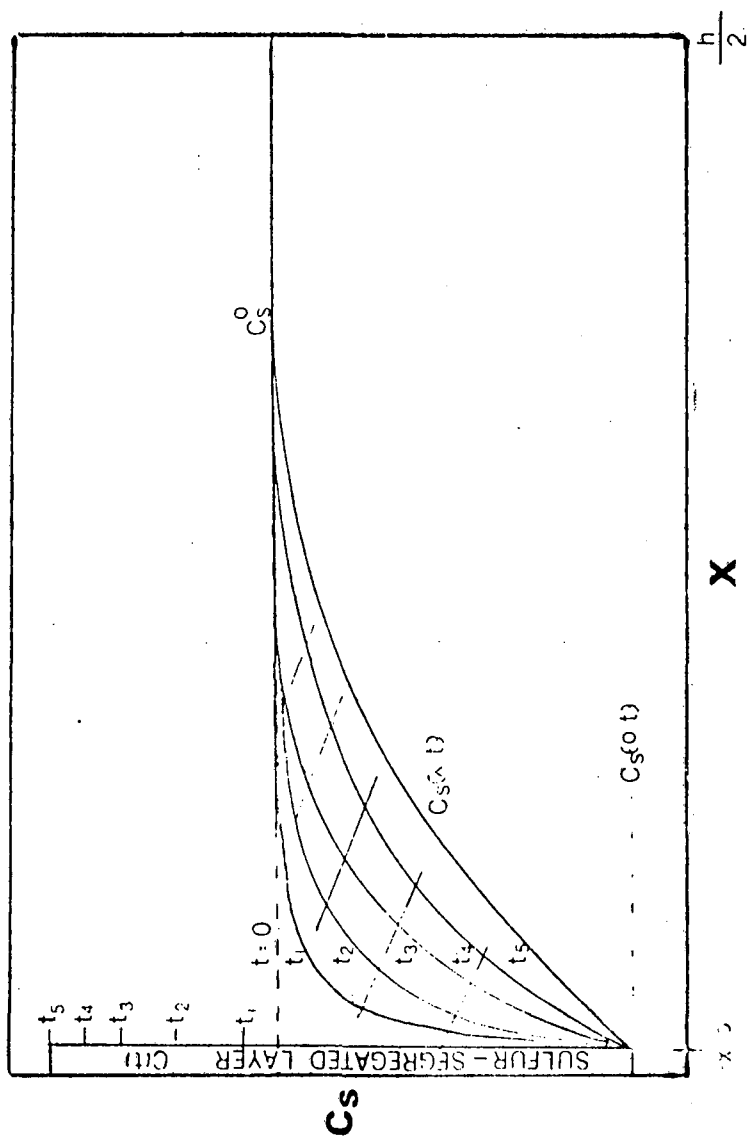


Figure 3.10 Concentration profiles during segregation.

A moment's study of this equation shows that each successive term is smaller than the preceding one. Thus, the concentration gradient of sulfur atoms across the slab is approximately

$$C_{(s)}(x, t) = \frac{4C^0_{(s)}}{\pi} \sin \frac{\pi x}{h} \exp \left(-\frac{\pi^2 D t}{h^2} \right) \quad (11)$$

The Auger peak height can be used to represent the amount of segregated species which has diffused out to the surface, and hence is considered to be proportional to the flux of sulfur atoms passed through the layer adjacent to the surface.

$$\text{Therefore } \int_0^t j_{x=0} dt = \int_0^t -D \left. \frac{\partial C_{(s)}(x, t)}{\partial x} \right|_{x=0} dt \quad (12)$$

and the total amount of segregated-sulfur at the surface during the period t , $C(t)$, is

$$C(t) = \frac{4C^0_{(s)} h}{\pi^2} \left[1 - \exp \left(-\frac{\pi^2 D t}{h^2} \right) \right] \quad (13)$$

$C(t)$ can be obtained by the Auger analysis (as shown in Figure 3.3). The diffusion coefficient of sulfur in the nickel crystal are plotted in Figure 3.11 (as shown in curve C). The temperature dependence of the diffusion coefficient D is as follows:

$$D = 3.5 \times 10^{-2} \exp (30,500/RT)$$

However, Pfeiffer (3-13) investigated the diffusion of S^{35} into pure nickel and used autoradiographic experiments to determine the diffusion coefficients over a temperature range of 1000°C and 1200°C. He reported the temperature dependence of the diffusion coefficient to be as follows:

$$D = 2.3 \times 10^6 \exp (-90,000/RT)$$

Pfeiffer suggested that the high activation energy represented a lattice or volume process. Later, Wang and Grabke (3-14) have determined the diffusion coefficients of sulfur in nickel using the sulfurization and desulfurization of metal foils by the reaction $H_2S(g) = H_2(g) + S(\text{dissolved})$ at temperatures between 700°C and 1000°C by measuring the changes of electrical resistance. They, however, reported the temperature dependence of the diffusion coefficient

176

°C

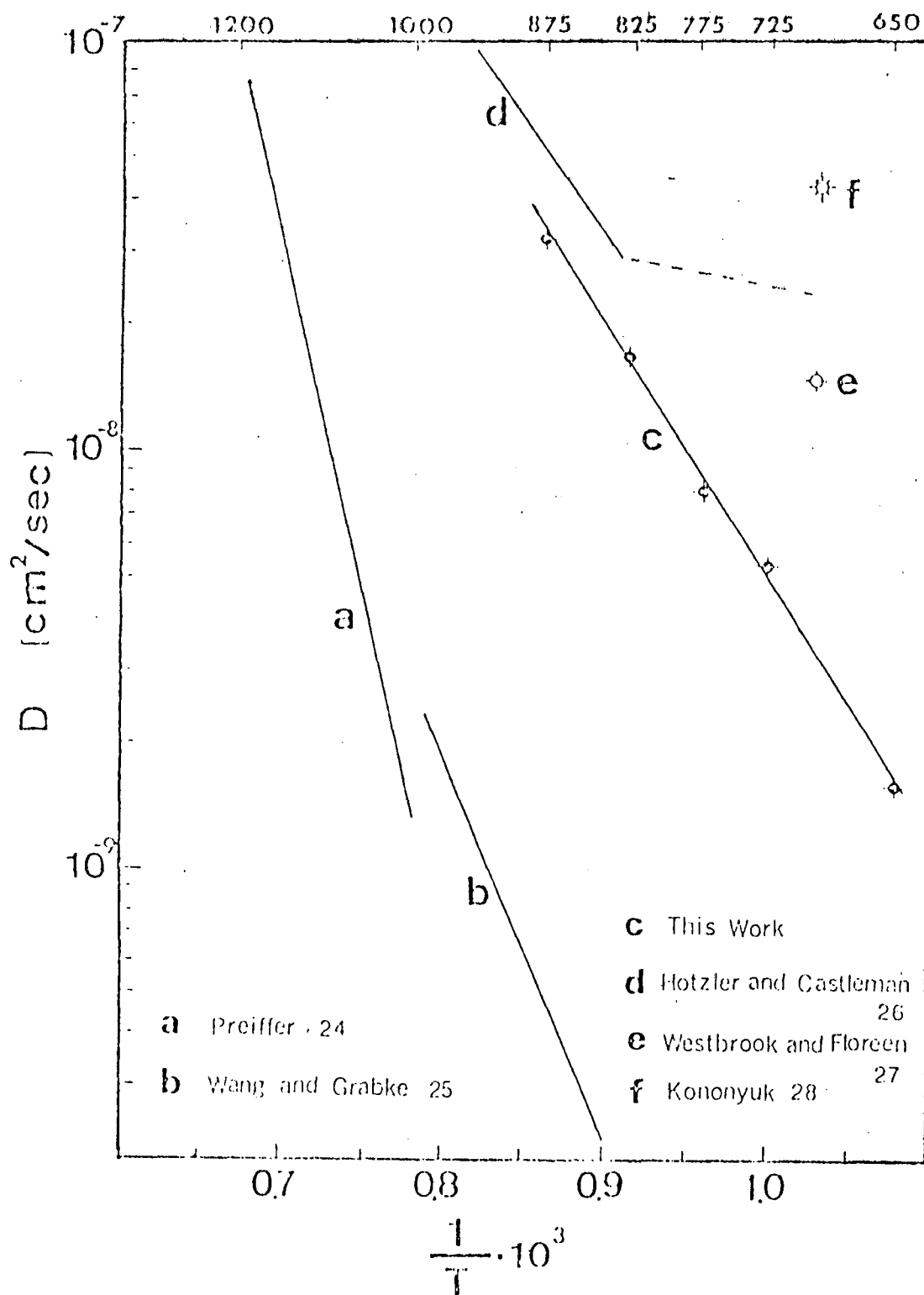


Figure 3.11 Diffusion coefficient of sulfur in nickel versus $1/T$.

to be as follows:

$$D = 0.2 \exp (-46,000/RT)$$

Wang and Grabke suggested that sulfur dissolved as a substitutional element and diffused via a vacancy mechanism. Hotzler and Castleman (3-15) have studied the diffusion of S^{35} into thoriated nickel (with 2.4 Vol. pct of ThO_2) by means of a surface intensity decrease technique. They found the activation energy of about 38,000 cal/mole at temperatures ranging from 925°C to 1150°C and less than 20,000 cal/mole at temperatures less than 925°C. They suggested that the diffusion of S^{35} in thoriated nickel occurs by more than one mechanism. They expected that lattice diffusion will predominate at high temperatures in pure nickel. Some single-point experiments of the diffusion of sulfur in nickel have reported the values $1.5 \times 10^{-8} \text{ cm}^2/\text{sec}$ at 700°C (suggested sulfur diffusion via dislocation forests) (3-16), and $4.4 \times 10^{-8} \text{ cm}^2/\text{sec}$ at 700°C (suggested sulfur diffusion via grain boundaries) (3-17).

In view of the complexities involved in the diffusion process, it is difficult to compare these experimental values. The apparent activation energy, 30500 cal/mole of sulfur diffusion in nickel single crystals in this study is less than that obtained by Pfeiffer (3-13), 90,000 cal/mole and that obtained by Wang and Grabke (3-14), 46000 cal/mole. In this study, it is suggested that the low activation energy of sulfur diffusion near the surface may be due to the extra dislocations (generated by the surface preparation) and higher concentration of vacant lattice sites than that in the far interior.

Generally, the empirical activation energy and frequency factor may be obtained from the Arrhenius equation in a number of ways. The "time to a given fraction method" (3-18) will be chosen as a tool to examine the kinetics of sulfur segregation.

The logarithmic form of the Arrhenius equation for t_y , time for the chosen value of y measured at each temperature, is

$$\log t_y = \text{Const.} - \log A_a + E_a/(2.303 RT) \quad (14)$$

If E_a (activation energy) and A_a (frequency factor) are constant a graph of $\log t_y$ against $1/T$ is linear. The slope of this graph is $E_a/(2.303 R)$. This is demonstrated in Figure 3.12. The procedure has been repeated for various values of y , 0.1 and 0.2 of NAPH S(150)/Ni(61) from Figure 3.3, to reveal the variation of E_a with y . It can be seen that E_a is independent of y and has a value of about 28,300 cal/mole. This value is close to that energy for sulfur diffusion, 30,500 cal/mole which was obtained from Figure 3.14. This may imply that the initial stage of sulfur segregation is diffusion controlled.

Electrochemical Behavior of Sulfur Segregated Nickel. The rationale for the effect of grain boundary segregation on intergranular stress corrosion and corrosion fatigue implies that the grain boundary composition can be markedly different from that of the matrix. Hence, the electrochemical behavior of the grain boundary may be expected to be quite different from that of the bulk material. For example, for a given set of environmental conditions the grain boundary region may be subject to rapid dissolution while the bulk material is in the passive range. This would naturally lead to intergranular attack.

The electrochemical behavior of sulfur segregated single and polycrystals of nickel was investigated in a sulfuric acid solution. The following paragraphs describe the effect of sulfur segregation on the polarization curves of single crystal and polycrystalline nickel.

Experimental Detail. Both nickel single crystals and polycrystals were used in this study. The specimen preparation was identical to that described in an earlier report.

Specimens were heated in the Auger chamber at a selected temperature to allow a build up of segregated-sulfur on the surface. They were then analyzed. Subsequently, a potentiostatic polarization test was carried out after the specimens were removed from the Auger chamber.

After Auger analysis, the sulfur-segregated specimens were spot-welded to a conduction wire. Only the specimen face of interest was exposed to the solution, as the remainder of the specimen was covered with a protective resin.

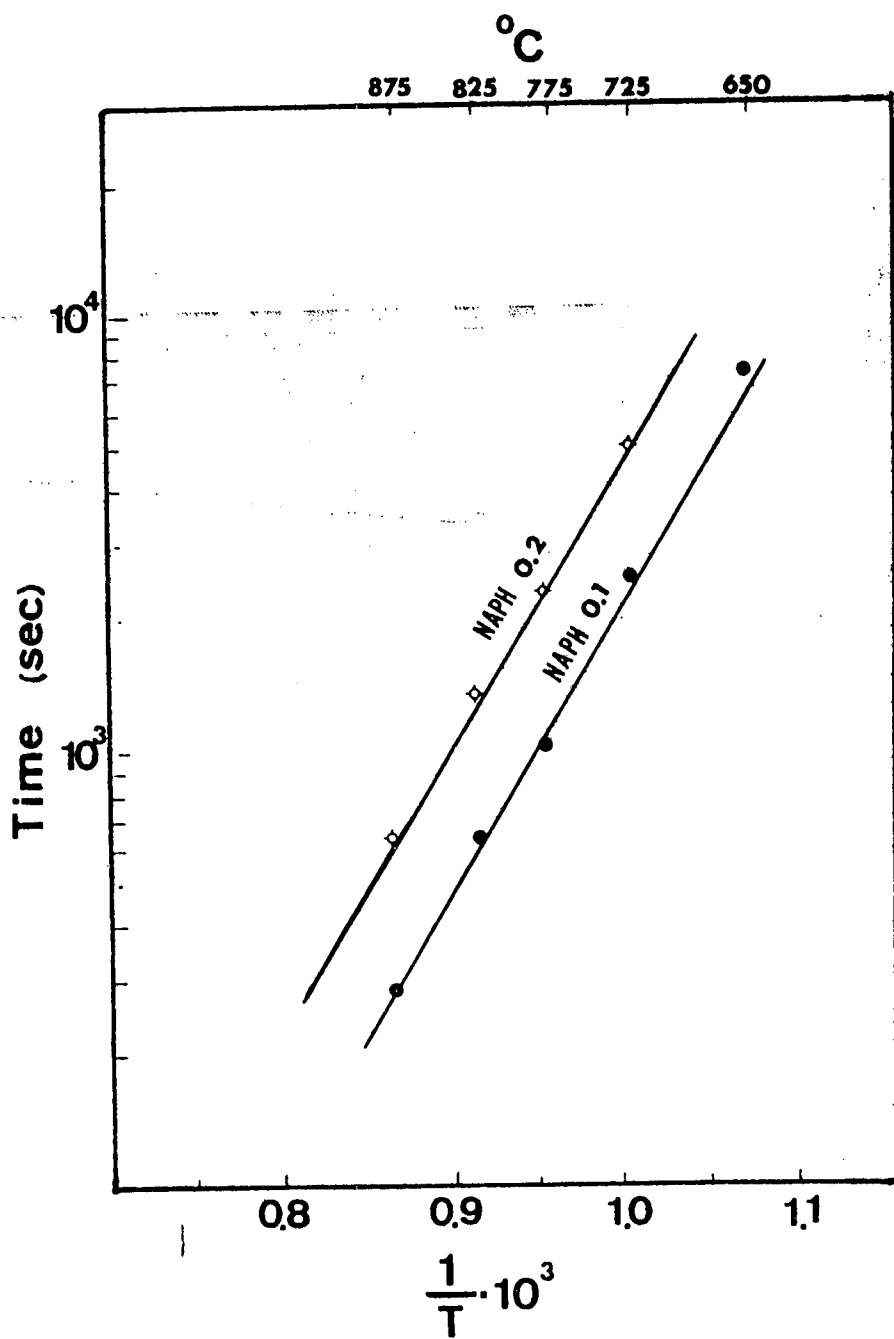


Figure 3.12 Plots of $\log t$ (t is time to a given fraction) versus $1/T$.

The test cell was an air-tight container of pyrex glass with a capacity of about 500 ml. It had two compartments, one for the specimen and one for an auxilliary platinum electrode. A sintered glass filter was provided to connect these two compartments in order to avoid diffusion of hydrogen gas from the platinum cathode to the surface of the specimen. A saturated calomel reference electrode (SCE) was used. This electrode was connected to the test cell by a salted bridge which was terminated in a Luggin capillary. Most experiments were carried out at room temperature. A one molar H_2SO_4 electrolyte was prepared from double distilled water and reagent grade sulfuric acid. The electrolyte was de-aerated with prepurified argon for at least 24 hours prior to any experiments. Polarization curves were determined potentiodynamically at a scan rate 200 millivolt per minute unless otherwise specified.

Results of Polarization scans. The polarization measurements of nickel in 1M H_2SO_4 solution were determined as a function of the temperature at which sulfur segregation was achieved.

Figure 3.13 shows the polarization behavior of the nickel single crystal (001) face in a 1M H_2SO_4 solution before and after sulfur segregation at 650°C and 850°C was about 10 and 30 at % respectively. Note the critical current density on the sulfur-segregated surface (after heating 30 min. at 850°C) was about an order of magnitude higher than that on an un-segregated surface. In addition, E_{pp} shifted to the more noble direction as the amount of sulfur increased. In the active to passive transition region of the polarization curves, a pseudopassivation was observed for the cleaned nickel. Surprisingly, the passive current density was reduced as the amount of sulfur increased.

Figure 3.14 shows the polarization behavior of nickel polycrystals in 1M H_2SO_4 before and after sulfur segregation at 550°C, 650°C, and 850°C for 30 minutes. For the case of polycrystals, the critical current density on the sulfur-segregated surface (after heating 30 min. at 850°C) was almost two orders of magnitude higher than that on un-segregated surface. Similarly, E_{pp} shifted in the more noble direction as the amount of sulfur increased. Again, no pseudopassivation was observed for sulfur-segregated surface except cleaned nickel. The resulting passive current density behaved irregularly.

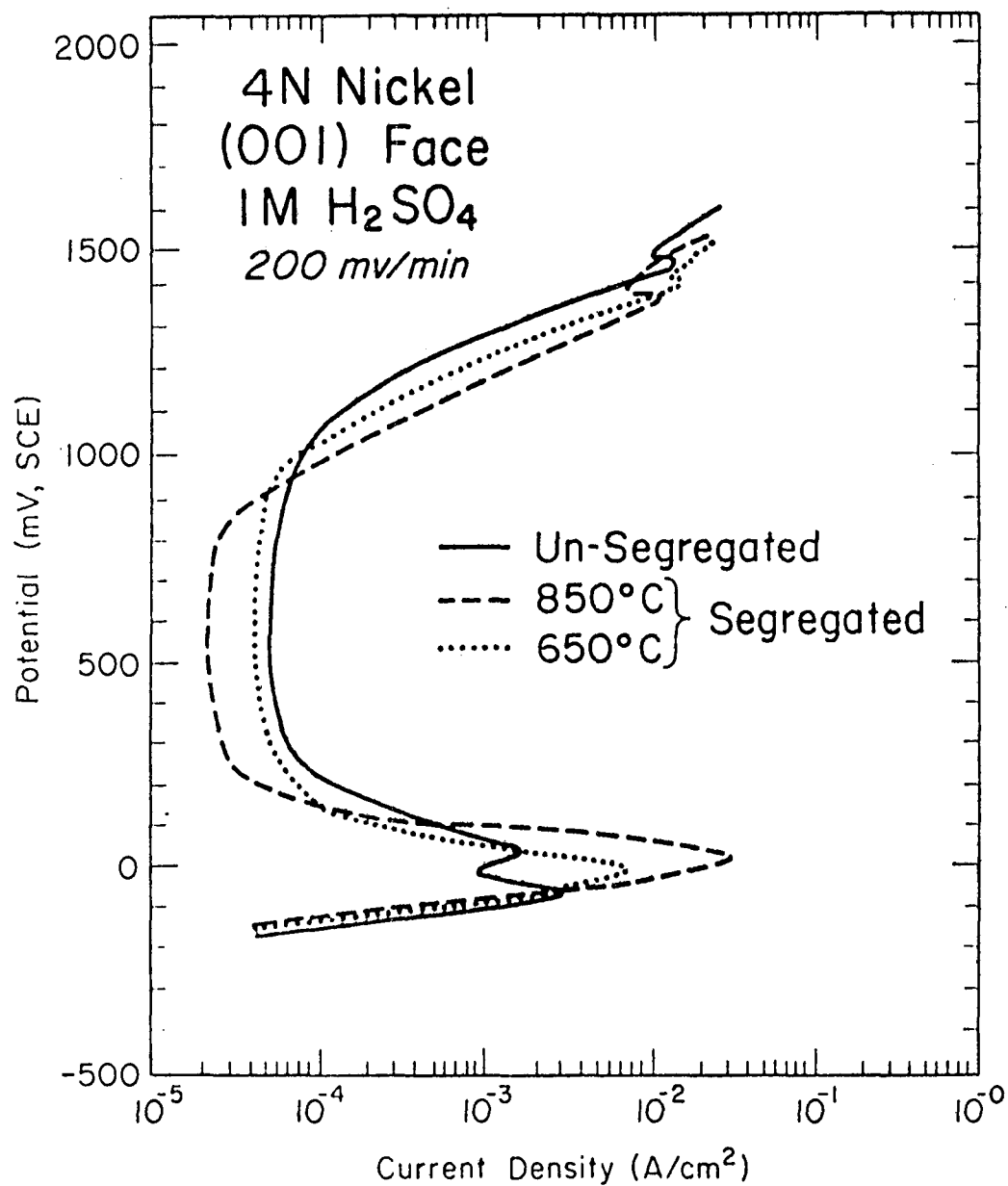


Figure 3.13 Polarization behavior of nickel single crystal (001) face in 1M H₂SO₄ solution and after sulfur segregation at 650°C and 850°C for 30 minutes.

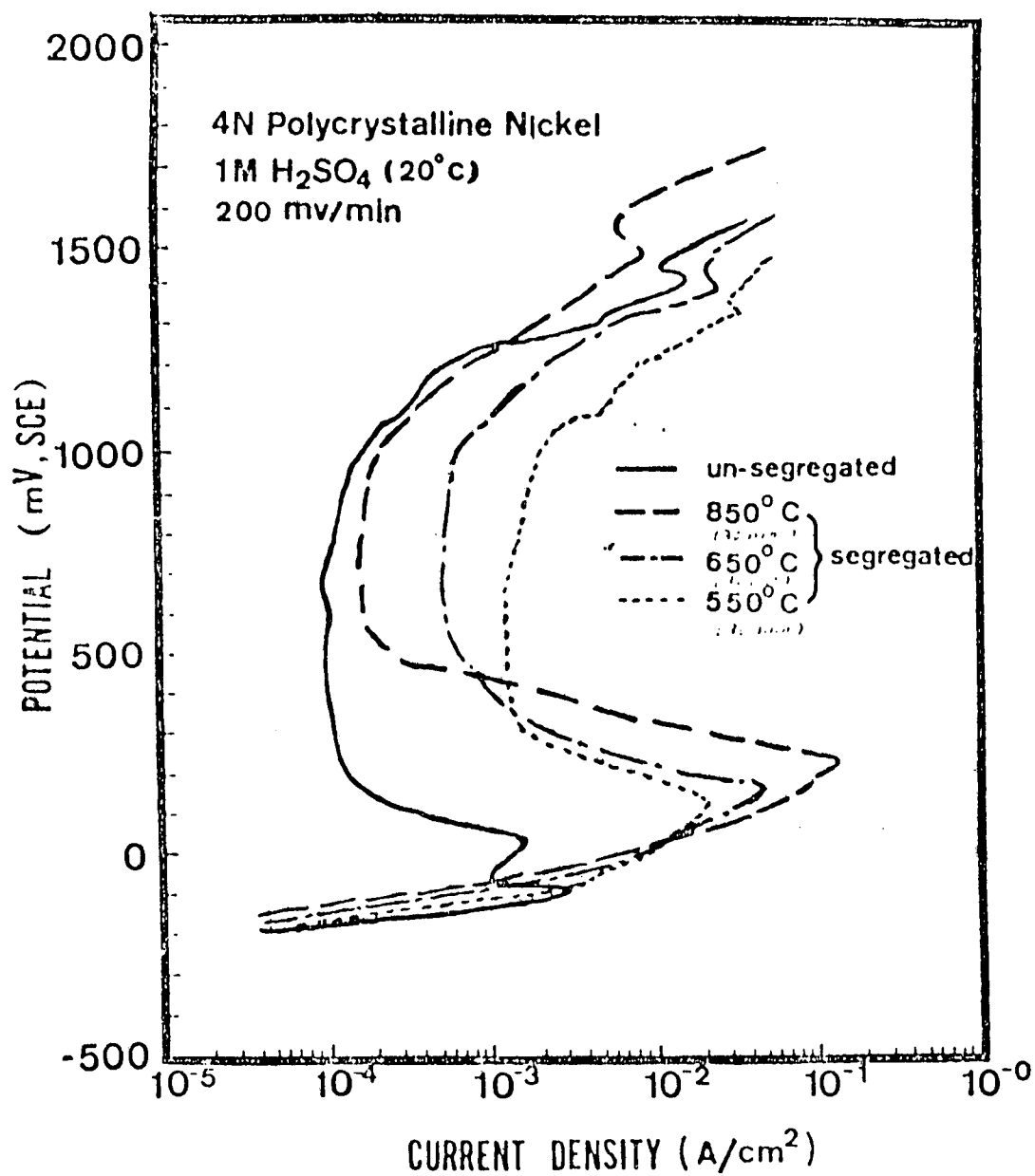


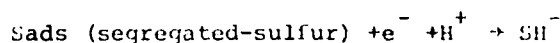
Figure 3.14 Polarization behavior of nickel polycrystals in 1M H₂SO₄ solution before and after sulfur segregation at 550°C, 650°C, and 850°C for 30 minutes.

The more pronounced effect on anodic current density in the polycrystal arises from grain boundary contributions. This can be seen from the following results. A specimen prepared by zone-refining had a large crystal with some smaller crystals around the edge of specimen, as shown in Figure 3.15. The specimen was 4N nickel heated 10 hours at 1150°C followed by furnace cooling to 650°C for 24 hours. The polarization behavior of this specimen is shown as the curve (a) in Figure 3.15. After running the polarization curve, the specimen was polished to a mirror-like finish with grade 000 emery paper and then diamond paste thus removing the segregated sulfur layer. The area B, containing small grains, was covered by a protective resin (e.g. microstop) and the remainder of specimen, area A, was exposed during a polarization run. Results are shown in curve (C) of Figure 3.15. In a similar fashion curve (b) shows the polarization behavior of area B.

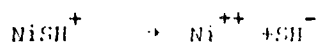
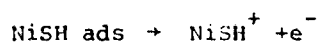
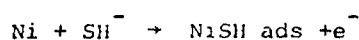
Thus, a comparison of curves (a), (b) and (c) of Figure 3.15 clearly shows the marked effect of grain boundary segregation of sulfur on the rate of dissolution of the grain boundaries in the active peak region. The specificity of the effect on segregated sulfur on electrochemical kinetics is illustrated by the fact that similar experiments with a nitric acid electrolytic did not produce any similar behavior.

Discussion. From the above results it can be concluded that segregated-sulfur plays an important role in the corrosion behavior of nickel. The effect of sulfur in nickel upon its corrosion properties in sulfuric acid has received attention in relation to the deterioration of electroplated nickel coating and dissolution of nickel anodes during electroplating and refining.

To define these results, a reaction scheme (3-19, 3-20) could be used as follows:



SH^- remains to stay at the metal surface to take part in the progress of dissolution as a catalyst.



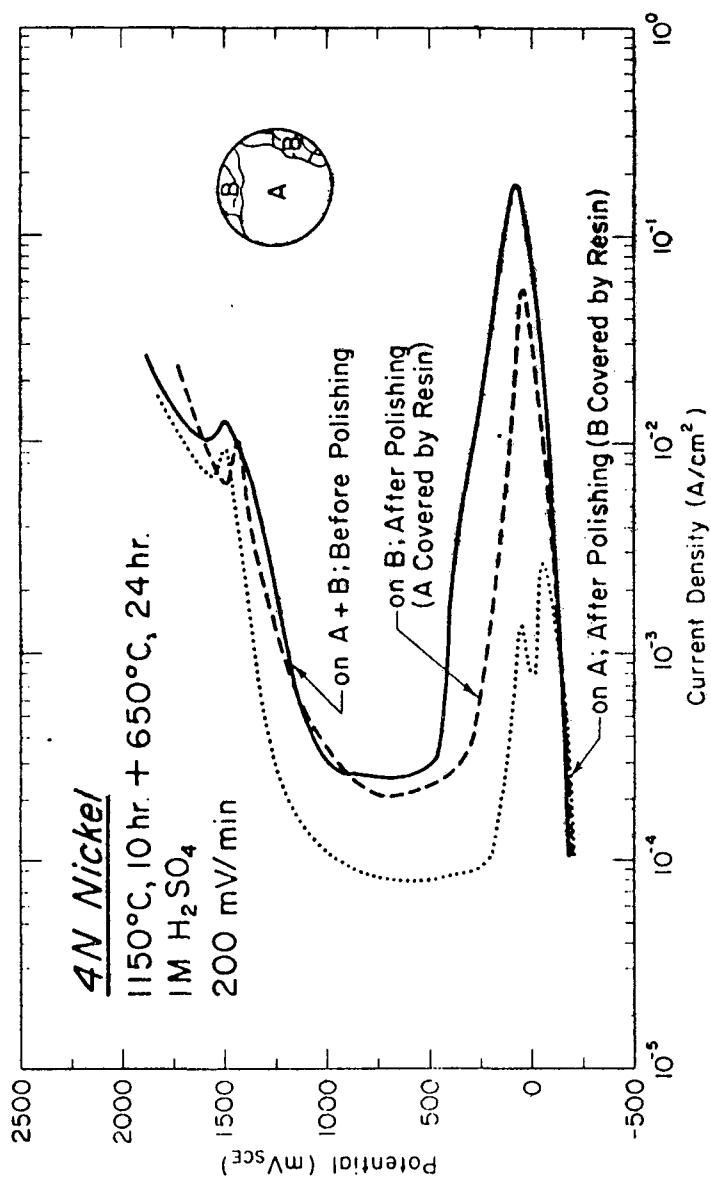


Figure 3.15 Polarization behavior of nickel in 1M H₂SO₄ showing a grain boundary segregation effect.

185-

According to the above scheme segregated sulfur in the nickel dissociates into SH^- which adsorbs on the nickel surface as a catalyst leading to the acceleration of nickel dissolution.

Another explanation may be based on the variation in activation energy of dissolution with sulfur on the nickel surface. This reasonable assumption results from the possibility that segregated-sulfur may act as a low energy site for cathodic hydrogen discharge. However, in practice it is probable that the mechanism of dissolution is complex and that other factors in addition to those mentioned above contribute to the effect of segregated-sulfur upon the dissolution of nickel.

Grain Boundary Segregation. With the advent of Auger analysis, it is now possible to measure compositional profiles if the grain boundaries can be suitably exposed, for example, by intergranular fracture. The present research was undertaken with the following objectives:

- o To develop techniques of exposing grain boundaries of nickel 200, Inconel alloy 600, and 304 Austenitic stainless steel.
- o To establish the identity and amounts of any species segregating to the grain boundaries.
- o To measure the compositional profiles of any species segregating to the grain boundaries.

Experimental Details. The materials, nickel 200, Inconel alloy 600, and 304 Austenitic stainless steel, used in this investigation had the following chemical composition in wt. pct.:

<u>Alloy</u>	<u>Ni</u>	<u>Fe</u>	<u>Cr</u>	<u>S</u>	<u>C</u>	<u>Cu</u>	<u>Si</u>	<u>Mn</u>
Ni 200	99.4	0.15		0.005	0.1	0.1	0.05	0.2
Inconel 600	76.0	8.0	16.0	0.005	0.08	0.2		
304 SS	8.0	72.2	18.0	0.006	0.08		1.0	

Samples for Auger electron spectroscopy were cut into 4.31 cm-long and 0.315 cm-diameter rods, round-notched 1.76 cm from one end with a depth of 0.157 cm and an angle of 60°. These were then given recrystallization and solution

annealing at 1250°C for 4 hours and 1300°C for 12 hours. They were then quenched in water to generate grain sizes of approximately 200 and 500 μ , respectively, and were subsequently aged between 550°C and 700°C with no further change in grain size. Note that the heat-treatments were carried out after encapsulation in quartz glass tubes evacuated and then pack-filled with argon.

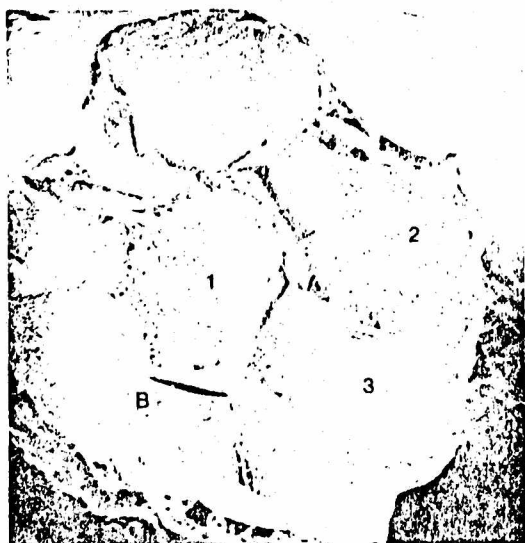
All samples were fractured at room temperature in the baked-out Auger chambers at pressure of 2×10^{-10} torr. The specimen fracture attachment used in this study, PHI Model 10-520 from Physical Electronics Industries, Inc., is designed for use in conjunction with cylindrical-Auger electron optics system with scanning Auger microprobe (PHI Model 545). The samples extended radially outward from the specimen manipulator rotation axis. The complete fracture attachment mounts on a 6" O.D. flange. The sample to be fractured was rotated over the fracture device and then lowered 0.5" into position for fracturing. The clean fracture surface was rotated in front of the coaxial cylindrical mirror analyzer for Auger analysis.

The scanning electron gun was mounted internally to the cylindrical Auger analyzer. Under normal operation the electron beam was scanned synchronously with the selected display device. This feature provided a means for easy specimen alignment when performing standard Auger analysis on selected areas of the specimen. The diameter of the electron beam was variable down to less than 5 μ m. Beam energy was variable up to 10 KeV, and beam current was variable from 50 nanoamps to 5 μ amps with a typical operating beam current of 0.5 μ amps. A TV monitor allowed continuous observation of the secondary electron micrographs.

The spectrum obtained experimentally was the derivative of the Auger electron distribution curve, i.e. $dN(E)/dE$. A 2KV electron beam was used. Auger peak amplitudes (peak-to-peak heights) were directly proportional to the amount of coverage. In the results reported herein Auger analysis was conducted along with sputtering by argon ion bombardment to obtain composition profiles of the segregated-zone. This technique entails the sequential removal of the fracture surface followed by AES analysis of the newly exposed layer.

The fracture surface of each Auger samples were examined in a scanning electron microscope after removal from the vacuum chamber. The fracture mode

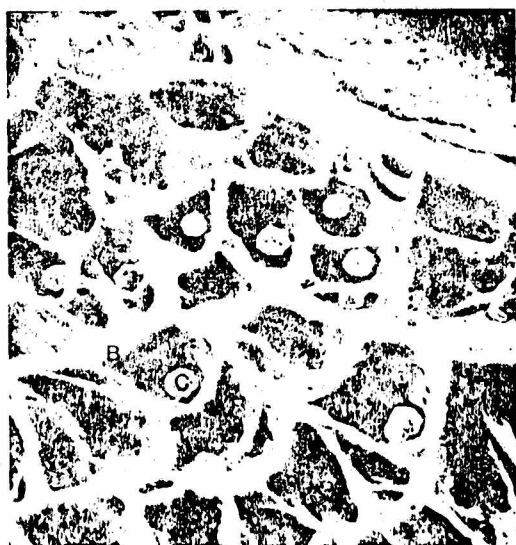
187



80X



800X



1800X

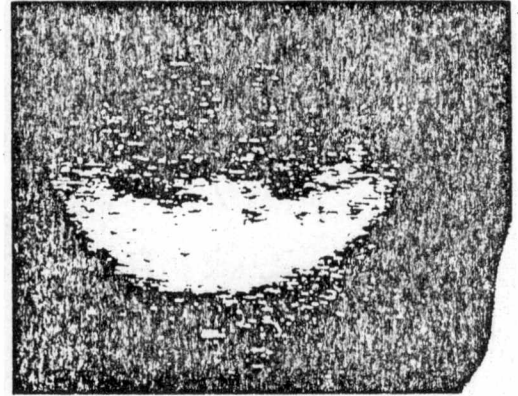


4000X

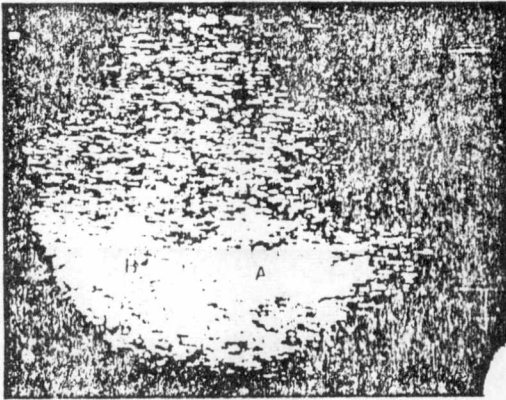
Figure 3.16 Fracture surface of Ni 200 (1250°C 4 hours + 585°C 48 hours WQ).



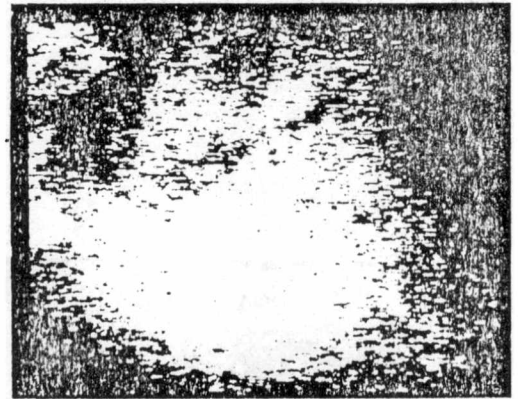
30 X



CADMIUM DISTRIBUTION



SULFUR DISTRIBUTION

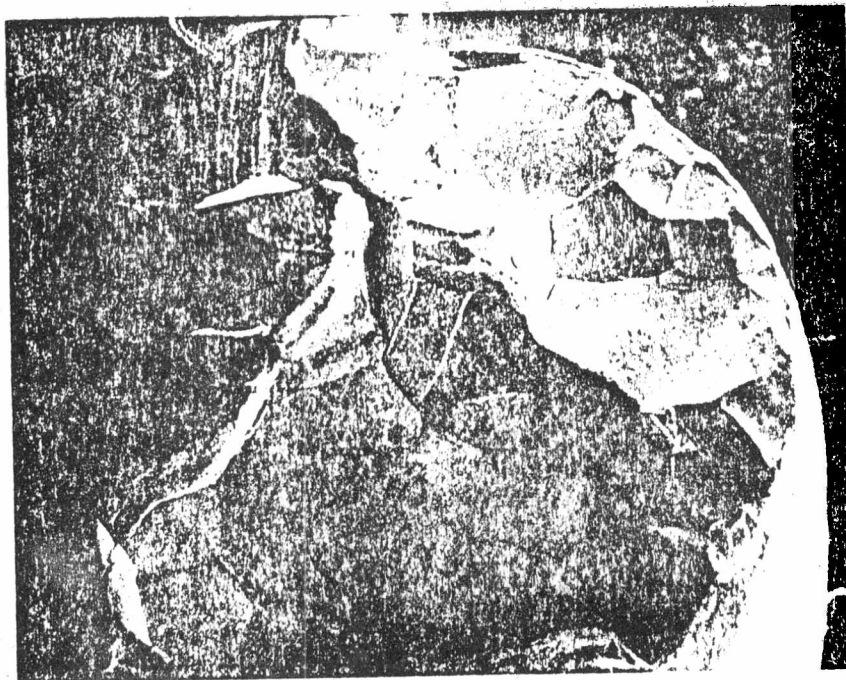


CARBON DISTRIBUTION

*Nickel 200 1100 °C + 1250 °C 4 Hours WQ
585 °C 120 Hours WQ*

Figure 3.17 Fracture surface of Ni 200 and scanning Auger traces.

189



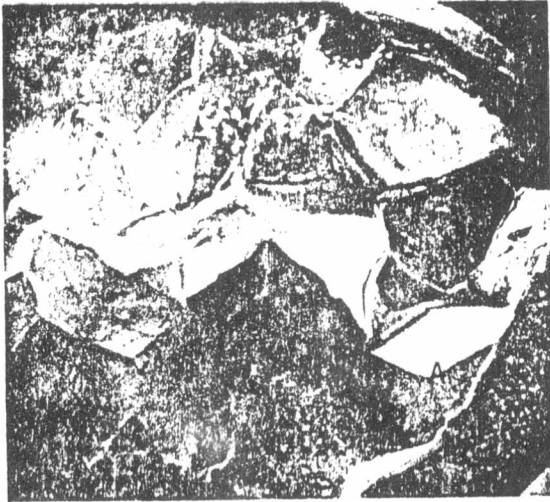
30X



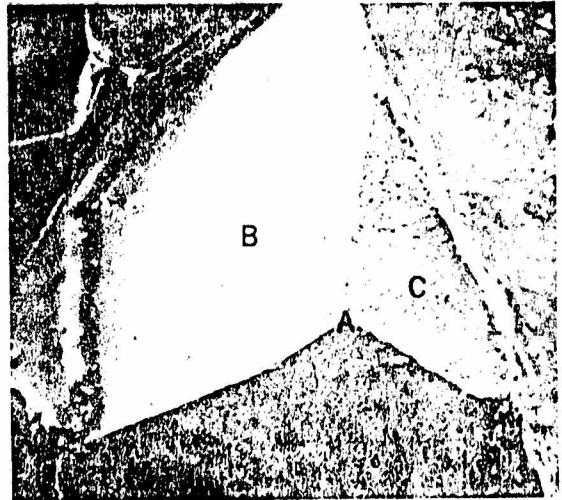
3000X

Figure 3.18 Fracture surface of Nickel 200 (1250°C for 4 hours + 625°C for 24 hours).

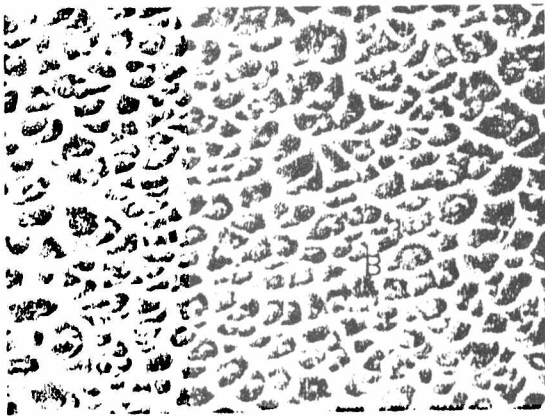
180



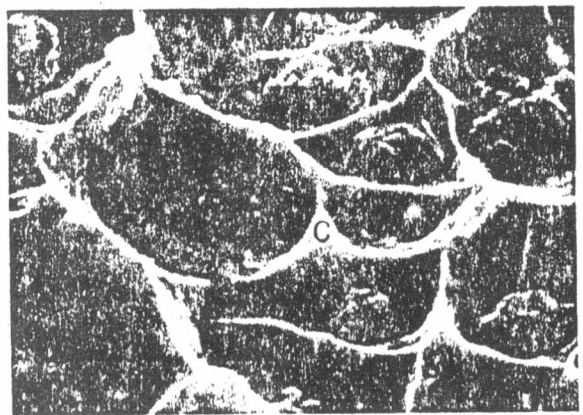
30X



120X



1000X



5000X

Figure 3.19 Fracture surface of Nickel 200 (1250°C for 4 hours + 600°C for 24 hours).

Nickel 200

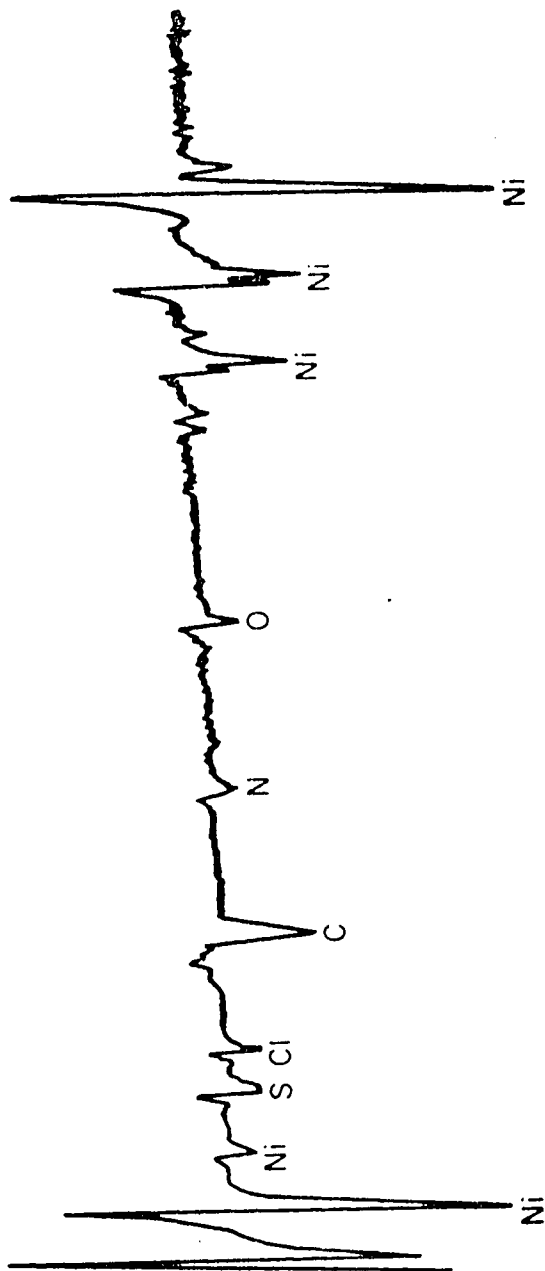


Figure 3.20 The representative Auger spectrum from the fracture surface of Nickel 200 (125°C for 4 hours + 565°C for 18 hours).

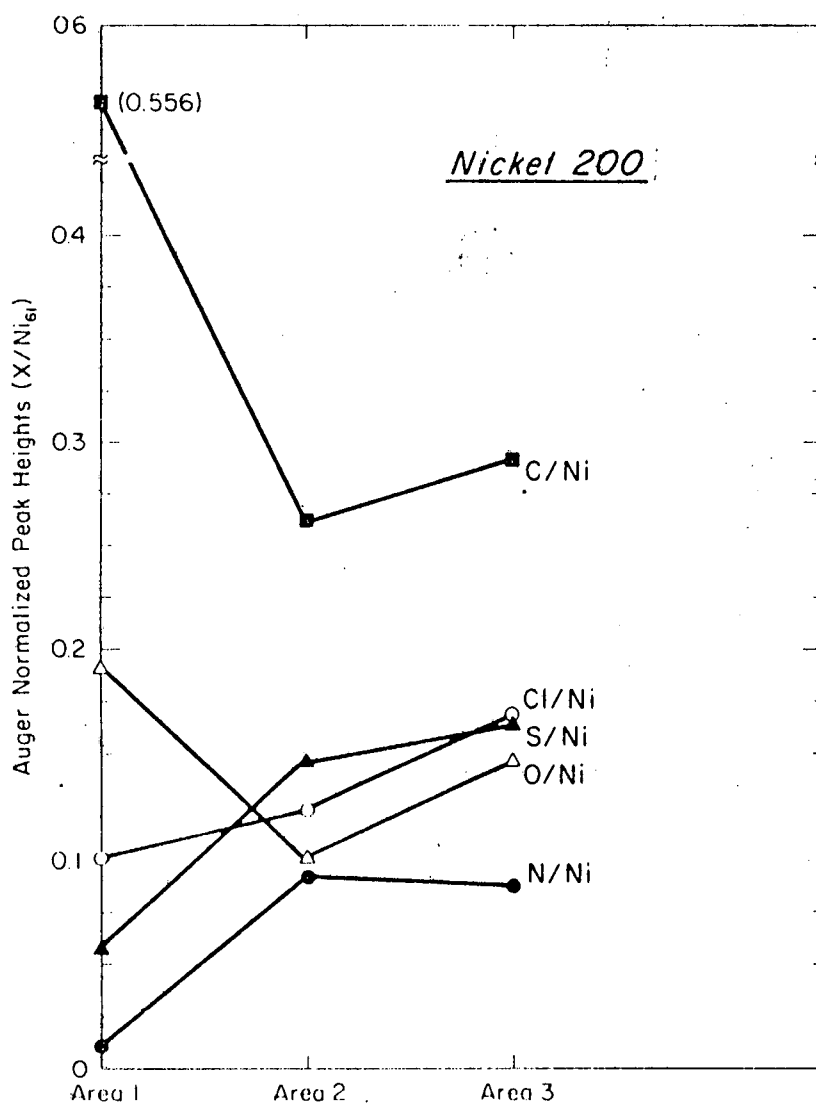


Figure 3.21 Auger spectroscopic analyses at the selected area (as shown in Figure 3.16) of the fractured surface.

Nickel 200

193

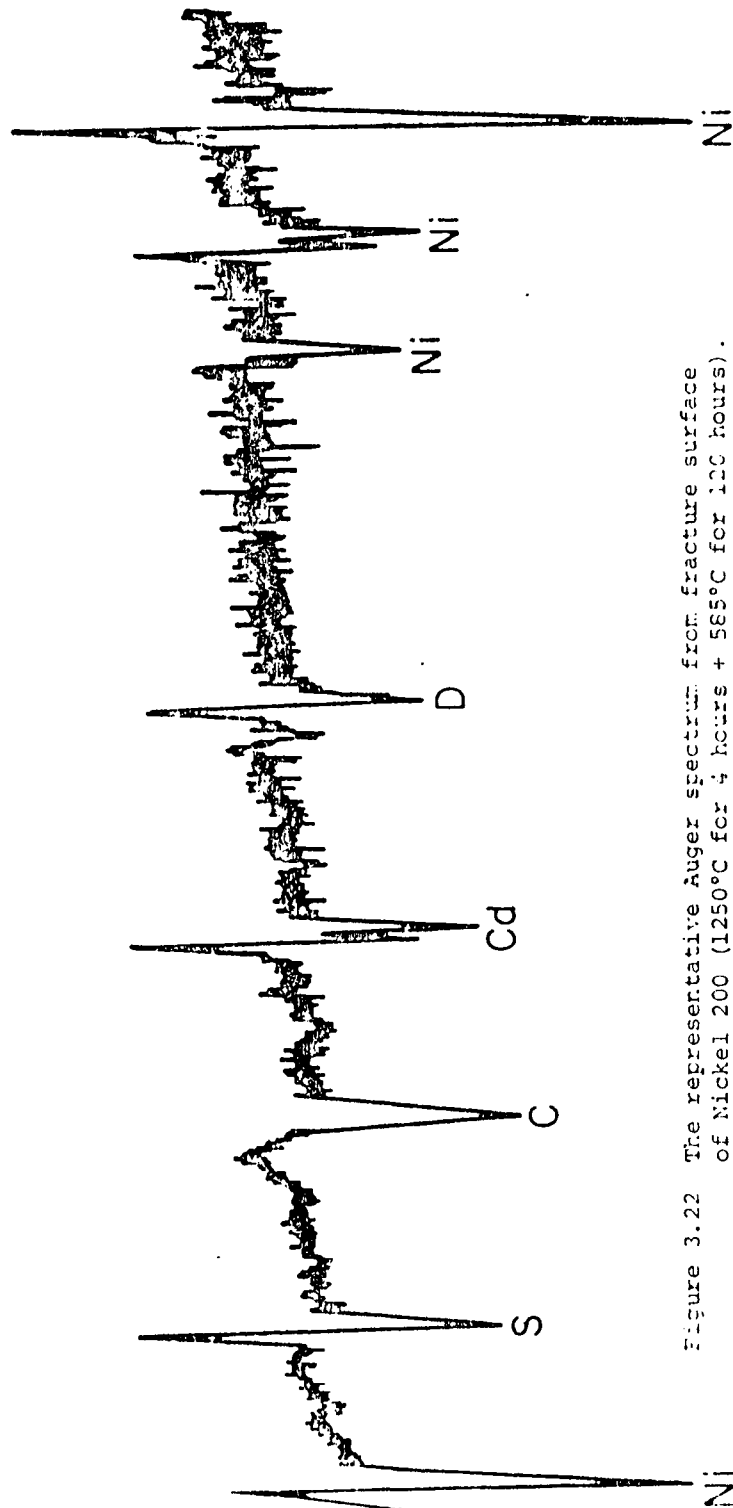


Figure 3.22 The representative Auger spectrum from fracture surface of Nickel 200 (1250°C for 4 hours + 585°C for 120 hours). Bright spot Area A, refer to Figure 3.17.

Bright - Spot (A)

Nickel 200

194

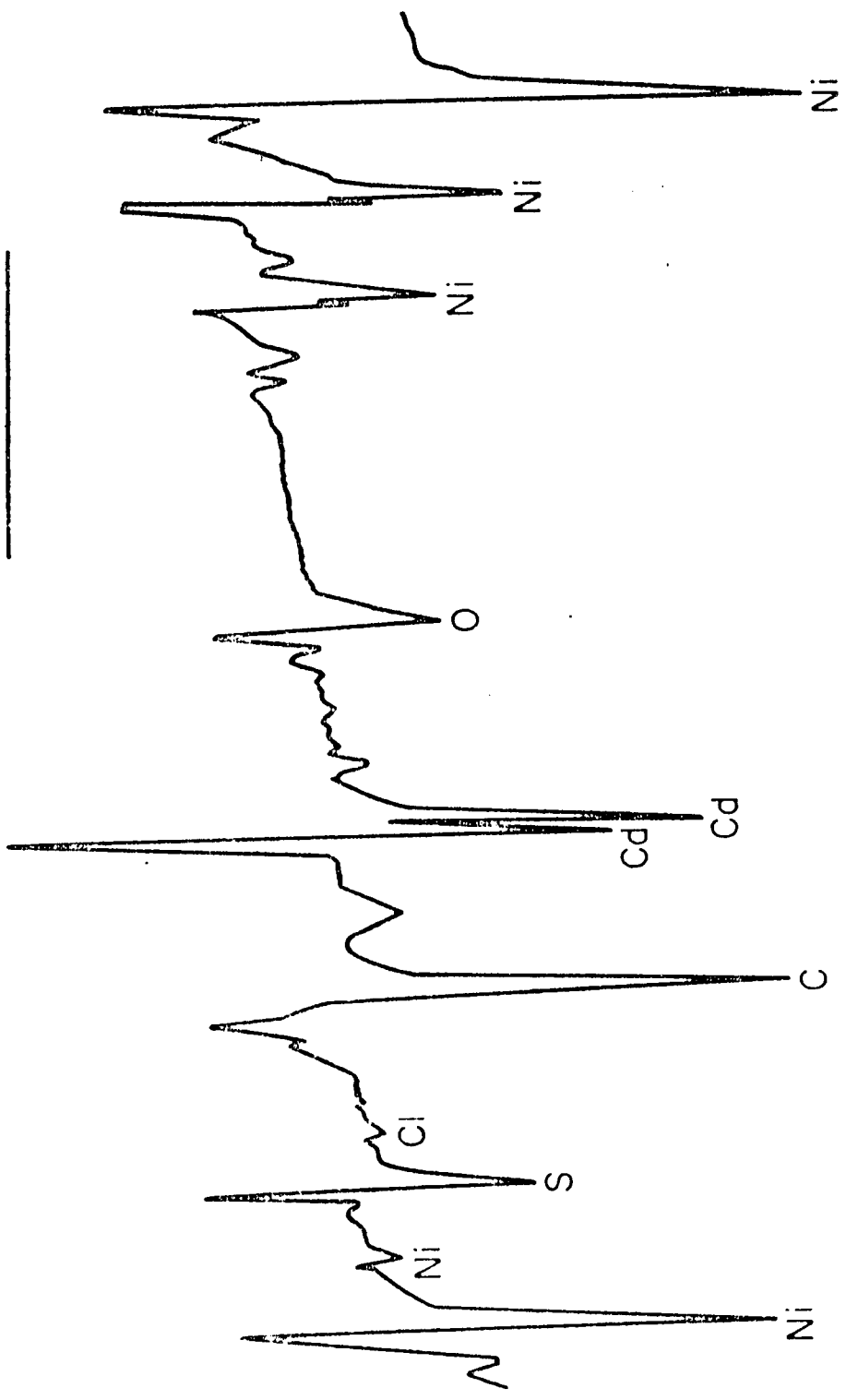
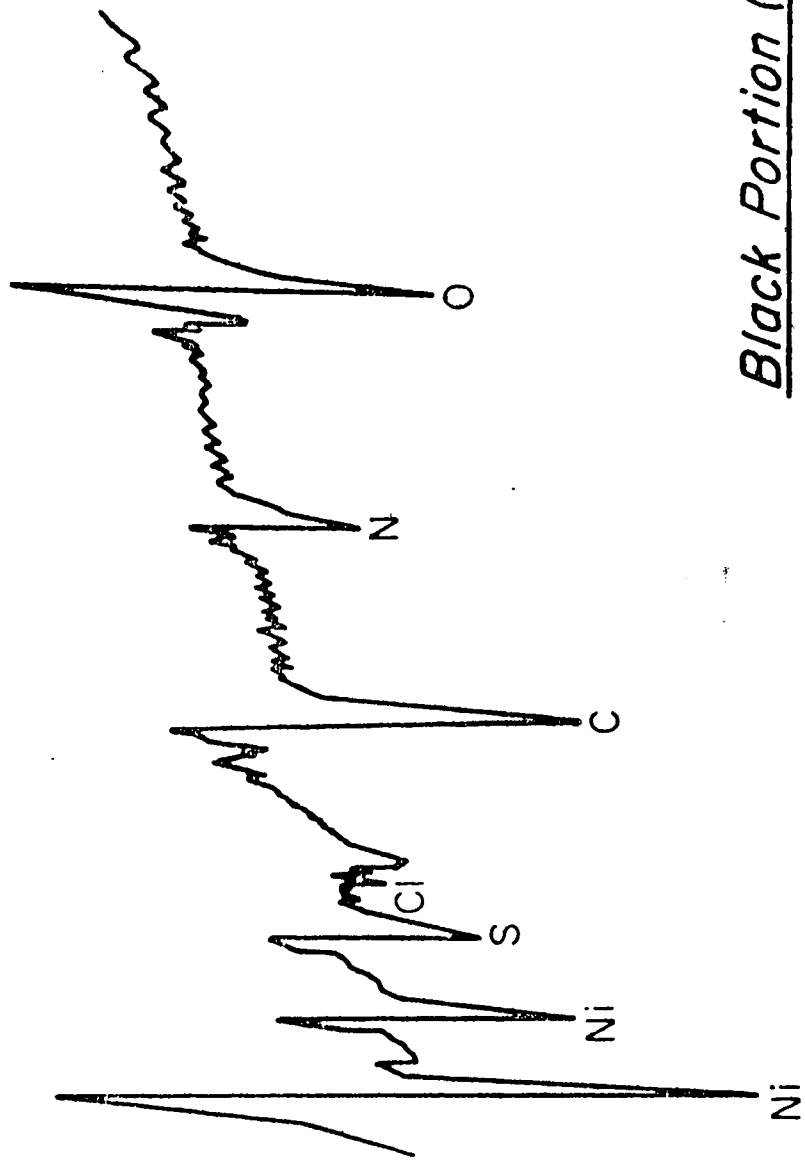


Figure 3.23 The representative Auger spectrum of fracture surface area B, refer to Figure 3.16.

Nickel 200

x 1 ← → x 5



Black Portion (C)

Figure 3.24 The representative Auger spectrum from fracture surface (Area C) in Figure 3.17 of Nickel 200 (1250°C for 4 hours + 585°C for 120 ksi).

was characterized and correlated with the material processing history and Auger results.

Results of Ni 200 In Situ Fractures. A change in fracture mode was observed with increasing aging time and/or temperature. Annealed and quenched specimens were found to be ductile and only fractured after large amounts of deformation. Samples intermediately aged at low temperature (say, 585°C) on the other hand, fractured in a more brittle manner with little deformation with an intergranular fracture mode. This failure mode is illustrated by an SEM fractograph (Figure 3.16) for nickel 200 aged 48 hours at 585°C after a solution treatment of 4 hours at 1250°C. Grain boundary facets indicative of intergranular failure are apparent. Similar results were obtained for samples aged 120 hours at 585°C (Figure 3.17), 24 hours at 625°C (Figure 3.18) and 24 hours at 600°C (Figure 3.19). Again, the failure mode was intergranular.

Figures 3.16 and 3.19 show that certain second phase particles are present on the fracture surface. The particles contained within the dimples are unable to be identified at the present time.

Figure 3.20 shows a typical Auger spectrum from the intergranular fracture surface of sample 1 (Aged 48 hours at 585°C). Auger analysis of the surface revealed segregation of sulfur, chlorine and carbon. Unfortunately, the presence of significant amounts of nitrogen and oxygen prohibits a quantitative rationalization. The distribution of segregants varies from area to area, as shown in Figure 3.21.

Upon further aging at 585°C (120 hours) cadmium segregation was observed on the fracture surface associated with increasing segregated-sulfur. The typical Auger spectra from three selected areas (referred to in Figure 3.17) are shown in Figure 3.22, 3.23, and 3.24. In all the Auger spectra, carbon and oxygen peaks were also observed. It is suspected that a major contribution to these peaks arises from contamination in the vacuum system. Work is continuing to investigate this possibility.

It can be seen from Figure 3.17 that the distributions of segregated sulfur and cadmium are not localized uniformly over fracture surface. In contrast, carbon distributes more uniformly. It is interesting to note that the regions enriched in sulfur also show cadmium enrichment. It should be mentioned

Inconel Alloy 600

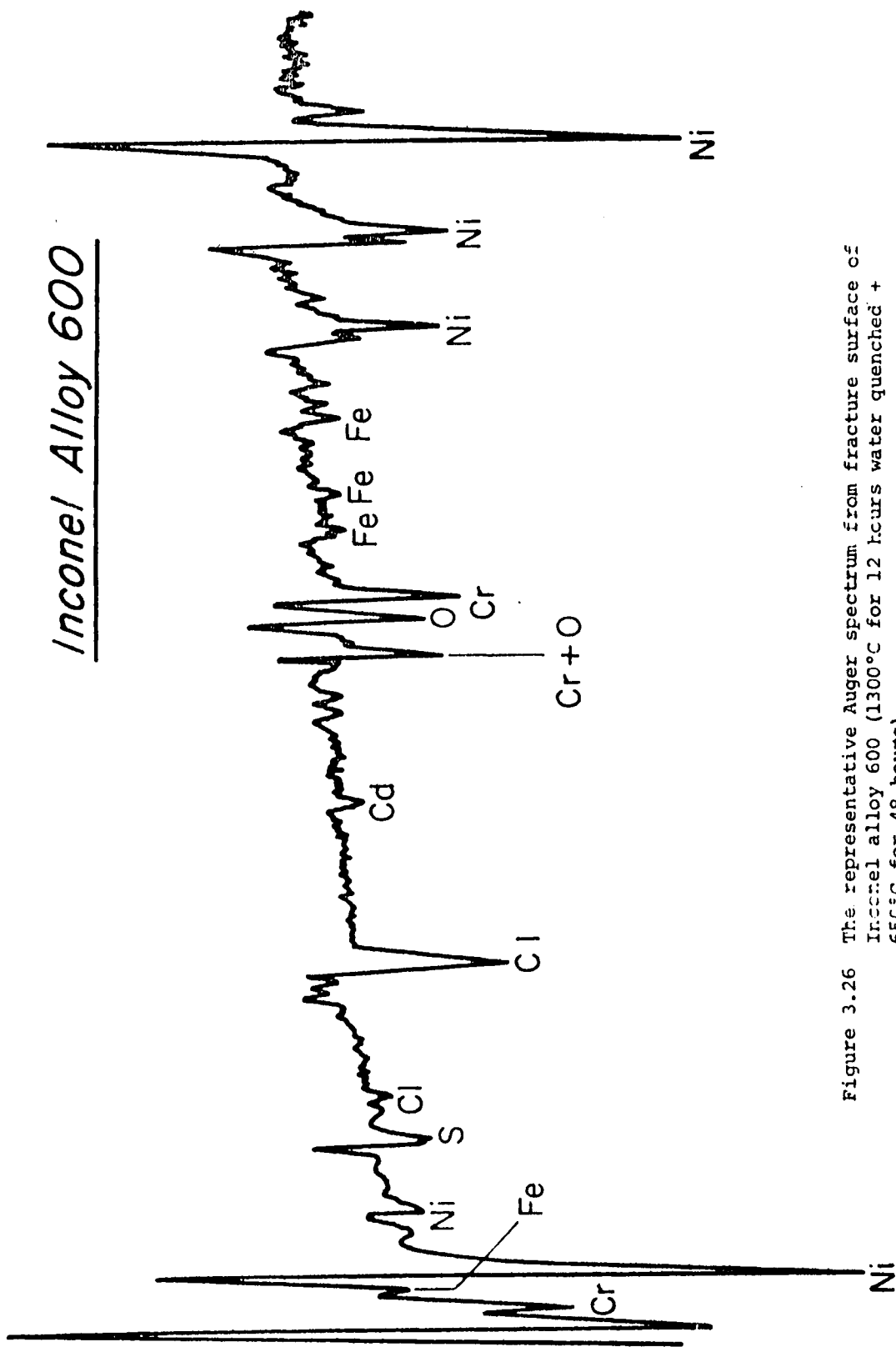


Figure 3.26 The representative Auger spectrum from fracture surface of Inconel alloy 600 (1300°C for 12 hours water quenched + 650°C for 48 hours).



40X

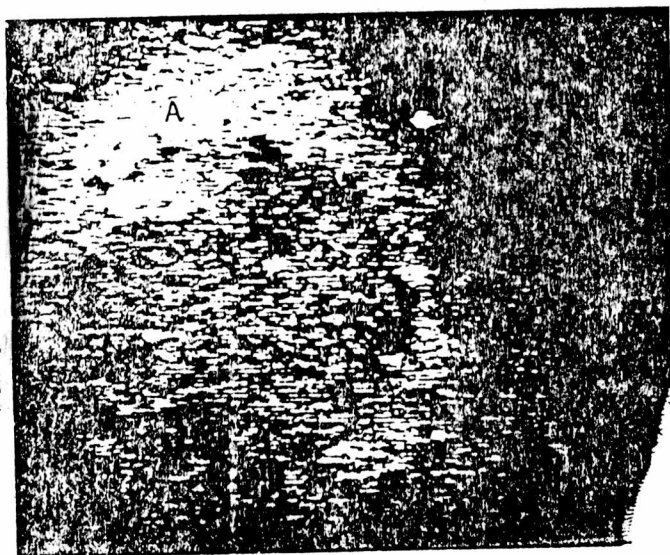


160X

Figure 3.27 Fracture surface of Inconel alloy 600 (1300°C for 12 hours, water quenched + 650°C for 124 hours, water quenched).



100X



Sulfur Distribution

Figure 3.28 Fracture surface and sulfur distribution on the fracture surface of stainless steel 304 (1300°C for 12 hours, water quenched + 650°C for 24 hours, water quenched).

Austenitic 304 Stainless Steel

201

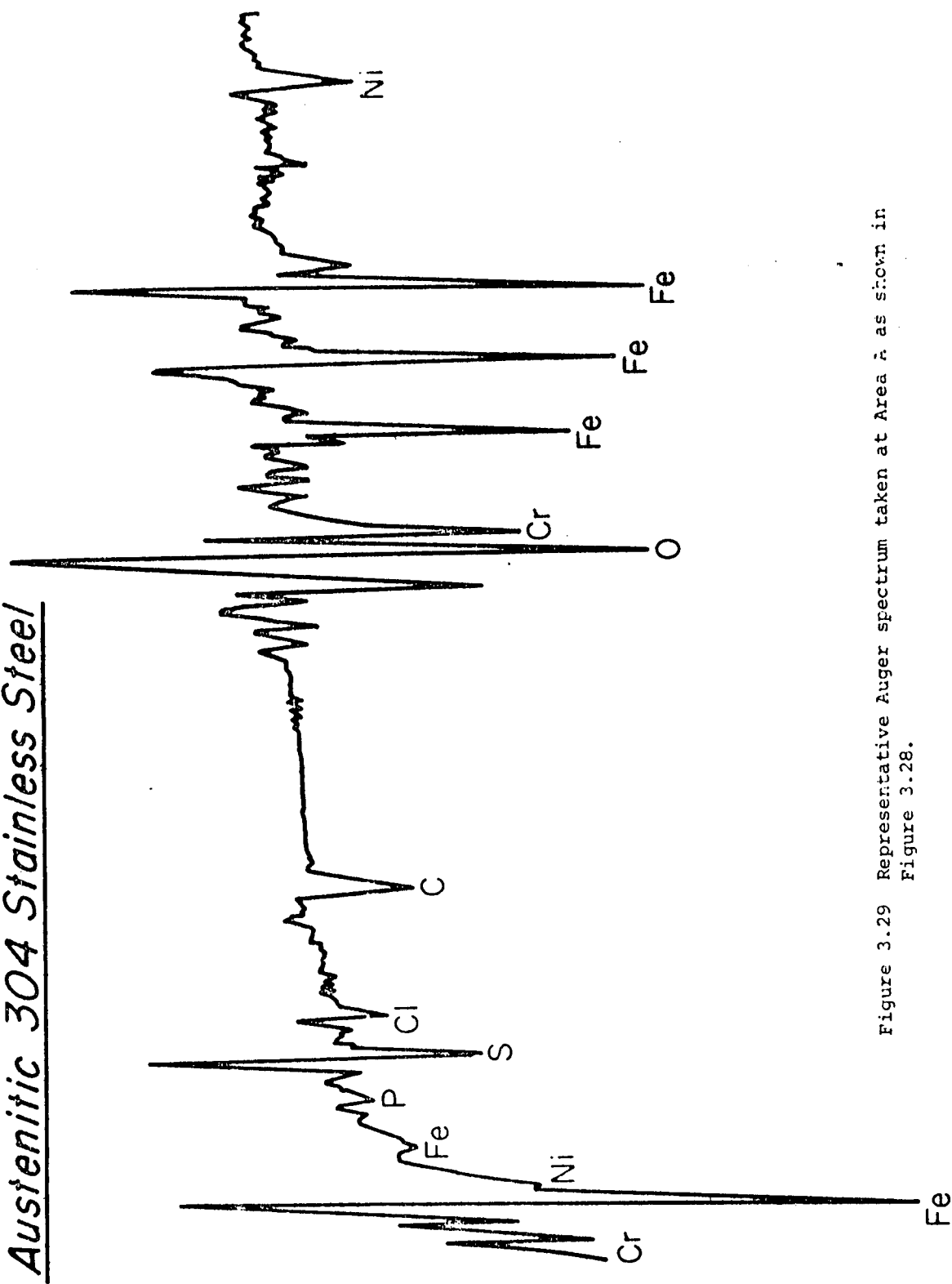


Figure 3.29 Representative Auger spectrum taken at Area A as shown in Figure 3.28.

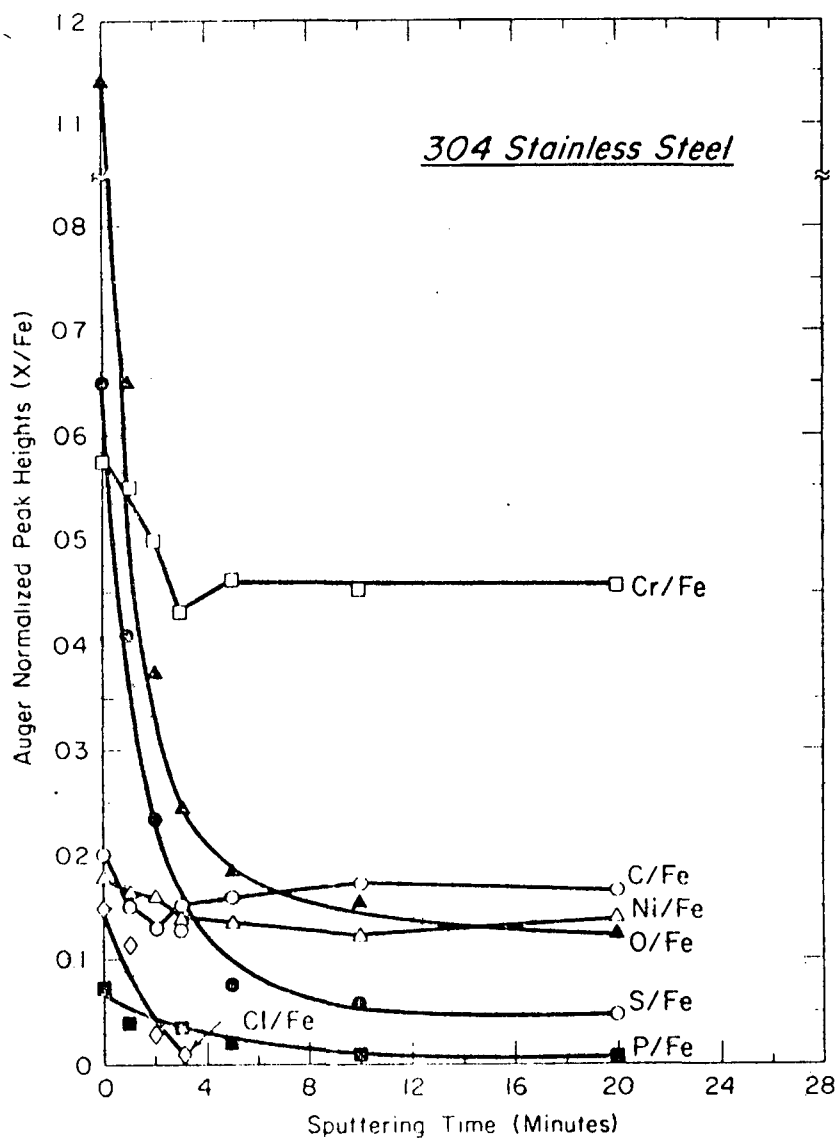


Figure 3.30 The depth-composition profile from fracture surface of 304 stainless steel (1300°C for 12 hours, water quenched + 650°C for 24 hours).

that the measurements from Auger analysis are actually lower than true value. This is because segregants localize on both fracture surfaces.

By sputtering off successive layers from the fracture surface, the profile of concentration of any segregant as a function of sputtering time (i.e. distance from the grain boundary) was established, as shown in Figure 3.25. The concentrations of all segregants dropped sharply to a low value within two minutes of sputtering (~ a depth of about $10 \text{ \AA}$ from fracture surface) and decreased steadily thereafter. This agrees with previous work on surface segregation.

Results of Inconel Alloy 600. The segregation of sulfur and cadmium were also observed on the fracture surface of Inconel alloy 600 (12 hours at 1300°C followed by water-quenched and then subsequently aged 48 hours at 650°C). The representative Auger spectrum is shown in Figure 3.26. Unfortunately, a scanning electron fractograph of this specimen was not taken due to damage of the specimen upon removal from the Auger chamber. However, a specimen (aged 24 hours at 650°C) broken in the atmosphere showed a tendency of intergranular fracture, as shown in Figure 3.27. More work will be carried out on this alloy in the next quarter.

Results of Austenitic 304 Stainless Steel. Dimples, which were formed by ductile tearing and linking of cavities were the main features observed on the fracture surface of austenitic 304 stainless steel, as shown in Figure 3.28. The Auger spectrum obtained from this type of fracture surface is shown in Figure 3.29. Besides the Cr, Fe, and Ni peaks, prominent peaks are noted for sulfur and oxygen. A carbide-like carbon peak is also shown in the spectrum. Segregation of chlorine and phosphorus are also observed. Again, it is suspected that a major contribution to oxygen and carbon peaks arises from contamination in the vacuum system. The source of chlorine is not known at the present time.

The distribution of species enriched on the fracture surface is again not uniform. The depth-composition profiles for various species near the fracture surface is shown in Figure 3.30. Both sulfur and oxygen dropped sharply within ten minutes of sputtering and then reached a plateau value. Chromium enriched at the region close to fracture surface then decreased deeper to the bulk. The depth-composition profile of carbon had the same tendency as chromium.

Discussion of In Situ Fracture Tests. The segregation of sulfur to grain boundaries in nickel has been clearly demonstrated in the present work. The segregation of sulfur to fracture surface in Inconel alloy 600 and austenitic stainless steel 304 type was also observed. The presently observed decay of the concentration of sulfur with distance from the fracture surface bears a very close similarity to that reported earlier for surface segregation. It is suspected that a major contribution to sulfur peak arises from the particles contained in the dimples shown in Figures 3.16 and 3.19. However, those particles still exist when the fracture surface shows no sulfur coverage after ion sputtering. Therefore, it is indisputable that sulfur segregation at nickel grain boundaries is not due to a second phase precipitate. The sulfur is confined to a narrow region ($< 10^{\circ}\text{\AA}$) in the vicinity of the grain boundary, probably in the elemental form.

The thermodynamic consideration of sulfur segregation to the grain boundaries of nickel can be rationalized by the same basis which has been discussed previously. The elastic misfit strain could be the driving force for this type of segregation. The concept of chemisorption is appropriate in considering sulfur segregation to grain boundaries. The specific function of temperature and time on grain boundary segregation of sulfur in nickel has not yet been established. However, it is reasonable to expect that the rate of sulfur segregation to grain boundaries is slower than that to the surface. This can be seen from Figure 1 that sulfur segregating to the nickel single crystal with (001) surface to a saturated value about 10 hours of heating at 585°C whereas sulfur segregating to grain boundaries to a value of one-third saturation (see Figure 3.21) for 48 hours of heating at 585°C.

On further ageing at 585°C (aged 120 hours) cadmium segregation was observed on the fracture surface associated with increasing segregated-sulfur (see Figure 3.17). It is surprising to observe cadmium segregation at nickel grain boundaries. Previous results of surface segregation on nickel had never shown any evidence of cadmium segregation. However, this strange result has been verified by the residual gas analysis in the SIMS. The cadmium vapor was measured and observed by SIMS technique when a nickel specimen was heated to the temperatures above 450°C. The mass spectrum of residual gas in the chamber of SIMS during heating a nickel specimen to 700°C is shown in

Figure 3.31. The existence of cadmium is indisputable. Cadmium may segregate on a nickel surface, but vaporizes during preheating prior to an Auger analysis. Thus, cadmium segregation was not observed in the work on nickel single crystals.

In most cases the fresh fracture surfaces were contaminated with oxygen and carbon. It is felt that longer times are needed for baking-out the Auger chamber to eliminate contamination.

Alloying Effects on Solute Segregation. The previous sections have illustrated the importance of solute segregation to grain boundaries as it affects intergranular corrosion processes. Late in the reporting period work was started in the area of alloying effects on solute segregation. The objective is to identify procedures to retard or eliminate deleterious segregation of impurity elements to grain boundaries.

Initial work will be directed to the investigation of the interaction of alloying elements with segregating species. Developing upon our broad base understanding of the nickel sulfur system, the segregation of sulfur will be studied in dilute binary nickel alloys. The alloying elements to be studied are Mn and Al. These alloys are now being prepared. Two alloy compositions have been chosen. The alloy concentrations will be 500 ppm and 1000 ppm.

Analogous to the nickel sulfur studies surface segregation of sulfur will be studied using Auger spectroscopy. The role of Mn and Al additions upon the extent and kinetics of sulfur segregation will be determined. Previous work has indicated that surface segregation studies provide a reasonable indication of what may be expected at grain boundaries.

TASK 1.0 CONCLUSIONS

A summary of the Task 1.0 studies for this reporting period are as follows:

- o Vacuum heating of nickel can lead to sulfur segregation. The chemistry of the sulfur-segregated surface was studied in a temperature range of 25°C to 950°C using an Auger electron spectroscopic technique.
- o Experimental results suggest that sulfur segregation exhibits behavior typical of chemisorption rather than physical adsorption.

206

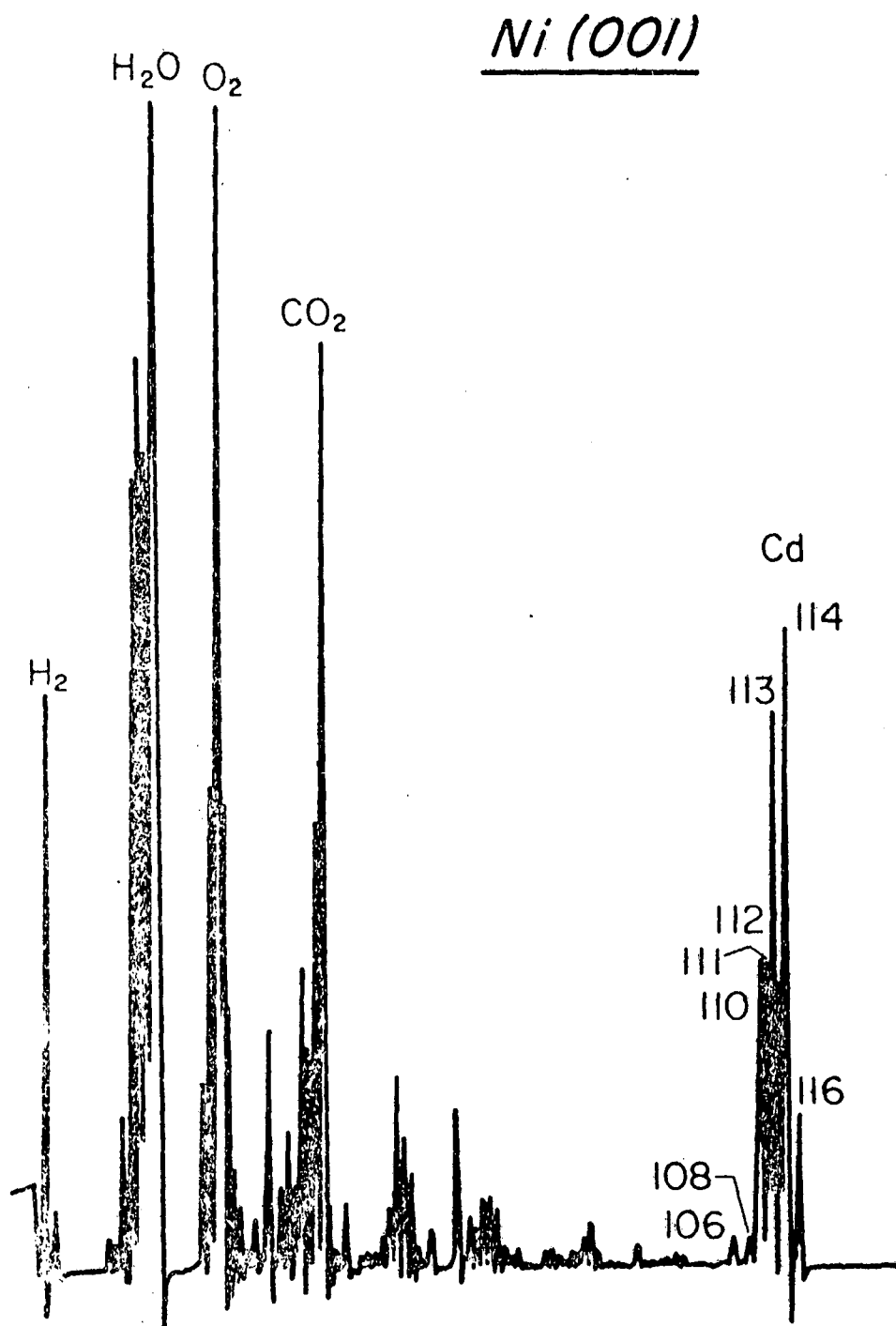


Figure 3.31 Mass spectrum for residual gas analysis (RGA), nickel single crystal (001) heated at 700°C.

- o Sulfur segregation does not follow a segregation (or adsorption) isotherm. This suggests that the concentration of sulfur (even though less than 10 ppm) in the nickel bulk is too high to follow an isotherm.
- o The extent of surface segregation has been expressed by the normalized Auger peak height (NAPH) which has been evaluated by Bishop and Riviere's formula and calibrated by a Ni_3S_2 standard. The approximate atomic concentration of segregated-sulfur on the nickel (001) face is 33 at.% which is enhanced relative to the matrix concentration by a factor of 1×10^3 to 3×10^4 .
- o The depth-composition profile of a typical region of the impurity segregated surface was obtained by inert ion (Ar^+) sputtering and expressed by a plot of normalized Auger peak heights versus sputtering time. The segregated layer has been estimated to be localized within a monolayer. This behavior is consistent with chemisorption and equilibrium segregation.
- o Diffusion plays an important role in the segregation process. It supplies the segregant atoms from the deeper bulk material. The amount of segregated-sulfur on the surface of nickel crystal increases linearly with time in the initial stage of the segregation process. This implies that sulfur diffuses from the nickel bulk at a constant rate. The diffusion coefficients of sulfur involved in segregation process have been estimated as

$$D = 3.5 \times 10^{-2} \exp (-30,500/RT)$$

The low activation energy for diffusion may be due to high dislocation density (which is generated by the surface preparation) and the higher concentration of vacancies in the region near the surface.

- o The influence of surface segregated-sulfur upon the anodic polarization behavior of nickel has been investigated. The critical current densities for both in single crystals and polycrystals in a one molar sulfuric acid solution increases as the content of segregated-sulfur increases.
- o Proper annealing and aging treatments lead to intergranular fracture of Ni 200. However, SEM fractographs show that second phase particles are present on the fracture surface. These particles have not been identified at the present time.
- o The segregation of sulfur to grain boundaries in nickel 200 has been clearly demonstrated in the present work. The segregation of sulfur to fracture surfaces in Inconel alloy 600 and 304 stainless steel has also been observed. In addition, cadmium segregation has been observed at nickel grain boundaries after long term aging at 585°C.
- o A study on the effect of alloying elements on the segregation of sulfur in dilute Ni-Mn and Ni-Mg alloys has just started. These alloys are now being prepared.

REFERENCES

- 3-1 J. W. Gibbs, "The Collected Works of J. Willard Gibbs," Vol. 1, p. 219, Yale University Press (1928).
- 3-2 E. A. Guggenheim, Trans. Faraday Soc. 36, 397 (1940).
- 3-3 D. McLean, "Grain Boundaries in Metals," p. 116, Oxford University Press, London (1955).
- 3-4 H. E. Bishop and J. C. Riviere, J. Appl. Phys. 40, 1740 (1969).
- 3-5 K. Ueda and R. Shimizu, Surf. Sci. 36, 789 (1973).
- 3-6 G. A. Somorijai, "Principles of Surface Chemistry," Prentice-Hall, Inc., New Jersey (1972).
- 3-7 "Handbook of Auger Spectroscopy," Physical Electronics Industries, Inc., (1972).
- 3-8 I. Langmuir, J. Am. Chem. Soc. 40, 1361 (1918).
- 3-9 J. P. Coad and J. C. Riviere, Proc. Roy. Soc., London A 331, 403 (1972).
- 3-10 G. E. Becker and H. D. Hagstrum, Surf. Sci. 30, 134 (1972).
- 3-11 J. E. Demuth, D. W. Jepsen, and P. M. Marcus, Solid State Communication 13, 131 (1973).
- 3-12 P. G. Shewmon, "Diffusion in Solids," p. 16, McGraw-Hill, New York (1963).
- 3-13 I. Pfeiffer, Z. Met. 46, 516 (1955).
- 3-14 S. J. Wang and H. J. Grabke, Z. Met. 61, 597 (1970).
- 3-15 R. K. Hotzler and L. S. Castleman, Met. Trans. 3, 2561 (1972).
- 3-16 J. H. Westbrook and S. Floreen, Canadian Met. Quart. 13, 181 (1974).
- 3-17 I. F. Koronyuk and M. M. Pavlyuchenko, Geterog Khim Reaktsii 231, (1961).
- 3-18 J. Burke, "The Kinetics of Phase Transformation in Metals," Pergamon Press, Oxford (1965).
- 3-19 J. Edwards, Trans. Inst. Metal Finishing 39, 33 (1962).
- 3-20 H. G. Feller, M. Festen, and J. Krupski, "Symposium on Third International Conference on Corrosion," edited by G. Okamoto, Tokyo (1972).

Section 3

TASK 1.0 METALLURGICAL STUDIES

(H. Chaung, M. H. Lee, J. B. Lumsden)

GENERAL OBJECTIVE

In this task both surface and grain boundary segregation are being measured as a function of temperature, time, and alloying. The correlation between the two types of segregation is being investigated so that relationships can be found which will eliminate the need to obtain intergranular fracture for grain boundary studies.

A second objective of this task is to identify those solutes which segregate or precipitate in grain boundaries causing an increase in susceptibility to stress corrosion cracking, corrosion fatigue, or intergranular corrosion. Ultimately relationships will be defined giving the amounts of these species in grain boundaries as a function of temperature, time, alloy composition, and alloy structure. This will permit a predictive capacity to be obtained. This understanding will lead to procedures which can be employed to eliminate intergranular failure.

PREVIOUS WORK

Much of the previous work has been concerned with investigating the changes in surface composition of nickel resulting from impurity segregation. This work has focused on sulfur, since it was found to be the most surface active and its presence on the surface catalyzed the anodic dissolution kinetics.

A relationship was found for the amount of segregated sulfur as a function of temperature and time. These investigations also showed that sulfur chemisorbed on the surface of nickel in monolayer concentrations. When the saturation coverage was attained, neither raising nor lowering of the temperature changed the surface concentration. A fast diffusion zone exists in the near surface layers in which diffusion coefficient is as much as three orders of magnitude greater than the bulk value. This region extends 50-75 μm below the surface. The consequence of this is that all the sulfur in this zone segregates to the surface in a matter of minutes when nickel is heated above 700°C. Thus, sulfur segregation cannot be prevented by using high purity alloys. This was demonstrated by using high purity nickel single crystals.

It was shown that segregated sulfur in the grain boundaries of nickel causes severe intergranular corrosion. Cadmium and carbon were also detected in the grain boundaries of nickel 200. Although carbon does not affect the stability of grain boundaries, the effects of cadmium are not clear.

CURRENT PROGRESS

Current progress under Task 1.0 is described in the following sections. The sections are organized according to the previous description of goals for this reporting period.

- o Grain boundary segregation in nickel.
- o Grain boundary in Inconel alloy 600.
- o Grain boundary segregation in 304 stainless steel.
- o Surface segregation on 4N Ni + 500 ppm Mn.

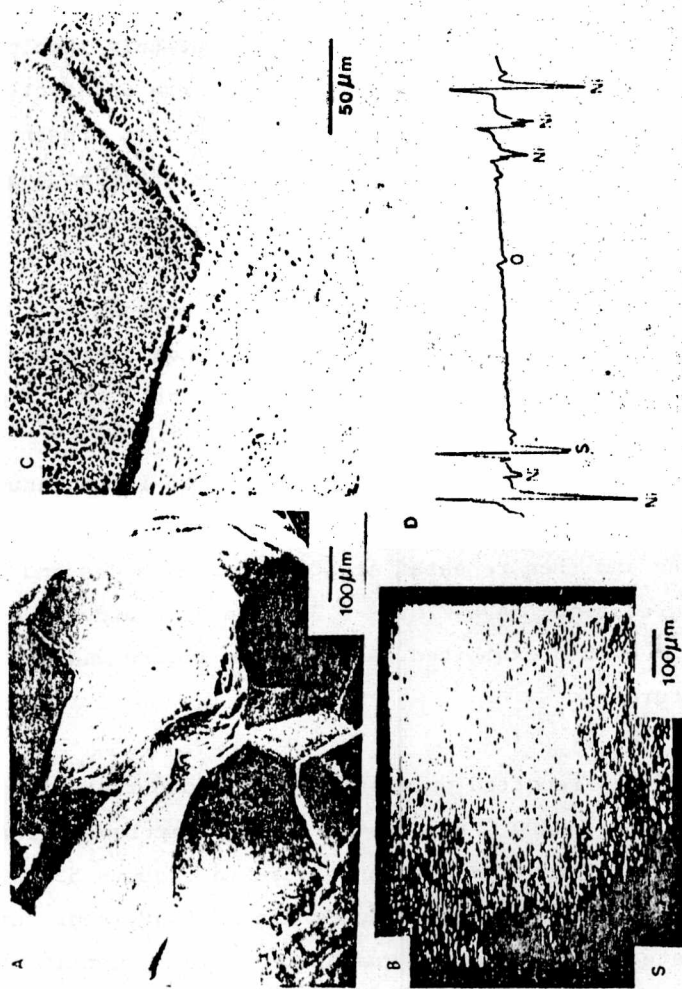
Grain Boundary Segregation in Nickel

In the following sections the results of our grain boundary composition studies are discussed. This work provides a fundamental understanding of the nature and extent of solute segregation in nickel and allows insights to the phenomena of solute segregation in commercial alloys. Some of the work on grain boundary segregation in Ni 200 has been previously reported. This report provides additional work and analysis of earlier results.

Experimental Details. The details of specimen preparation and the Auger electron spectroscopy techniques have been reported previously and will not be discussed here.

Test Results. Included herein is an outline of some representative results of grain boundary composition.

Sulfur Segregation. Figure 3.1 shows the scanning Auger results and scanning electron fractographs obtained from an intergranular fracture surface of Ni 200 which was solution annealed at 1250°C for 10 hours followed by water-quenching. Very prominent in the Auger spectrum besides the Ni peaks, is that of S. The normalized Auger peak height (NAPH) S/Ni is approximately 0.63. This value is approximately that obtained for segregated sulfur on a Ni single crystal surface after saturation coverage had been reached. The approximate atomic concentration of the saturated, segregated-sulfur has been estimated to be 33 at.%.



Nickel 200
Grain Boundary Composition
600°C 24 Hours
(After Growing Large
Grains at 1250°C 10 Hr)

Figure 3.1 Sulfur segregation in a Ni 200: (a) and (c) scanning electron micrographs; (b) sulfur surface; and (d) Auger spectrum of sulfur-enriched region on the fracture surface.

The left-bottom picture in Figure 3.1 shows the sulfur Auger image of the fracture surface which indicates the distribution of segregated sulfur. It should be noted that variations occurred in the NAPH S/Ni from area to area ($S/Ni \sim 0$ to 0.63). The sulfur decreased rapidly with depth during argon ion bombardment. This suggests that the segregated layer at the grain boundary is less than a monolayer which bears the same characteristic as that of surface segregation.

The SEM fractographs in Figure 3.1 give the fracture mode of this specimen. Grain boundary facets indicative of intergranular fracture are apparent. Dimples which are characteristics of a ductile fracture are also present. This shows that the fracture is still "ductile" but followed the grain boundaries. This phenomenon seems to be characteristic of "weak embrittlement."

Most of the specimens were heated in the temperature range between 500°C and 650°C, as shown in Figure 3.2. The experimental results to date are insufficient to assess quantitatively the trend of sulfur segregation.

Carbon Segregation. Figure 3.3 is the Auger spectrum from an intergranular fracture of Ni 200 which was also solution annealed at 1250°C for 10 hours followed by water quenching and then reheated at 500°C for 24 hours and water quenched. Only carbon segregation, NAPH C/Ni ~ 0.35 , was observed. The fracture surface of this specimen also exhibited, as shown in Figure 3.4, an intergranular dimpled rupture.

The surface segregation results reported previously have shown that carbon segregates with a maximum value, NAPH C/Ni ~ 0.45 , in the temperature range between 450°C and 550°C and no longer appears on the surface above 550°C. It seems that the results of surface segregation and grain boundary segregation for carbon tend to correlate with each other qualitatively and quantitatively.

Cadmium Segregation. It has been reported previously that cadmium was observed on the fracture surface of Ni 200. However, there has been no further observation of cadmium segregation in grain boundaries.

In the previous report it was also shown that cadmium segregated to the surface of a Ni single crystal, but it evaporated. The evaporated cadmium was detected

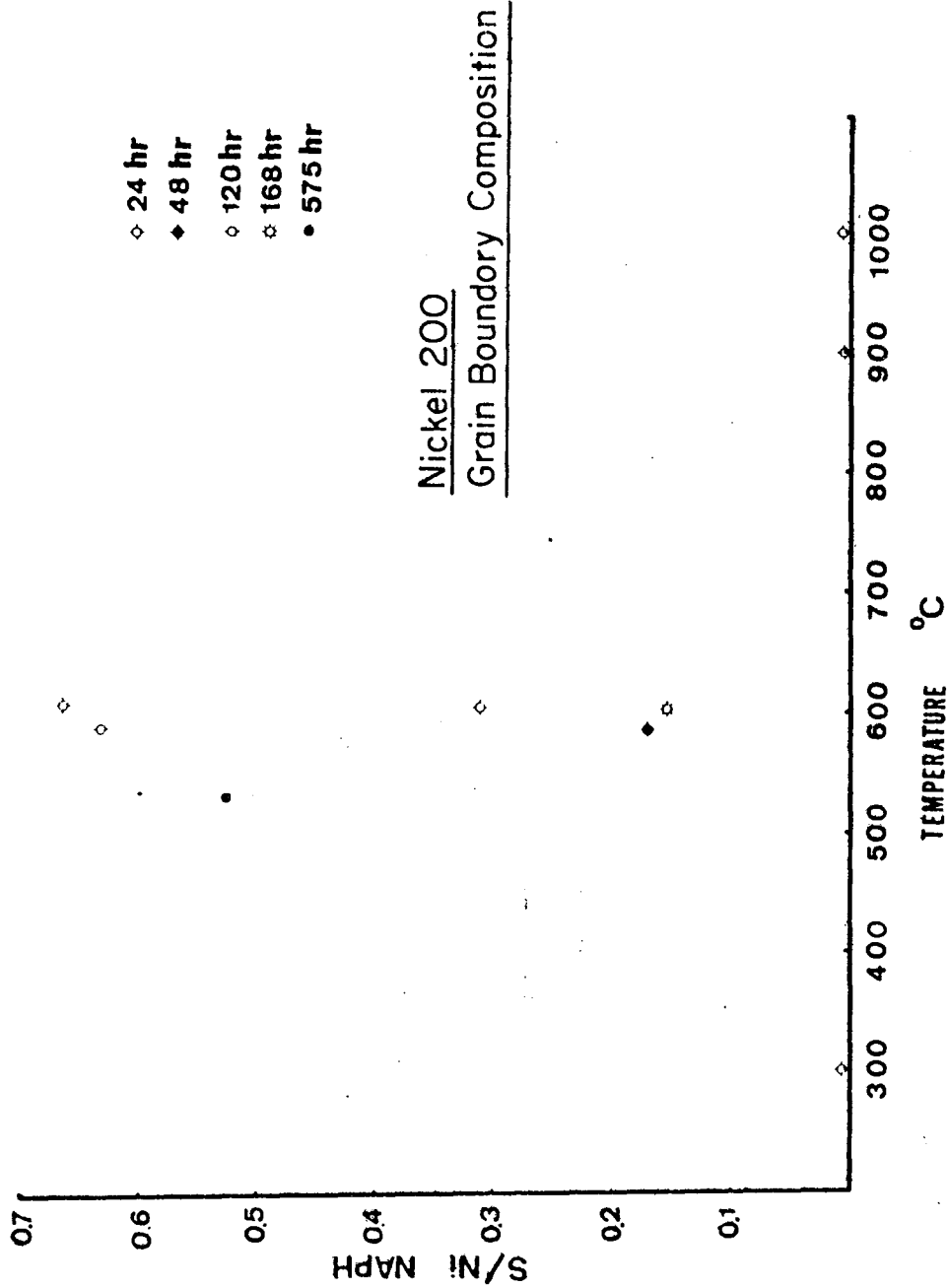


Figure 3.2 Sulfur segregation at grain boundaries of Ni 200 as a function of temperature.

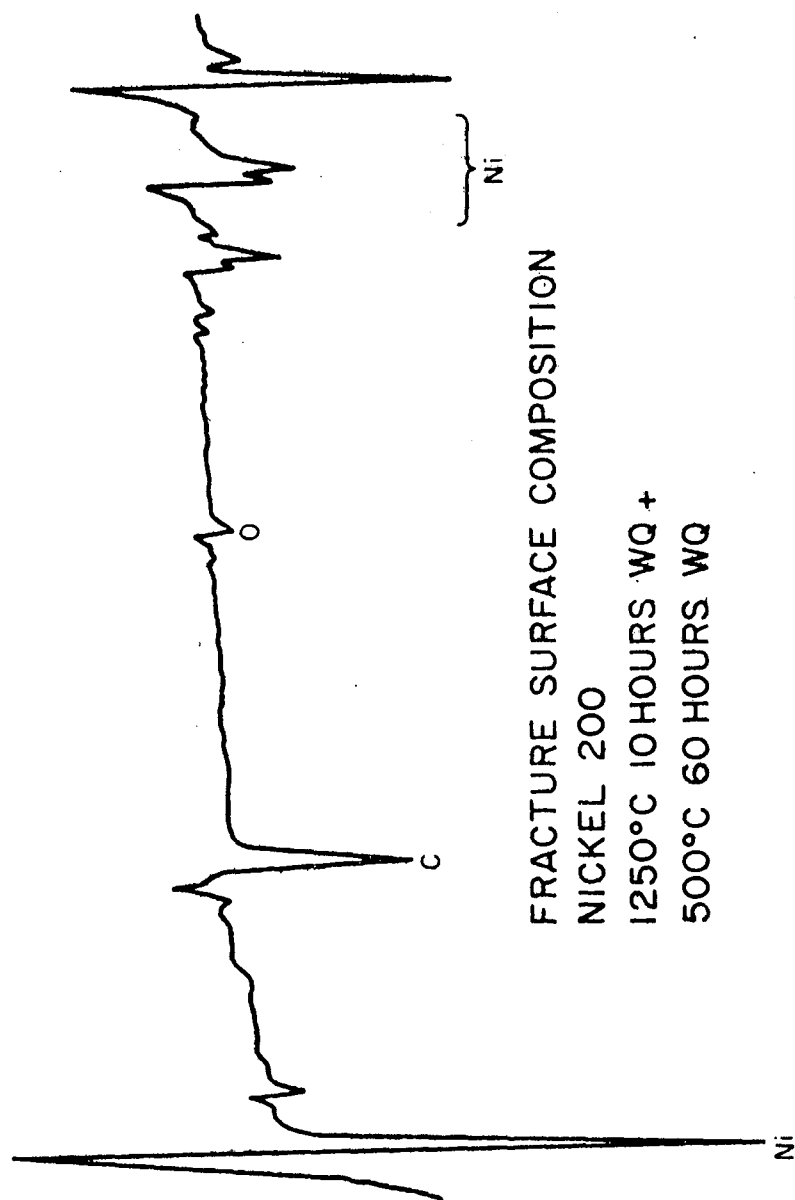


Figure 3.3 Representative Auger spectrum of the fracture of Ni 200 showing carbon segregation.

215

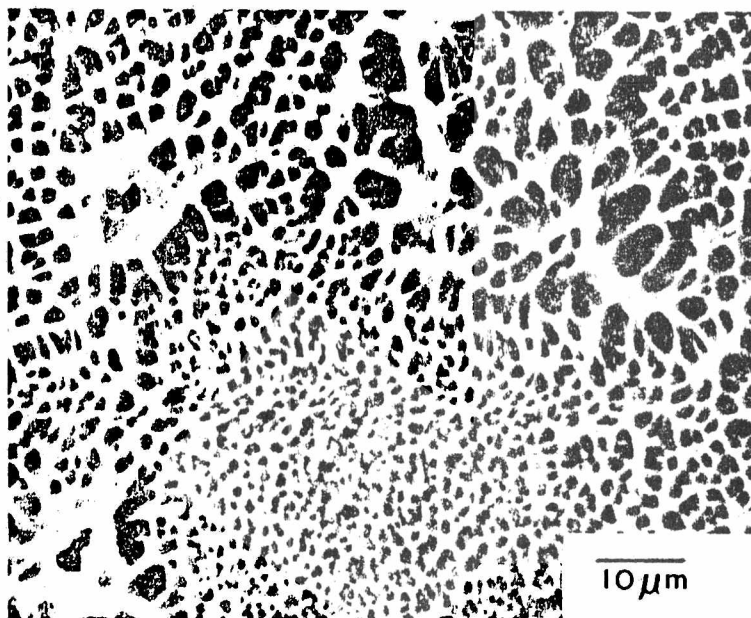
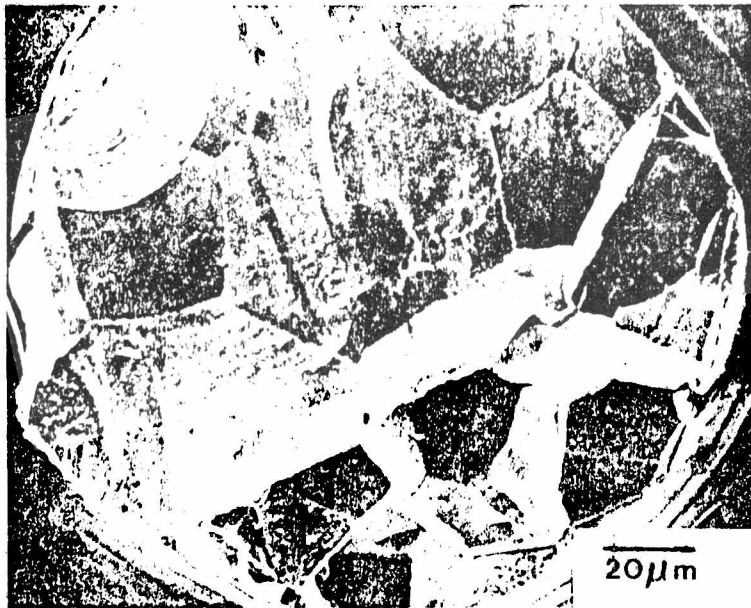


Figure 3.4 SEM Fractographs of Ni 200 with carbon segregation.

using a mass spectrometer. Figure 3.5 shows that cadmium does exist on the surface of Ni at low temperatures. This figure gives the surface composition of a Ni (111) face during cooling through the temperature range between 25°C and 75°C after two hours of heating at 650°C.

These results demonstrate conclusively that cadmium does segregate. However, the failure to detect it in the grain boundaries reproducibly suggests that its segregation kinetics are very complex possibly depending upon the annealing temperature, quench rate and site competition with other segregated species.

Boron and Nitrogen Segregation. Figure 3.6 is the fracture surface composition of nickel 200 which was heated at 1250°C for 10 hours followed by water quenching. It was then reheated at 600°C for 96 hours and water quenched. Small amounts of boron and nitrogen were observed on the fracture surface. The morphology of the fracture was the same as that shown in Figures 3.1 and 3.4.

The segregation of boron and nitrogen have also been found on the nickel single crystal surface during heating times longer than 5000 seconds at 650°C, (Figure 3.7). It is interesting to note that the presence of boron is always associated with that of nitrogen. The kinetics of boron and nitrogen segregation have not been studied.

Chlorine Segregation. The segregation of chlorine has also been observed on the fracture surface of nickel 200. The sample was solution annealed at 1350°C for 24 hours followed by water quenching. It was reheated at 550°C for 72 hours and water quenched. Figure 3.8 is an Auger spectrum showing chlorine segregation. The segregation of chlorine was accompanied by the segregation of sulfur. Under argon ion bombardment the segregated chlorine levels decreased rapidly with depth away from the fracture surface.

Effect of Boundary Migration. The accumulation of sulfur at grain boundaries may also occur as a result of the sweeping action of migrating boundaries during recrystallization (3-1). Auger analyses for the fracture surface of nickel 200 which was 30% cold-rolled followed by recrystallizing at 600°C for one hour revealed the segregation of sulfur and magnesium, as shown in Figure 3.9. The fractograph of this specimen is shown in Figure 3.10. It

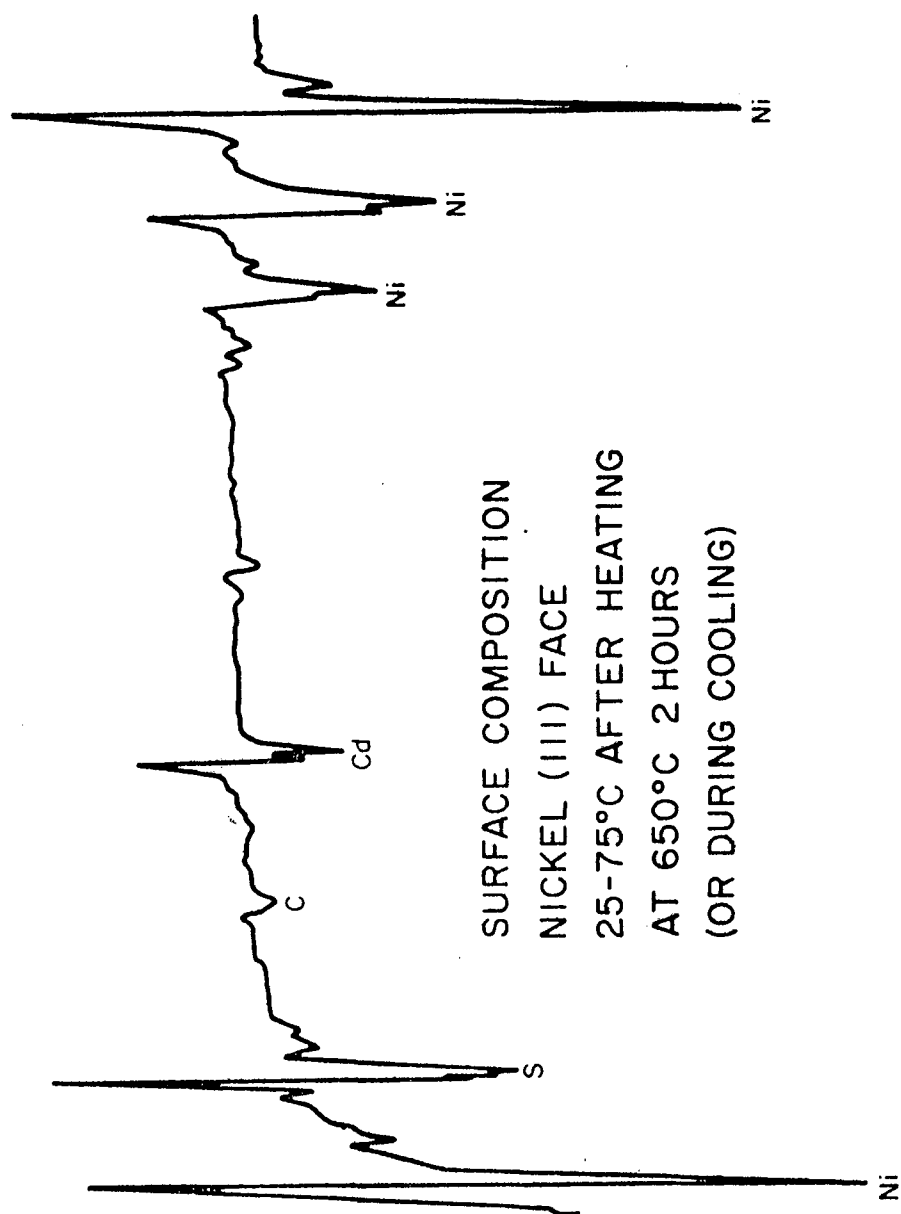


Figure 3.5 Representative Auger spectrum of the surface composition of a nickel (111) face during cooling after 2 hours of heating at 650°C.

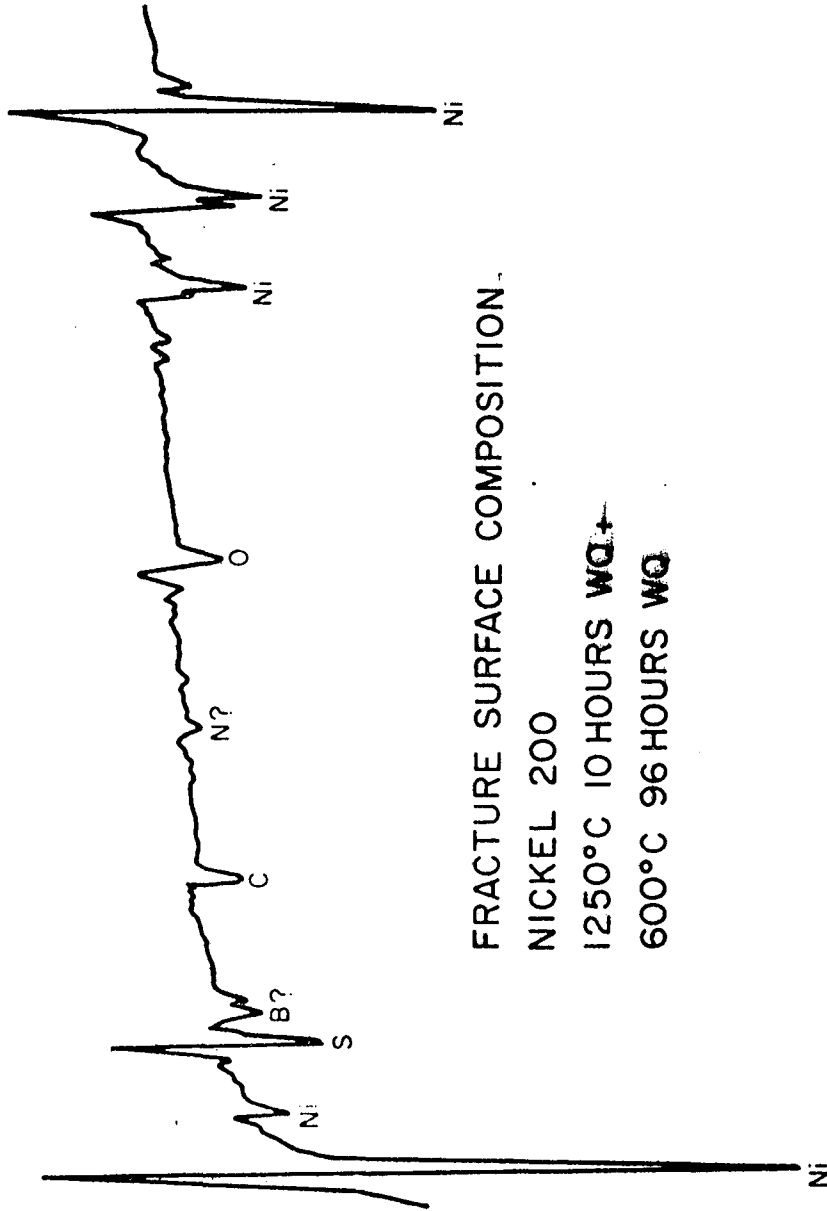


Figure 3.6 Fracture surface composition of Ni 200 showing boron and nitrogen segregation.

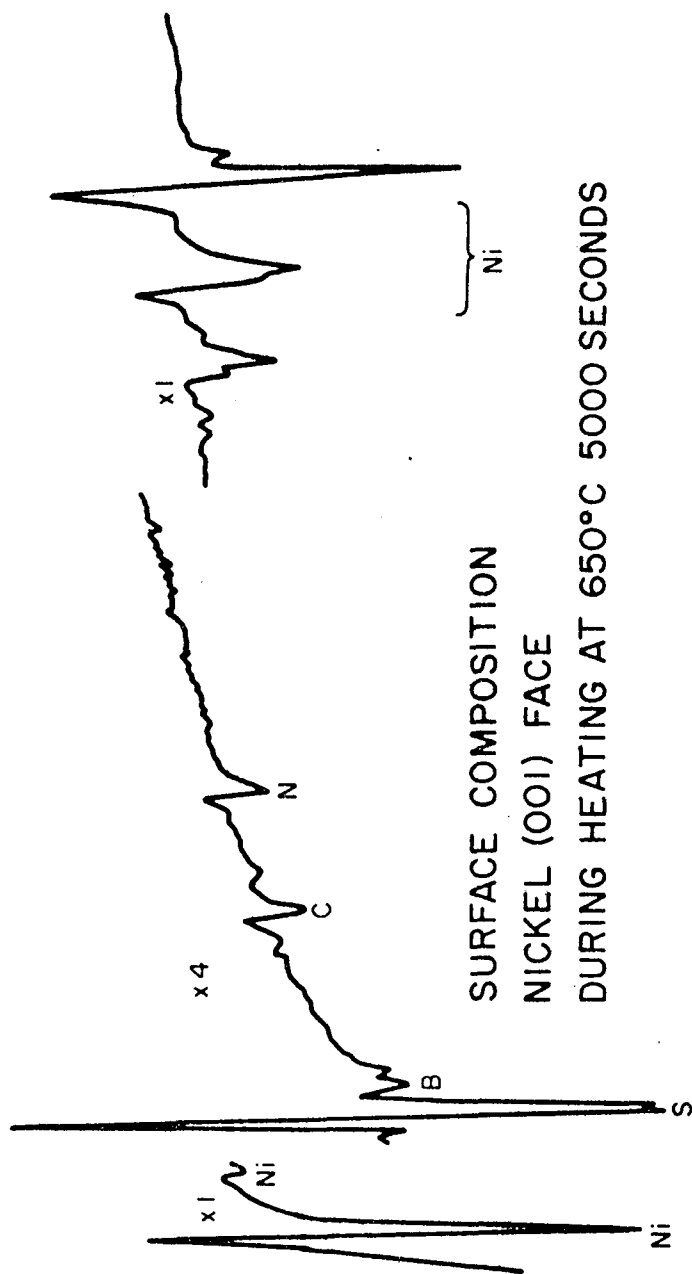


Figure 3.7 Surface composition of nickel (001) face showing boron and nitrogen segregation.

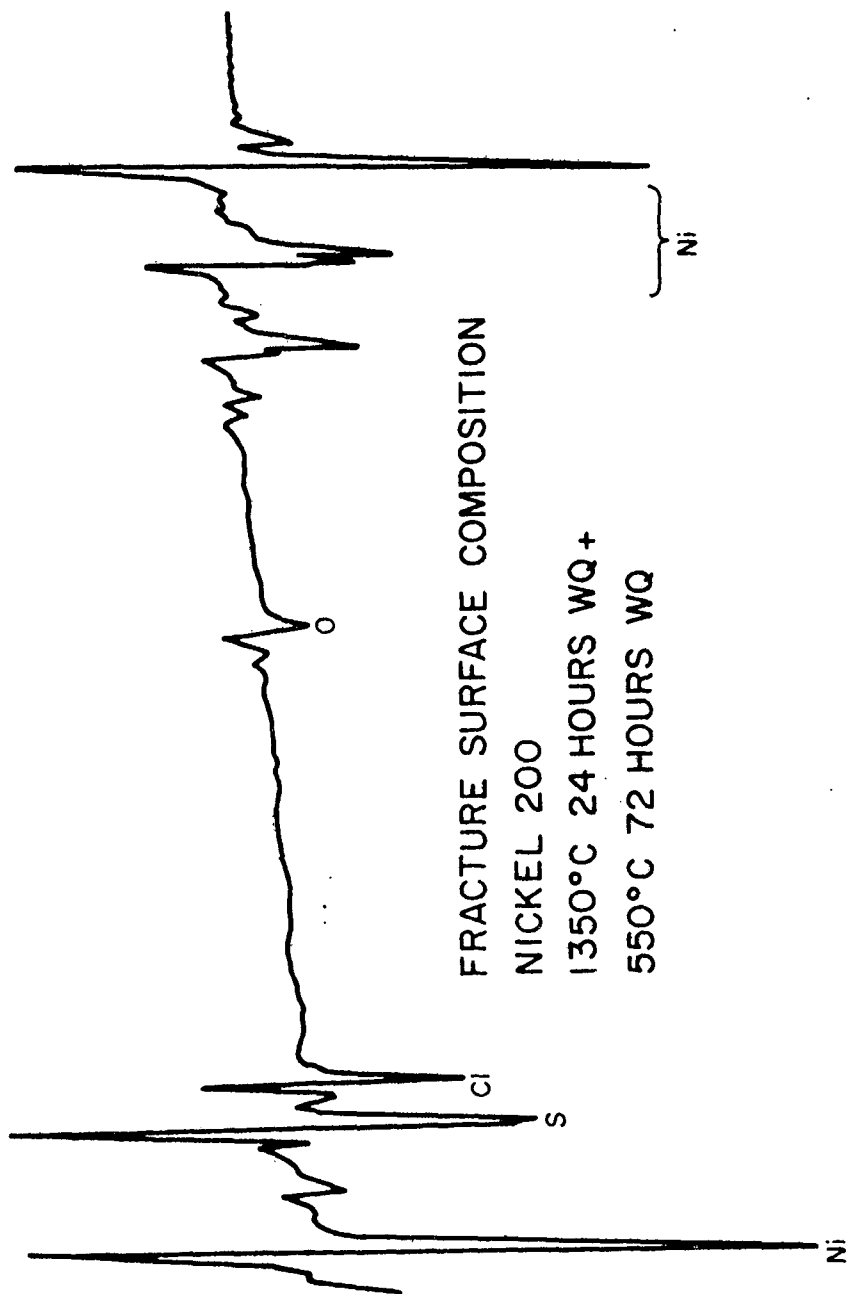


Figure 3.8 Fracture surface composition of Ni 200 showing chlorine segregation.

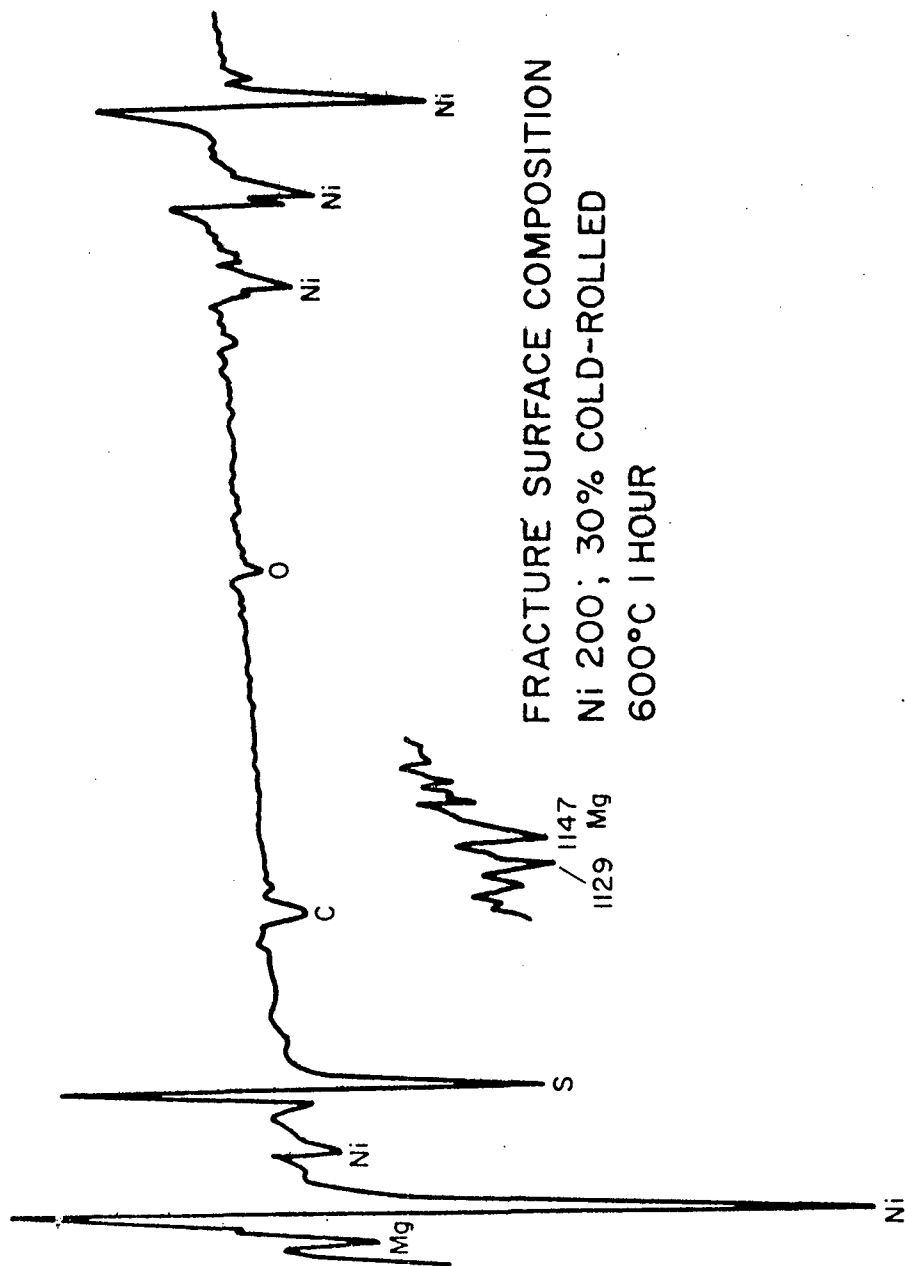


Figure 3.9 Representative Auger spectrum showing recrystallization effects on solute segregation in Ni 200.

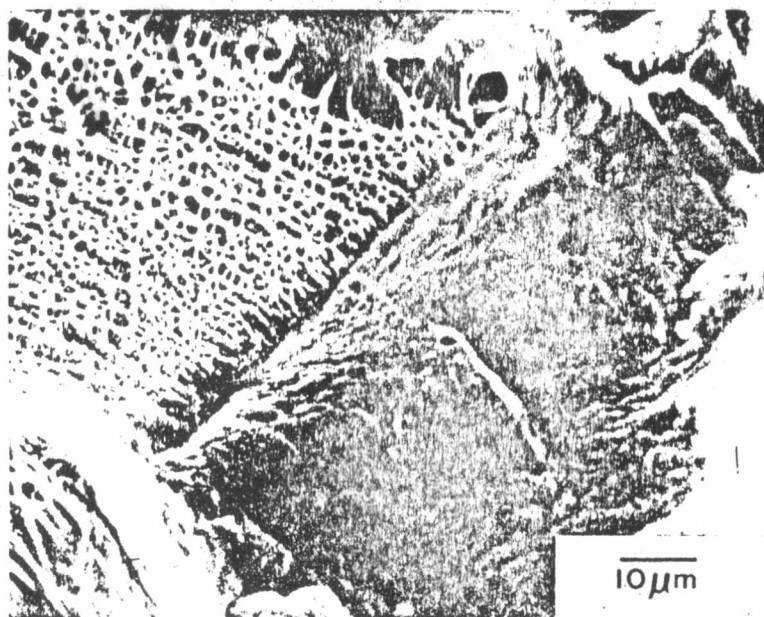


Figure 3.10 The SEM fractograph obtained from recrystallized Ni 200.

can be seen that two kinds of fracture modes are present. One exhibited the typical intergranular dimple rupture. The other was flat and contained large amounts of sulfur. The presence of Mg with S suggests that MgS has precipitated in the grain boundaries.

Segregation in "Embrittled" Nickel. Production of an intergranular surface of a face centered cubic material such as nickel in an ultrahigh vacuum condition by simple impact fracture (the experimental technique being used here) is not an easy task. To date, it has been only partially successful to obtain intergranular fracture. In all cases the fracture follows the grain boundary but the fracture surface has a dimple structure. The higher magnification of a SEM fractograph shows that second phase particles are contained within the dimples. Attempts to identify these particles using microprobe analysis have been unsuccessful. The particles are too small to be resolved by the scanning Auger.

The addition of an embrittling element such as a bismuth to the nickel can shift the intergranular dimpled rupture to a smooth intergranular fracture.

Figure 3.11 shows the representative Auger spectrum, Auger images, and SEM fractographs of nickel 200 which was doped with 100 ppm Bi and heated at 600°C for 24 hours followed by water quenching. Grain boundary facets indicative of intergranular fracture are apparent. The high magnification of the SEM fractograph indicates no dimples or second phase particles on the grain facets. Auger analysis shows a large segregation of sulfur and bismuth. The Auger map of sulfur indicates that the distribution of the segregated sulfur is not uniform.

DISCUSSION

The segregated species observed except cadmium are residual non-metals which have low solubility in nickel and differ in atomic size. The size difference contributes to the driving force for segregation. These elements may be present in nickel as impurities. There have been many investigations of the effects of sulfur on the properties of nickel, but the mechanisms and kinetics of sulfur segregation are not yet understood. In addition, segregation of cadmium, nitrogen, chlorine, and carbon are not well documented.

Summarizing the experimental results, sulfur is the primary specie which segregates to the grain boundaries and surface of Ni. This may be attributed to the very low solubility of sulfur (less than 10 ppm at room temperature), the large electronegativity difference between sulfur (2.44) and nickel (1.75), and the high strain due to the misfit of the sulfur atom in the regular nickel lattice (about 0.4 Å). Therefore, sulfur would tend to segregate onto the nickel surface or grain boundaries in order to minimize the free energy of the system (2) if sulfur atoms receive the necessary energy to overcome the activation energy for diffusion.

It was demonstrated in a previous report that the structure in the negative excursion of the S Auger peak is indicative of chemical bonding between S and Ni. This structure is observed both for sulfur segregated on a Ni surface and in the grain boundaries. This suggests that in both cases chemisorption and not physical adsorption occurs.

The largest value of $N_{\text{APH S/Ni}} \sim 0.65$ for grain boundary segregation is close to the $N_{\text{APH S/Ni}} (-0.66 \pm 0.05)$ for saturated surface segregation. This may

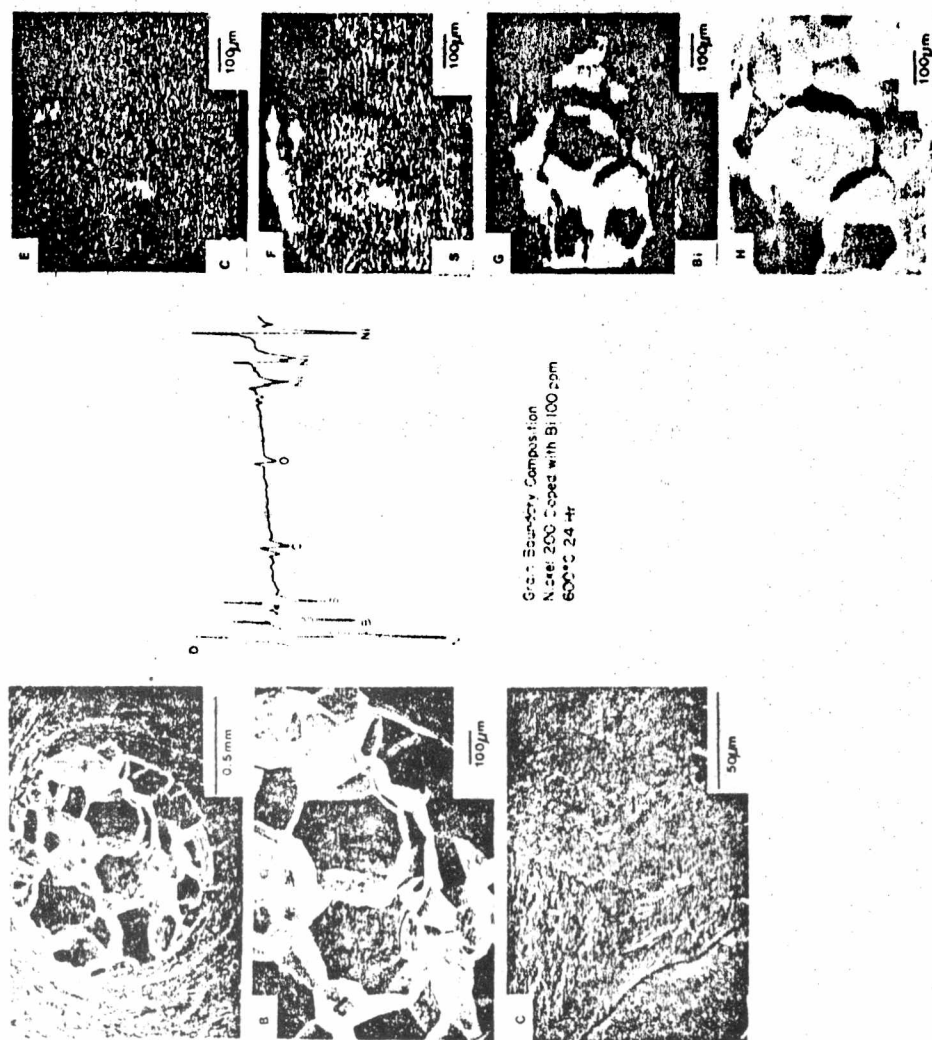


Figure 3.11 Grain boundary composition and fractographs of a Ni 200 doped with 100 ppm bismuth: (a) through (c) scanning electron micrographs; (d) Auger spectrum showing sulfur and bismuth segregation; (e) through (g) Auger images of C, S, and Bi, respectively; and (h) absorbed current micrographs of fracture surface.

imply that there is the same saturation limit for sulfur both on surface segregation and grain boundary segregation. However, most observed values for the NAPH S/Ni in grain boundaries are smaller than that of the saturation limit.

Considering the two main segregants (sulfur and carbon), sulfur sits on a substitutional site in the matrix, whereas carbon sits at an interstitial one. It is expected that the diffusion of carbon is more rapid than sulfur. Therefore, carbon levels are higher at low temperatures than those of sulfur. At high temperatures segregated C does not appear on the surface. It is not clear whether this is due to the influence of S or whether it is a property of the Ni-C system. The latter case will exist if the temperature is above that at which graphite precipitates. However, the results do indicate that sulfur can influence carbon segregation since carbon does not segregate after a saturation coverage of sulfur occurs.

The discussion of segregation of boron and nitrogen will be made in the section concerning the grain boundary segregation in Inconel alloy 600. The results to date are not sufficient to define the conditions under which cadmium and chlorine segregate.

Grain Boundary Segregation in Inconel 600

Experimental Details. The details of specimen preparation and the Auger electron spectroscopy technique have been given in an earlier report.

Test Results. Included herein is an outline of several representative results of grain boundary composition obtained from the fracture surface of Inconel 600.

Figure 3.12 shows the Auger spectrum and the SEM fractographs obtained from the fracture surface of a specimen which was heated at 1350°C for 2 hours followed by water-quenching and then re-heated at 600°C for 24 hours (or 72 hours) followed by water-quenching. The fracture surface exhibited a mixture of ductile and flat grain boundaries. The flat area is less than 20% of the total fracture surface of the specimen. This area had high concentrations of sulfur, nitrogen, titanium, phosphorus, carbon, and chromium enrichments. The

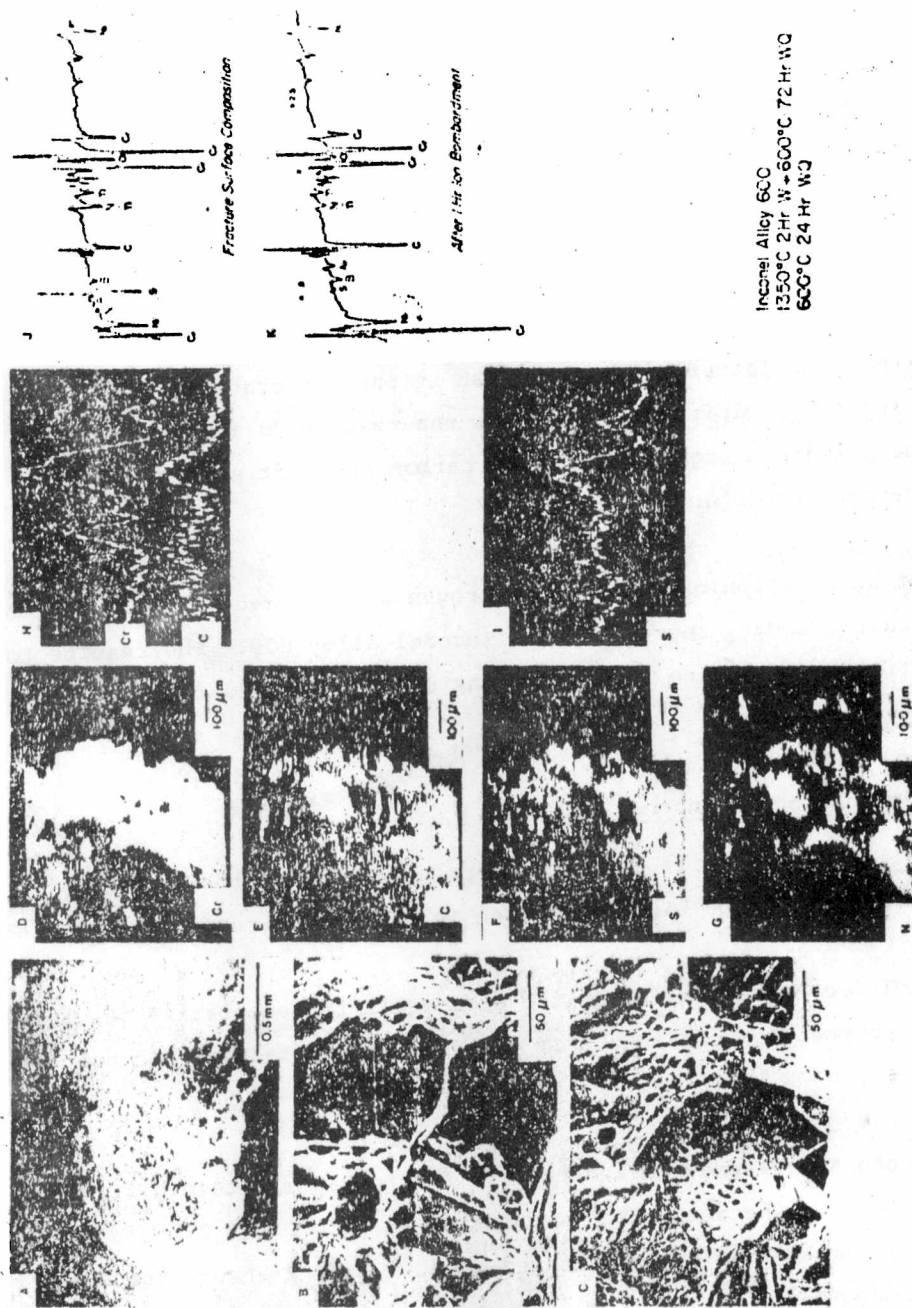


Figure 3.12 Grain boundary composition and fractographs of an Inconel 600 alloy: (a) through (c) scanning electron micrographs; (d) through (g) Auger images of Cr, C, S, and N, respectively; (h) and (i) line deflections of Cr, C, and S, respectively; (j) and (k) Auger spectra of fracture surface composition and after one hour ion-sputtering respectively.

variation in enrichment from area to area is likely due to the changes in fracture mode. The upper spectrum in Figure 3.12 is the representative Auger analysis showing the segregation of impurities and solutes. The most prominent peak is sulfur. However, chromium and carbon peaks become prominent after one hour of argon ion bombardment; this can be seen from the bottom Auger spectrum in Figure 3.12.

The depth-composition profiles of sulfur, carbon, and chromium are shown in Figure 3.13. Argon ion bombardment did not remove the segregated-sulfur as rapidly as in the case of sulfur segregation on nickel. It took longer than 10,000 seconds of ion bombardment to sputter off the segregated sulfur from the fracture surface. The segregated-carbon and -chromium levels increased as a function of ion-sputtering reached a maximum value and then decreased. Both maximum levels of carbon and chromium were at about 1,000 seconds of ion-sputtering. It is assumed that the high carbon and chromium is due to chromium carbide. From scanning Auger images as shown in Figure 3.12, the area showing high sulfur concentration has high chromium and carbon concentrations, but not vice versa.

Results have been obtained from several heat treatments: (1) 1350°C for 2 hours followed by water quenching and reheating at 600°C for 72 hours followed by air cooling; (2) at 1350°C for 2 hours (water quenched), (3) 1350°C for 2 hours, furnace cooled to 550°C for 350 hours; (4) 1050°C for 24 hours followed by water quenching and reheating at 600°C for 160 hours (water quenched) and (5) 1050°C for 24 hours followed by water quenching reheating at 600°C for 20 hours followed by water quenching. The amounts of segregation expressed in NAPH are shown in Figure 3.14. It can be seen that the specimen as quenched without further heating shows no significant segregation. In addition, the specimens preheated at 1350°C have higher segregation levels than those preheated at 1050°C.

Discussion. Interpretating the variation of grain boundary chemistry in Inconel alloy 600 should concern interaction between segregated impurities and trace (or minor alloying) elements at or near the grain boundaries. The possibilities of forming non-metallic inclusions such as carbides, sulfides, nitrides, borides, and oxides, or complexes should be considered.

Bieber and Decker (3-3) made a systematic study of the influence of trace elements and minor alloying additions in nickel and its alloys and classified

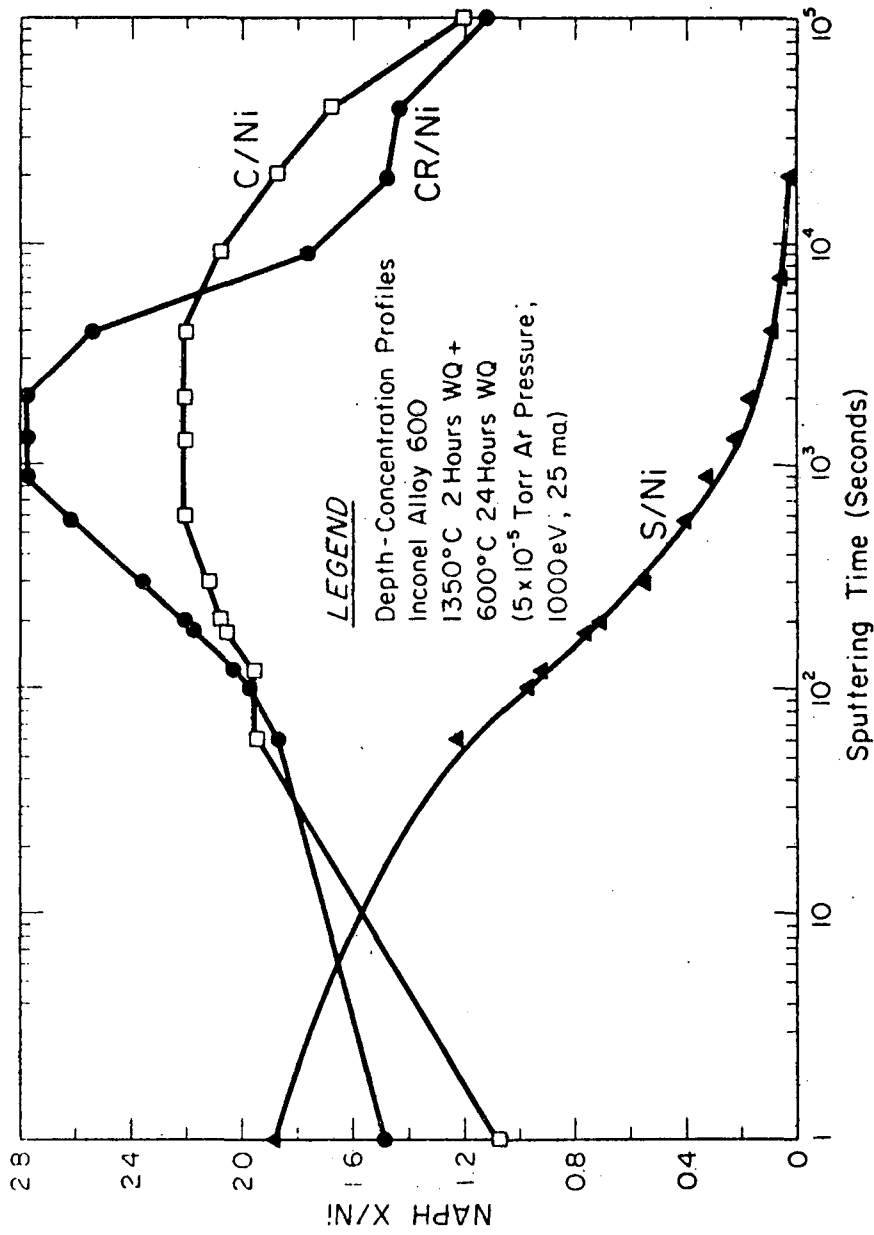


Figure 3.13 Depth composition profiles of segregated sulfur, carbon, and chromium of Inconel 600.

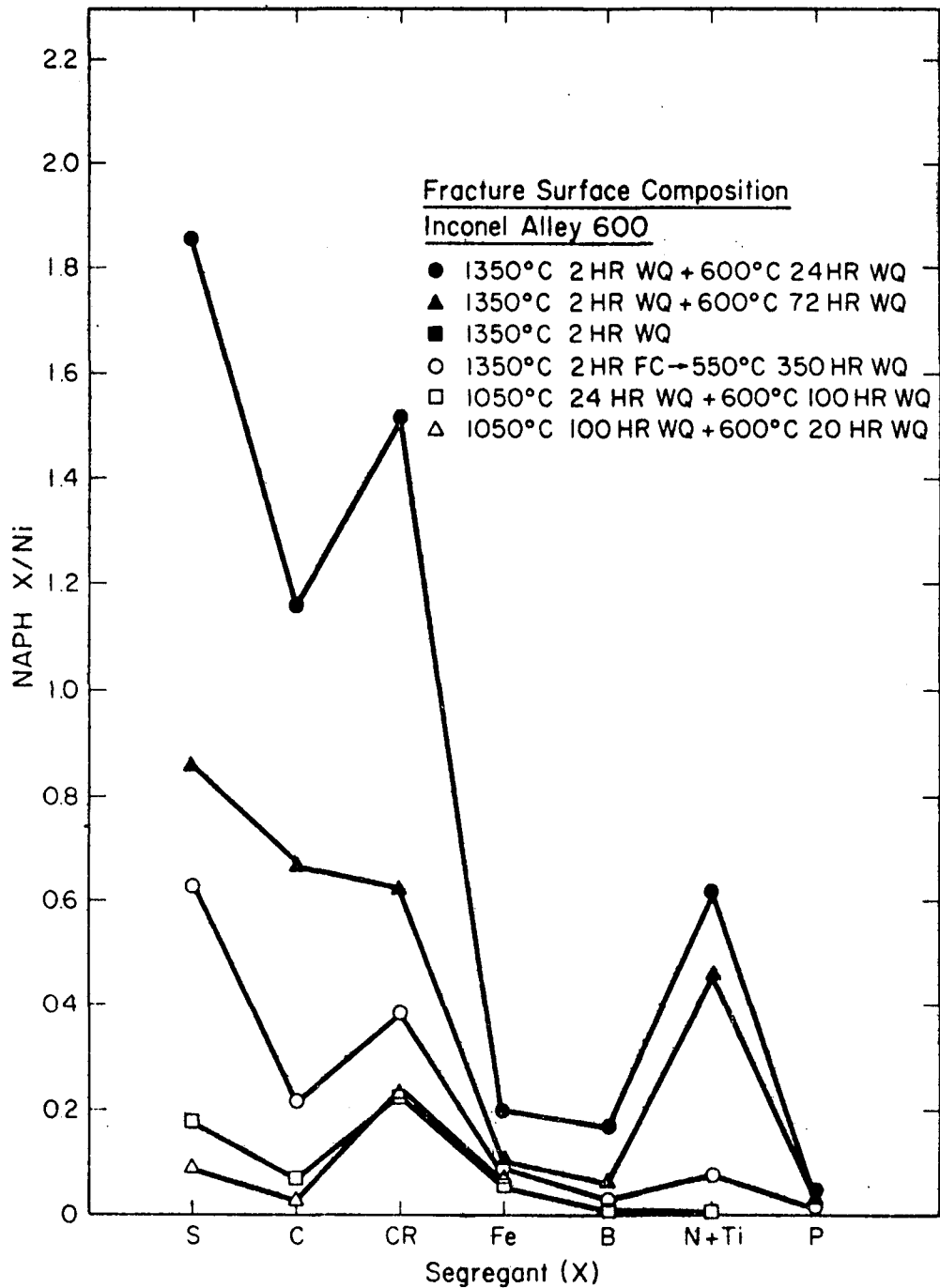


Figure 3.14 The fracture surface compositions of Inconel 600 at various heat treatments.

55 elements into three groups as detrimental elements, neutral elements, and beneficial elements. These trace elements and impurities may interact with each other depending on thermodynamic considerations and complex kinetic processes. More complicated interactions occur when more elements are present.

The segregation of sulfur at grain boundaries in Inconel alloy 600 may more or less bear the same characteristic as that in pure nickel. However, the fine structure observed in the negative excursions of the Auger peak from sulfur in the grain boundaries of nickel was not present in the spectra from that in the grain boundaries of Inconel 600. This suggests that the bonding is different, and thus the effects on the anodic dissolution kinetics may differ from those of nickel. Also, the AES ion sputtering profile (see Figure 3.13) shows that measurable amounts of sulfur levels extend far below the fracture surface (longer than 10,000 seconds of sputtering). Usually, in the pure nickel case, it took about 300 seconds to sputter off segregated sulfur from the fracture surface. This could imply that sulfur is associated with the formation of second phase chromium carbide.

The experimental results have shown that boron segregates to both surface and grain boundaries of Inconel alloy 600. Boron has a low solubility in nickel, iron, and austenitic steels, and so is expected to segregate to the available lattice defects in these materials. In the late 1950's it was realized that trace additions of boron and zirconium introduced to nickel base alloys substantially improve their hot-working behavior and creep-rupture properties (3-4). Boron is a beneficial element in small amounts but harmful in larger additions. Evidence for boron segregation to grain boundaries in a nickel base alloy by secondary ion mass spectrometry has been found by Walsh and Kear (3-5). They observed that many of the intergranular regions contained massive Cr-rich M_3B_2 boride particles. In our AES results, the boron Auger peak has shifted from 168 eV to 179 eV before and after ion bombardment. It suggests that boron may form a boride at the grain boundaries. This phenomenon has also been found for some cases in pure nickel.

Nitrogen was also found in the grain boundaries of Inconel 600. The solubility of nitrogen in nickel is small (~ less than 10 ppm). Therefore, it is not surprising that nitrogen segregates to the grain boundaries and surfaces of nickel alloys. Nitrogen is considered detrimental to malleability even in

small additions. It is known (3-6, 3-7) that nitrogen will react with titanium to form brittle TiN particles which may act as nuclei for the precipitation of MC carbides and some nitrogen may displace carbon in carbide to form carbonitrides. From the AES results, it can be seen that the nitrogen and Ti peaks are present in the spectrum after one hour of ion sputtering. This may indicate that particles of TiN form at the grain boundaries.

A small phosphorus peak has been observed in the Auger spectrum obtained from the fracture surface. The solubility of phosphorus in nickel is small (about 0.32%) but higher than that of sulfur in nickel (about 10 ppm). This is why sulfur segregation is more prominent than phosphorus segregation. No information has been documented on possible interactions between phosphorus and alloying elements. Phosphorus is detrimental in larger additions to some properties of Inconel alloy 600. Vermilyea et al. (3-8) have shown that additions of phosphorus to Inconel 600 type alloys cause susceptibility to intergranular attack in strongly oxidizing media. This intergranular attack was believed to be associated with segregation of phosphorus to grain boundaries. In addition, the deleterious effect of phosphorus in acid solution has been rationalized (3-9) on the basis of an increase in the effective number of grain boundary carbide precipitates and the activity of pre-existing corrosion paths. From the previous report, it can be seen that vacuum heating of Inconel alloy 600 results in surface layers rich in sulfur and phosphorus. The results showed site competition between segregated sulfur and phosphorus. This has not been observed in grain boundary segregation.

Carbon plays a major role in the segregation process. Very prominent in the Auger spectrum from the fracture surface besides the Cr, Ni, and S peaks, is that of C at approximately 272 eV. An examination of the ion sputtering profile suggests that carbon must be present in the form of carbides instead of graphite. High carbon levels are always associated with unusually high chromium enrichment before and after ion bombardment. Accordingly, precipitation of the chromium-rich carbide ($M_{23}C_6$) probably occurred along the grain boundaries when the specimen was sensitized. The nature and extent of the interaction between the precipitation of carbides and the presence of segregated impurities is a challenging problem. The results to date are insufficient to make any further discussion.

Grain Boundary Segregation of 304 Stainless Steel

Intergranular attack is a principal mode of failure for austenitic stainless steel. Although solute segregation or the depletion of alloying elements at grain boundaries is thought to be a contributing cause, no direct evidence is presently available to correlate between susceptibility to intergranular attack and grain boundary composition. The main difficulty is due to the lack of a suitable technique for studying grain boundary chemistry.

Test Results

Figure 3.15 shows the Auger spectrum and SEM fractographs obtained from the fracture surface of a 304 stainless steel which was heated at 1400°C for 24 hours followed by water quenching and sensitizing at 600°C for 24 hours (water quenched). The fracture surface of the specimen exhibited a mixture of ductile and flat grain boundaries. The amount of flat boundaries is approximately 30% of the total surface area. Three different types of chemical compositions were observed. One area exhibited a strong sulfur segregation. Some areas appeared high in carbon associated with segregated phosphorus. The rest of the surface did not show any significant enrichment. The microstructure of this specimen is that of a two-phase material. The sample was magnetic indicating the second phase as δ . Two different sets of segregation may be attributed to two kinds of boundaries--sulfur segregation to γ - γ boundary and phosphorus and carbon segregation to the γ - δ boundary. Figure 3.16 shows the Auger spectrum obtained from a fracture surface of 304 stainless steel which was heated at 1250°C for 44 hours followed by water quenching. In addition to sulfur, nickel enrichment was observed. The fracture mode of this specimen was like that of the previous specimen. It is interesting to note that nickel enrichment disappeared when the specimen was re-heated at 600°C for one hour and water quenched.

TASK 1.0 CONCLUSIONS

The metallurgical studies of solute segregation have shown that (1) evidence for surface segregation and grain boundary segregation in nickel, Inconel alloy 600, and 304 stainless steel has been developed using Auger electron spectroscopy. (2) Sulfur exhibits strong and prominent segregation to surface and grain boundaries in nickel, Inconel alloy 600, and 304 stainless steel when the bulk concentration is as low as a trace. The sulfur segregation bears chemisorption behavior. (3) Table 3.1 shows details of some of

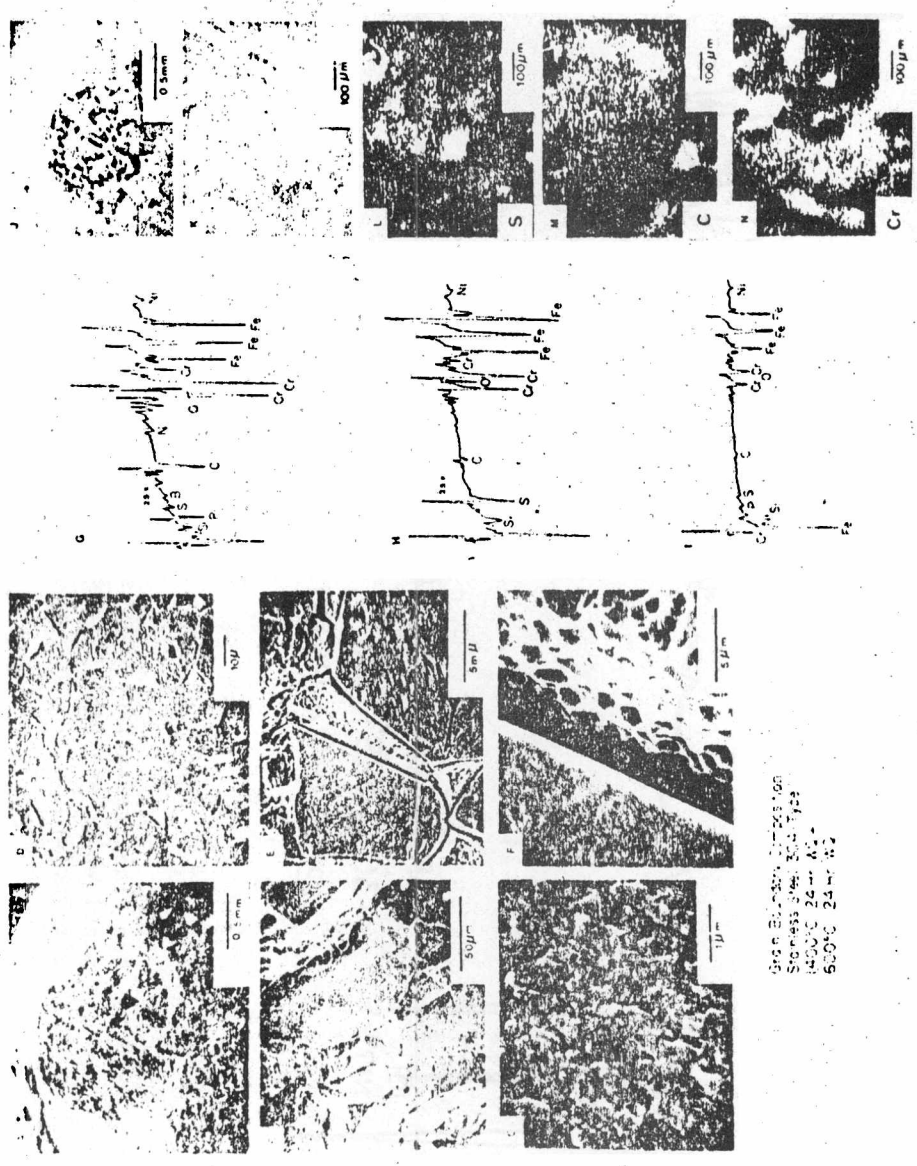


Figure 3.15 Grain boundary composition and fractographs of a stainless steel 304-type: (a) through (c) scanning electron micrographs; (d) through (f) metallographs; (g) through (i) Auger spectra showing representative composition of fracture surface from selected areas; (j) and (k) absorbed current micrographs of fracture surface; and (l) through (n) Auger images of S, C, and Cr, respectively.

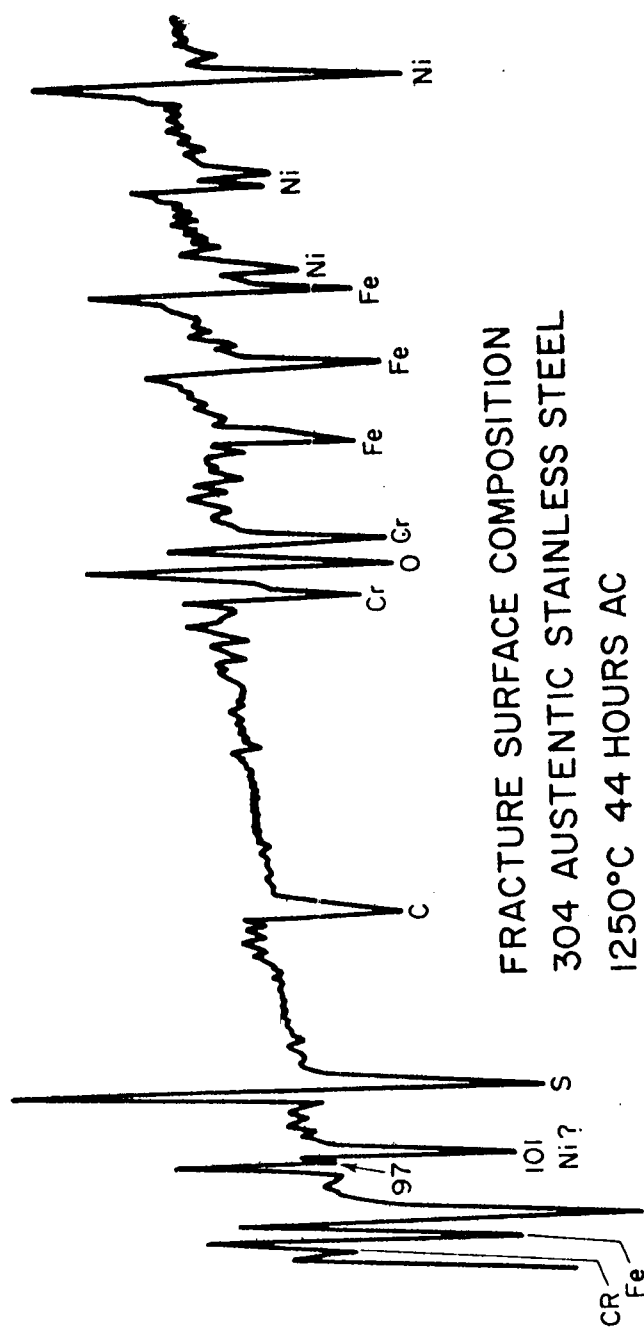


Figure 3.16 The fracture surface composition of a 304 austenitic stainless steel which was heat treated at 1250°C for 44 hours followed by air cooling.

the results. These results show that at least surface segregation can be used to predict grain boundary segregation qualitatively. The same elements which segregated to the surface were found at grain boundaries. (4) Quantitative correlation should exist between surface segregation and grain boundary segregation since the same theoretical expressions apply for both. However, the results to date are insufficient to correlate each other. (5) Exposing smoother grain boundaries can be made by techniques such as doping with embrittling elements or introduction of pre-cracked specimens. More work of optimizing procedures for exposing grain boundaries of face centered cubic alloys will be searched.

REFERENCES

- 3-1 K. M. Olsen, C. F. Larkin, and P. H. Schmitt, Jr., Trans ASM 53, 349 (1961).
- 3-2 D. McLean, "Grain Boundaries in Metals," p. 116, Oxford University Press, London (1955).
- 3-3 C. G. Bieher and R. F. Decker, Trans. AIME 221, 629 (1961).
- 3-4 R. F. Decker and J. W. Freeman, Trans. TUS-AIME 218, 277 (1960).
- 3-5 J. M. Walsh and B. H. Kear, Met Trans 6A, 226 (1975).
- 3-6 A. Taylor and K. Sachs, Nature 169, 411 (1952).
- 3-7 S. T. Wlodek, Trans ASM 57, 110 (1964).
- 3-8 D. A. Vermilyea, Corrosion 3, 222 (1975).
- 3-9 A. R. McIlree, H. T. Michels, and P. E. Morris, Corrosion 31, 441 (1975).

Chemical Instrumentation

...a



feature

Edited by GALEN W. EWING, Seton Hall University, So. Orange, N. J. 07079

These articles are intended to serve the readers of THIS JOURNAL by calling attention to new developments in the theory, design, or availability of chemical laboratory instrumentation, or by presenting useful insights and explanations of topics that are of practical importance to those who use, or teach the use of, modern instrumentation and instrumental techniques. The editor invites correspondence from prospective contributors.

LXX. Electron Spectroscopy Instrumentation (Concluded)

Claudio A. Lucchosi and Joseph E. Lester, Department of Chemistry, Northwestern University, Evanston, Illinois 60201

SPECTROMETERS

The purpose of this section is to summarize and to compare the main design features of electron spectrometer systems which are currently commercially available in the United States. The essential components of an electron spectrometer system are shown in the schematic diagram of Figure 1. A comparison of the functions of the components used to make up the six commercial instruments is given in Table 2. The performance specifications of the spectrometers are listed in Table 1.* The information cited is based upon the manufacturer's literature and upon written

and verbal consultations with company scientists and engineers. The tables only contain data for those features and accessories actually deliverable to users as of January, 1973. No value judgments of the spectrometer systems are intended since valid judgments can be made only after extended testing of each instrument under the intended use conditions of the prospective purchaser. Furthermore, new developments are occurring so rapidly that certain comparisons may not be valid for long. Additional detailed information about a given instrument may be obtained by contacting the manufacturers listed at the end of this article. Photographs of commercial spectrometers are shown in Figures 8 through 13.

Source. The ideal source would be a monochromatic source of variable wave-

length with high power output at an energy of at least 900 eV so that one would be able to excite the 1s shells of the second row elements. This energy also is sufficient to excite at least one inner shell of all the heavier elements. The simplest compromise between power and monochromaticity is the use of a characteristic x-ray emission line of one of the lighter elements. The $K\alpha$ doublet of magnesium or aluminum has been chosen by the instrument builders because these lines have reasonably narrow composite linewidths of 0.75 eV and 0.95 eV, respectively (18). As pointed out previously these linewidths are adequate for most chemical studies. The $K\alpha$ lines of the heavier elements have considerably larger halfwidths (for example, Cu $K\alpha$ FWHM $\sim$ 2.6 eV, Mo $K\alpha$ FWHM $\sim$ 6 eV) which makes them unattractive for chemical shift measurements. The heavy element $K\alpha$ lines can be useful for the production of Auger electrons since higher power is available when heavy metal targets are used and since the photon linewidth is not related to the Auger linewidth. Of course, the linewidth of any x-ray source can be improved at the expense of intensity by suitable monochromatization.

The basic x-ray source consists of a heated filament at -5 to -20 kV and an Al or Mg water-cooled anode at ground potential. The geometry of the target varies from instrument to instrument. The AEI ES100 (Figure 4) and McPherson ESCA 36 use a planar anode at a small take-off angle to the target direction. This geometry results in a high intensity line source when viewed from the sample position. In the AEI ES200 the filament is at ground potential and the anode is at a high positive potential. This arrangement reduces scattering of electrons at the anode. In the

Table 1. System Performance Specifications^a

	Element	Sensitivity Parameters					Sensitivity (cps/%)	Resolution ^b (eV)	Peak Position	
		Peak Intensity (counts/sec)	FWHM (eV)	Power ^c (watts)	S/B	S/N			Accuracy (eV)	Reproducibility (eV)
AEI ES 200	Au 4f	140,000	1.30	500	11	350	1300	0.86	0.1	0.05
	Ag 3d	25,000	0.90	500	12	500	230			
	C 1s	40,000	1.0	500	70	500 (20 sec/eV)	390			
DuPont 650	Au 4f	300,000	1.20	350	7	2500 (20 sec/eV)	2600	0.9	0.1	0.05
	Ag 3d	100,000	1.15	350	8	1250 (20 sec/eV)	---	---	---	---
	C 1s	60,000	1.15	350	10	1250 (20 sec/eV)	---	---	---	---
Hewlett-Packard ESCA-5950A	Au 4f ^e	120,000	0.8	400 (Al)	120	---	1200	---	---	---
	Ag 3d	26,000	0.87	750 (Al)	33	---	250	---	---	---
	C 1s	12,000	0.8	800 (Al)	200	1500	120	0.57	0.1	0.03
McPherson ESCA-36	Au 4f	75,000	1.35	750	14	350	700	---	---	---
	Ag 3d	18,700	0.88	750	19	270	180	0.88	0.04	0.015
	C 1s	14,500	1.0	1000	53	470 (22 sec/eV)	140	---	---	---
Vacuum Generators, Ltd. ESCA-2	Au 4f	30,000	2.36	500 (Al)	na	na	---	---	---	---
	Ag 3d	na ^d	---	---	---	---	---	---	---	---
	C 1s	10,000	1.83	500 (Al)	na	na	---	1.0	0.1	0.05
Varian VIER-15	Au 4f	1,000,000	1.6	2600	7	na	8800	0.9	0.1	0.03
	Ag 3d	24,000	0.88	2400	13	na	220			
	C 1s	11,700	1.0	1000	17	na	110			

Data obtained from manufacturers; ^b Best reported system resolution; ^c X-ray power with magnesium target except where indicated to be ^d Not available; ^e Known to be cleaned by Ar⁺ bombardment; ^f For silicon 2p doublet.

(Continued on page A270)

237 Chemical Instrumentation

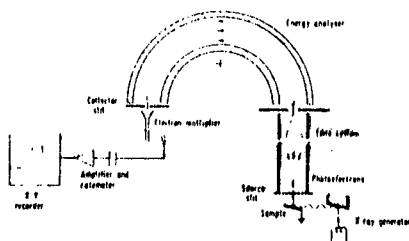


Figure 4. Schematic diagram of the AEI ES100 Spectrometer.

Du Pont and Varian instruments an annular target surrounding the sample (which in these cases is a disc and a cylinder, respectively) is used. With this geometry these manufacturers achieve a larger x-ray target area and higher photon flux at the sample surface. This is one reason for the considerably higher counting rates exhibited by these instruments.

In all five of the above instruments the x-ray target and the sample are separated by a thin aluminum or beryllium window. This window serves to exclude electrons scattered from the x-ray target from the sample chamber. In the case of an aluminum window and an aluminum target, the window effectively filters the $K\beta$ line and the background radiation without significantly attenuating the $K\alpha$ doublet. However, the aluminum window, when used with other x-ray targets, will produce undesired photoelectron lines excited by the Al $K\alpha$ x-rays from the aluminum window.

The vacuum requirements of the x-ray source are not stringent—a pressure of less than 10^{-5} torr is adequate if hydrocarbon vapors which produce target contamination are excluded. Another target contaminant is tungsten from the filament; thus, tube geometries in which the anode is not in a direct line with the filament may extend the operating time between shut-downs for target cleaning.

The Hewlett Packard 5950A spectrometer (shown schematically in Figure 5) produces an x-ray source with an effective line width of less than 0.5 eV by dispersing the Al $K\alpha_{1,2}$ x-rays on a Rowland circle via a bent crystal diffraction "grating." The $K\alpha$ line is spatially dispersed across the target so that the photoelectrons ejected from a level in the sample have different kinetic energies depending on the posi-

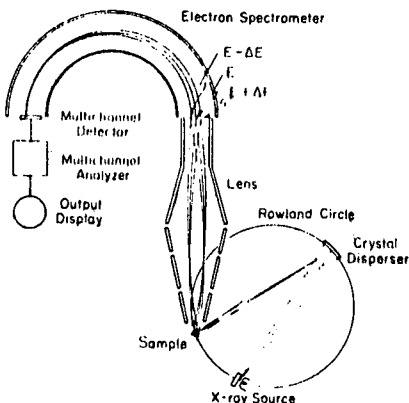


Figure 5. Schematic diagram of the Hewlett-Packard Spectrometer.

tion across the sample from which they originated. In the lens system and energy analyzer this dispersion results in all photoelectrons from one level being focused on the same line at the exit plane of the analyzer. (The theory of this system is discussed in Ref. 1, Appendix 10 for a magnetic energy analyzer and in Ref. 19 for an electrostatic energy analyzer.) In addition to compensating for the intrinsic source linewidth, the dispersed source also significantly reduces the background in the spectrum since the Bremsstrahlung photoelectrons and the $K\alpha_{3,4}$ satellite lines are eliminated. For studies of many chemical systems this feature of the dispersed source may be more important than the reduced linewidth since one should have lower detection limits with the improved signal-to-background. It can be advantageous to have a source of small linewidth if an element exists in several oxidation states in a sample and it is desired to extract the binding energies of each of these oxidation states. (AEI has announced as an accessory for their spectrometers a monochromatized x-ray source. Preliminary performance data for an ES200 equipped with this source are as follows for a gold sample: $I_p = 60,000$ cps at FWHM of 0.8 eV and at an x-ray power of 1500 watts. The S/B for this sample was 75. The system resolution is reported to be 0.5 eV.)

If only outer shell excitation is desired, then the ultraviolet resonance lines of helium at 21.2 or 40.8 eV and linewidths of less than 0.01 eV may be used. Recently, other sources such as monochromatized cyclotron radiation ($E < 100$ eV) (20) and rare earth M lines (21) having small half-widths have been used as valence shell excitation sources. Electron guns are frequently used as excitation sources for Auger electron analysis (6) since high intensities of electrons of several kilovolts energy are easily produced and since the energy of exciting radiation does not affect the Auger electron energy. It is important to have at least two alternate x-ray sources in order to distinguish photoelectron peaks from Auger peaks. When a different x-ray energy is used the photoelectron peaks shift in kinetic energy but the kinetic energies of Auger peaks are constant.

Sample and Sample Chamber. Solid, liquid, and gaseous samples can be studied by ESCA. However, the practical restriction that the sample have a low vapor pressure makes the study of solids most convenient, and consequently, liquids (and gases) generally are examined after freezing. It is possible, of course, to vaporize the liquid and to study it as a vapor if a differentially pumped cell is used. The reason for the low vapor pressure restriction is the requirement that the sample chamber vacuum be of the order of 10^{-5} torr (or better) in order to eliminate scattering of the emitted electrons. In those cases where very clean sample surfaces are necessary, the residual gases in the sample chamber must be about four orders of magnitude lower in pressure.

In addition to the low vapor pressure requirement, solid samples should be chemically stable in the spectrometer and

(Continued on page A271)

should be in electrical equilibrium with the spectrometer. For many studies it is essential to lower the sample temperature to minimize possible changes in the sample when it is exposed to high vacuum and/or to exciting radiation. Study of radiation-sensitive materials by ESCA requires special care. The sample temperature is controlled by use of a variable temperature sample probe with which the temperature may be varied from liquid nitrogen temperatures (-190°C) to about $+250^{\circ}\text{C}$. The exact temperature ranges of the probes provided with each spectrometer are shown in Table 2. Probes which go to higher temperatures are available as accessories.

Solids are most conveniently handled as flat pieces with the dimensions given in Table 2. Very frequently, however, solids are received for examination in pulverized form; in this case 10 to 15 mg. of sample is adequate. The pulverized material may be pressed into a disc, spread onto a metallic backing (such as an abraded aluminum plate), or dusted onto conducting tape (such as double-sided adhesive tape). In all of these sampling techniques, it is essential that the sample be in good electrical equilibrium with the spectrometer so that the Fermi levels of the two coincide and Equation 1 holds. Samples that are electrical insulators may become positively charged during irradiation with x-rays because electrons are being emitted. This increase in surface potential is called the "charging effect" and can lead to apparent binding energy shifts of many volts. In most spectrometers, however, a sufficiently large number of secondary (background) electrons are present in the sample chamber to stabilize surface charge at a small value. Furthermore, "radiation damage" during irradiation of the sample may increase electrical conductivity sufficiently to provide charge transport through the sample.

The "charging problem" has been accentuated in the Hewlett-Packard ESCA 5950A due to the use of a dispersed x-ray source. Because of this source there is a significant reduction in the number of secondary electrons in the sample chamber which normally serve to neutralize the surface charge. In a recent paper, it was reported that the Hewlett-Packard sample-charging is being controlled by use of an electron gun in the sample chamber (22). In cases where the charging effect cannot be eliminated (for example, in thick insulating samples), it is important to find a reference line for which the shift due to the charging is identical with that of the line under study. If there is no internal reference element, an external standard must be found. This may be accomplished by mixing the sample with a suitable reference standard or by *in situ* deposition of some reference material (such as gold) on the sample. Dianis and Lester (23) and Swartz *et al.* (24) have discussed this problem.

Sample accessibility and versatility are important considerations in the use of an electron spectrometer. All of the commercial instruments except the McPherson

ESCA-36 have at least three access ports either in the sample chamber or in a sample pre-treatment chamber. The McPherson system, however, is unique in that it has a large modular sample inlet system which can accommodate odd-shaped samples up to 27 cubic inches in size. The sample chamber routinely holds an eight-position sample wheel which can be controlled manually or automatically. All of the spectrometers except the Du Pont 650 and the Vacuum Generators ESCA-2 have multiple sample capability as may be seen in Table 2.

A means for cleaning or chemically modifying the sample prior to obtaining a spectrum without exposure to air between treatment and examination may be vital in the study of many chemical systems. As shown in Table 2, pretreatment chambers are available for four of the six instruments listed. In the AEI and McPherson spectrometers sample preparation is done directly in the sample chamber. Common accessories for sample treatment include ion bombardment guns for cleaning the surface of solid samples, evaporators for deposition of metals on sample surfaces, and gas-handling systems for *in situ* sample treatment. The availability of these accessories is indicated in Table 2.

The vacuum system in the sample chamber should be designed to produce high vacuum without contamination of the sample. If the sample chamber also is used for sample treatment, then the sample chamber, the analyzer and the source should be separately pumped and isolatable from each other. If a sample pretreatment chamber is used then it is only necessary that it be separately pumped. Separate pumping of the sample pretreatment region removes some restrictions on the gases that may be used in the chemical modification of a sample surface. If one wants to produce and maintain atomically clean sample surfaces, then it is necessary that the partial pressure of any reactive residual gas be less than 10^{-9} or 10^{-10} torr in any of the regions to which the sample is exposed; i.e., ultra-high vacuum conditions must be maintained. At 10^{-9} torr pressure of reactive gas the sample surface may be covered with a monolayer of contaminant in 15 minutes. In actuality it is not the pressure of the gas but the flux of reactant (molecules per cm^2 per sec) impinging on the sample surface that is critical. Therefore, care must be taken in the choice of materials from which the sample chamber is constructed if clean surfaces are to be examined. A system can exhibit quite low pressures and still contaminate samples because high outgassing rates of the chamber walls are compensated for by high pumping speeds.

Several types of pumping systems are compatible with clean surface studies; each has its own advantages and disadvantages. The most common ultra-high vacuum (UHV) pumps are titanium sputter-ion pumps which are used by Hewlett-Packard and Varian. The advantage of these pumps is the absence of pump fluids; the disadvantage is the low gas throughput. McPherson uses a turbomolecular pump in its standard pumping system, and combines this with a cryopump

Chemical Instrumentation

in its UHV package. This combination yields extremely high pumping speeds and low sample chamber pressures. It is claimed that clean surfaces maintain their integrity for hours in this system. AEI, Du Pont and Vacuum Generators use the more conventional diffusion pumps. One does have the possibility of pump oil contamination in these systems, but properly designed liquid-nitrogen-cooled cold traps should eliminate this problem. AEI has reported sample chamber pressures as low as 10^{-11} torr in the ES200 spectrometer. The advantage of diffusion pumps is their high gas throughput which makes them particularly attractive for studies involving gas treatment of the sample. At present, Du Pont does not offer UHV capability for their spectrometer. In general, the suitability of a particular type of pumping system depends on the kinds of studies envisioned by the experimenter. Most of the studies of chemical compounds done to date have been done in vacuum systems only capable of about 10^{-7} torr.

Electron Energy Analyzer. The heart of any electron spectrometer is the energy (or momentum) analyzer. One wants an analyzer with both high resolving power and high transmission. A number of different types of electron energy analyzers are suitable for ESCA spectrometers: (a) uniform field magnetic sector; (b) double focusing magnetic sector [first described by Siegbahn (25)]; (c) double focusing hemispher-

ical electrostatic analyzer (26); (d) cylindrical electrostatic (27); (e) cylindrical mirror (28, 29); (f) electrostatic non-dispersive energy filters (30, 31, 32).

Reviews of the theory of several of these analyzers are given by Siegbahn (1) and Sevier (17). Although the first spectrometer used for ESCA had a magnetic momentum analyzer, all commercial spectrometers currently available contain electrostatic energy analyzers. The reason for choosing the electrostatic analyzer over the magnetic analyzer lies in the difficulty of reducing stray magnetic fields to acceptable levels (ca. 10^{-4} gauss) in a magnetic analyzer since three sets of mutually perpendicular Helmholtz coils must be used. For an electrostatic analyzer magnetic shielding may be used and the size and complexity of the stray field cancellation devices is considerably reduced. Another restriction on the environment of the analyzer is that the pressure must be less than 10^{-5} torr in order to minimize electron scattering from the theoretical trajectories by residual gas molecules. Since the vacuum requirements in the sample region are the most stringent, any of the pumping alternatives adopted for that portion of the spectrometer will suffice in the analyzer.

Since all but one of the commercial instruments utilize a double focusing electrostatic analyzer (shown schematically in Fig. 6), some of its properties are discussed in detail. The electrostatic field is radial. If the radius and potential of the inner and outer spheres are a , V_a and b , V_b , re-

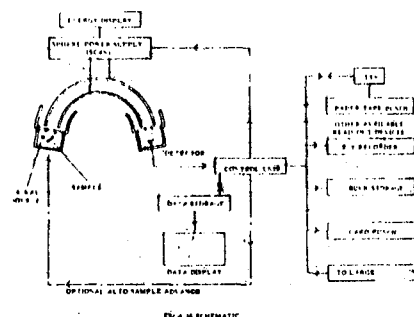


Figure 6. Schematic diagram of the McPherson ESCA 36 Spectrometer with some data handling options.

spectively, then the field ($\mathcal{E}$) is given by:

$$\mathcal{E} = (V_b - V_a)ab/[r^2(b - a)] \quad (5)$$

The solution of the equation of motion in this field for a 180° sector is of the form (17):

$$r_0/r_{180} = \{2Er(1 + \alpha^2)/Er_0\} - 1 \quad (9)$$

where E is the energy of the electron traversing the median radius, $r = (a + b)/2$, r_0 is the entrance radius and r_{180} is the exit radius of an electron of energy E . There is a reciprocal relationship between transmission and resolution in this analyzer. The resolving power, R , is given by:

$$1/R = \text{FWHM}/E = \Delta E/E = W/2r + \alpha^2/4 \quad (10)$$

where W is the width of both the entrance and exit slits (presumed equal) and α is the analyzer acceptance angle. For an analyzer of mean radius $r = 30$ cm, R of 1000 can be obtained for $W \sim 0.36$ mm and $\alpha \sim 2^\circ$. Siegbahn (1) reported a transmission of 0.29% for this R at an electron energy, E , of 1000 eV.

The McPherson ESCA 36 (Figure 6) contains an analyzer which is essentially identical to the 36 cm analyzer described by Siegbahn (1). Electron trajectories are defined by entrance and exit slits and a baffle which limits the acceptance angle. The instrument may be operated with a resolving power of $E/\Delta E = 5000$ at energies up to 4000 eV. This analyzer is conceptually the simplest commercial analyzer, but it must be of large dimensions in order to obtain adequate sensitivity at useful resolution values.

Since the important quantity in an ESCA experiment is the FWHM and not R , one can see from Equation 10 that lowering the electron energy, E , would allow one to operate at lower R but higher transmission. Several manufacturers have adopted this approach--AEI, Hewlett-Packard, Vacuum Generators, and Varian. In all of these instruments the electrons leaving the sample are retarded so that they enter the analyzer at some lower energy. Thus, the desired value of the FWHM can be obtained at a lower value of R . Therefore, a smaller monochromator or wider slits can be used. Although the retarding lens magnifies the source image at the entrance to the analyzer, the resulting intensity loss may be more than compensated for by the higher transmission through the analyzer. The first three instruments use a retarding lens and a hemispherical analyzer. The Varian analyzer (33) is of cylindrical symmetry best described as two concentric spheres with solid segments removed along the axis. In this geometry electrons of all azimuthal angles are accepted.

The Hewlett-Packard spectrometer is unique in that the retarding lens-analyzer system has been designed for the dispersed x-ray source described above (19). The complete system is shown in Figure 5. X-rays are dispersed across the sample with the higher energies closer to the center of the analyzer. Thus, the photoelectrons ejected from an energy level have energies that depend on the position on the sample from which they originate. The retarding lens performs two functions. It retards the electrons to an energy of approximately 115 eV; and it reimages the electrons leaving the sample with a magnification of about five, with the higher energy electrons at larger analyzer radii. In order to accomplish these functions, the sample surface must be inclined by a calculated angle with respect to the entrance plane of the analyzer. The higher energy electrons have trajectories with larger values of r than the lower energy electrons. By properly matching the dispersion of the x-ray optics with the retarding lens potentials and the analyzer dispersion, all of the electrons from one binding energy in the sample are imaged at a single radius at the exit focal plane of the spectrometer. Therefore, the contribution of the x-ray

Chemical Instrumentation

241

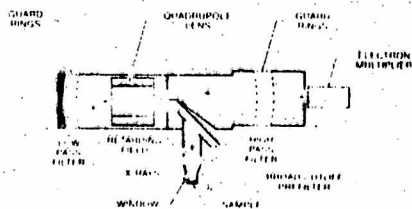


Figure 7. Schematic diagram of the Du Pont Spectrometer.

source to the observed linewidth can be significantly reduced. Theoretically the contribution can be made zero, but aberrations in the x-ray dispersing crystals and in the lens lead to an estimated linewidth contribution of from 0.2 to 0.3 eV. One other feature of this system is that it oper-

ates simultaneously at maximum resolution and maximum sensitivity since there is no entrance slit to the analyzer.

The Du Pont instrument does not use a dispersive analyzer. Instead the analyzer shown in Figure 7 is composed of an electron mirror which reflects electrons of energies less than some fixed value E_1 (≤ 70 eV) and a high pass filter which only passes electrons of energies greater than some higher fixed value E_2 (≥ 70 eV). Tracing the path of electrons through the spectrometer, one sees that photoelectrons ejected from the sample are retarded and enter a low resolution "pre-filter" (low resolution parallel plate analyzer) which deflects the electrons of a chosen energy range through an aperture toward the low-pass filter. Those electrons of energies less than E_1 are reflected and imaged on an aperture in the center of the analyzer tube. Those of higher energies strike the mirror

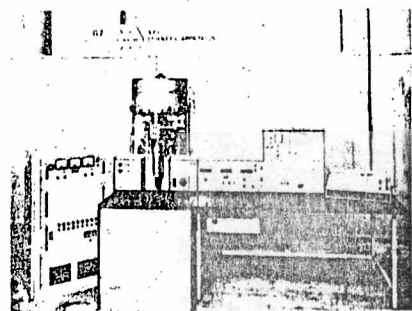


Figure 8. Photograph of AEI ES100 Electron Spectrometer.

surface and are either absorbed or scattered out of the main path. A quadrupole lens aids in alignment of the beam of reflected electrons on the aperture. Those electrons passing through the aperture encounter a high-pass electron filter set at a voltage V_2 , corresponding to energy E_2 slightly lower than E_1 . Those electrons of energy greater than E_2 pass through the filter and are detected. The resolution of the analyzer is determined by the difference between E_1 and E_2 and by the shape of the transmission function of the mirror and filter. A system resolution of better than 1 eV for energies up to 1200 eV has been obtained. The real advantage of this analyzer scheme is that the acceptance angle is large ($\sim \pi/25$ steradians) and that the filter transmission function improves as the acceptance angle is increased. From the specifications in Table 1 the only apparent disadvantage is a high spectrum background.

An explanation of one entry in Table 2 is possibly necessary. By "scan mode" is denoted the set of instrument potentials that are varied in order to bring photoelectrons of different energies into focus on the detector. "Retarding voltage" implies that the potential(s) of the retarding lens(es) are varied in order to scan electron energies. "Hemisphere voltages" imply that the potentials on the inner and outer spheres of the analyzer itself are varied.

Detectors. The electrons that traverse the analyzer are detected in the AEI, Du Pont, McPherson, and Vacuum Generators

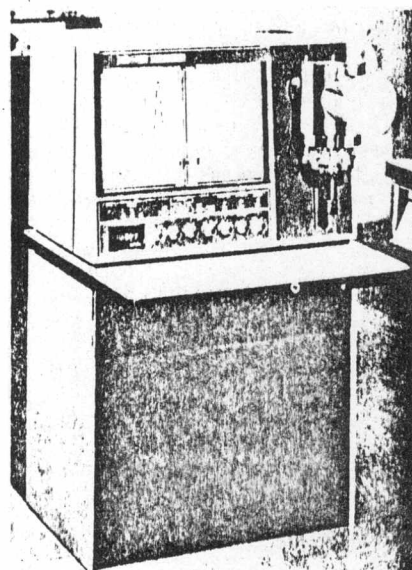


Figure 9. Photograph of Du Pont 650 Electron Spectrometer.

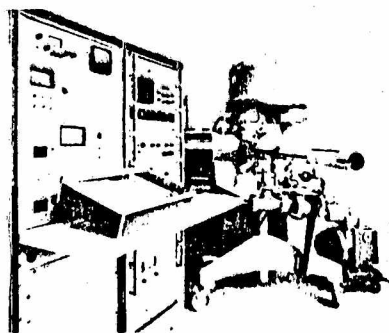


Figure 10. Photograph of Hewlett-Packard 5950A spectrometer system.

spectrometers by channel electron multipliers. In the Varian instrument the electron multiplier is a discrete dynode multiplier. In all of these instruments the electrons leaving the analyzer exit slit (or filter) are amplified by the electron multiplier with a gain of 10^6 to 10^8 . The resulting pulses are fed into an amplifier and pulse-height discriminator and then into a counter, computer or ratemeter. In the Hewlett-Packard spectrometer the detector is an array of channel multipliers called a Channelplate which is placed at the exit image plane of the analyzer. Impingement of an electron on one of the channels of the array results in a pulse of electrons exiting from that channel and striking a phosphor screen mounted on a glass plate in the vacuum system. The light pulses emitted by this screen are detected by a vidicon tube (television camera) outside the window. The position of

the light pulse on the array corresponds to a known electron kinetic energy and detection of a light pulse results in a count being stored in the channel of a multi-channel scaler corresponding to that energy. The use of this parallel detector with which electrons of energies over approximately a 10 eV energy range can be simultaneously detected is necessary because of the low x-ray intensity striking the sample in this instrument. Since there are approximately 150 channels across an energy range of 10 eV, the contribution of the detector aperture to the observed line-width is negligible. However, the simultaneous counting reduces the data acquisition time by a factor equal to the number of channels in which counts may be simultaneously stored.

Data Acquisition and Presentation. There are two basic data acquisition and/or presentation modes in the commercial spectrometers— analog or digital. In an analog system the pulses from the discriminator go to a ratemeter which drives the Y-axis of an X-Y recorder. The X-axis is driven by the analyzer voltage generator. Thus, a spectrum of counting rate versus kinetic energy is produced directly. The operator has control over the usual parameters: scan magnitude, scan speed, full-scale count rate and time constant. As shown in Table 2, this type of display is the normal mode of operation for the AEL, Du Pont and Vacuum Generators spectrometers.

In the digital systems the pulses from the discriminator go to a channel in either a computer memory or a multichannel an-

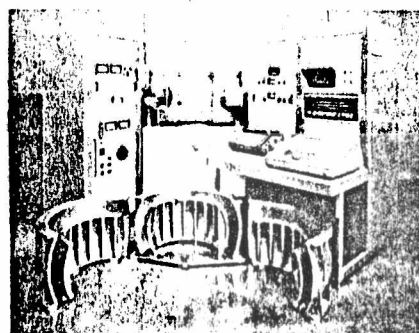


Figure 11. Photograph of McPherson ESCA-36 with three analyzer assemblies in the foreground.

alyzer. The channel is selected on the basis of the analyzer voltage. The contents of the memory are then recalled when the operator wants to observe the spectrum. Hewlett-Packard, McPherson and Varian have this mode as their normal mode of operation. In the Hewlett-Packard spectrometer the storage device is a multi-channel scaler. The scan amplitude, number of channels used, and dwell time per channel are the important parameters in this type of data acquisition system. In the McPherson and Varian instruments the storage device is a mini computer which also controls the spectrometer functions. In these three spectrometers the spectrum is displayed on a CRT screen during data acquisition so that the operator can observe the build-up of signal in

(Continued on page A284)

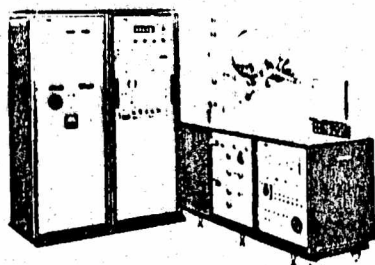


Figure 12. Photograph of the Vacuum Generators ESCA-2.

the spectrum. When a scan is completed, the spectrum may be plotted on an X-Y recorder. The contents of the scaler or memory also may be punched onto paper tape for future manipulation. AEL, Hewlett-Packard and Vacuum Generators have computer control and data acquisition as options for their spectrometers. The presence of a dedicated mini-computer allows the operator to perform some data handling operations, e.g., smoothing, satellite subtraction, or deconvolution. Also, with the computer the spectrometer may be set up to scan a number of binding energy ranges sequentially without any intervening operator action. One also may make multiple scans of one region to enhance the signal-to-noise ratio of the spectrum. The computer may be used for data de-

convolution to remove the contribution of the x-ray source to the spectral peaks. At present, AEL and Varian offer fast-Fourier-transform algorithms in their software packages for this purpose. In general, the utility of a computer on an ESCA spectrometer in terms of data acquisition and manipulation is worth the additional cost.

FUTURE DEVELOPMENTS

ESCA is a relatively new and high-cost technique which is undergoing rapid development. Nevertheless, the present instrumentation has advanced to the stage where the major impetus to continued growth must come from significant new applications of the method. Widespread use in the study of the chemistry of surfaces of solids will assure its place in chemical instrumentation. Certainly, its application to problems in catalysis and surface coatings shows great promise. One area in which much work needs to be done is sample cleaning and pretreatment leading to reproducible sample surfaces. Use of ion sputtering to obtain composition depth profiles will become important. Since ESCA is one of the very few techniques by which the second row elements (and their oxidation states) may be determined, future developments towards quantitative methods for these elements are quite probable.

Developments in the instrumentation itself will probably be weighted by the applications trends. The addition of multi-channel detectors to dispersive instru-

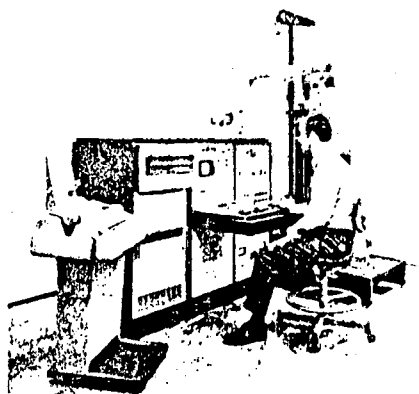


Figure 13. Photograph of the Varian VIEE-15 spectrometer system.

ments without the simultaneous addition of a monochromator could increase sensitivity by up to 100 fold. Certainly, monochromatized sources will become more common (for the reasons outlined in the text). The use of electron flood guns or other means of surface charge control will spur the utilization of monochromatized sources in commercial spectrometers. Alternate photon sources will be developed; e.g., sodium or yttrium x-ray sources. Probably, the most useful developments in instrumentation will be the expansion of computer software for data analysis and signal recognition and retrieval.

ACKNOWLEDGMENTS

The authors wish to thank Howard Harrington of Hewlett-Packard, John Rendina of McPherson, William Riggs of du Pont, and Alan Wolstenholme of AEI for helpful discussions. The spectra were obtained with an electron spectrometer obtained, in part, with funds from NSF Grant GP-28134. J.E.L. acknowledges support from NSF and PRF for photoelectron spectroscopy research.

MANUFACTURERS

AEI Scientific Apparatus, Inc.
500 Executive Blvd.
Elmford, N.Y. 10523

E. I. du Pont de Nemours and Co., Inc.
1500 S. Shamrock Ave.
Monrovia, Calif. 91016

Hewlett-Packard
Scientific Instruments Division
1601 California Ave.
Palo Alto, Calif. 94304

McPherson Instrument Corp.
530 Main Street
Acton, Mass. 01720

Vacuum Generators, Ltd.
Charlwoods Road
East Grinstead, Sussex
England

Varian Associates
611 Hansen Way
Palo Alto, Calif. 94302

LITERATURE CITED

18. Norrland, E., Ekstig, R., Kallne, E., and Chetal, A. R., *Metrologia*, **5**(3), 80 (1969).
19. Siegbahn, K., Hammond, D., Fellner-Feldleg, H., Barnett, E. F., *Science*, **176**, 245 (1972).
20. Eastman, D. E., and Cashion, J. K., *Phys. Rev. Lett.*, **27**, 1520 (1971).
21. Krause, M. O., *Chem. Phys. Lett.*, **10**(1), 65 (1971).
22. Amy, J. W., and Baitinger, W. E., Abstracts of 44th Eastern Analytical Symposium, Paper No. 6, 1972.
23. Dinnis, W. P., and Lester, J. E., *Anal. Chem.* (in press).
24. Swartz, W. E., Watts, P. H., Watts, J. P., Brasch, J. W., and Lippincott, E. R., *Anal. Chem.*, **44**, 2001 (1972).
25. Svartholm, N., and Siegbahn, K., *Ark. Mat. Astr. Fys.*, **33A**, 21 (1946); Siegbahn, K., and Svartholm, N., *Nature*, **157**, 872 (1946).
26. Purcell, E. M., *Phys. Rev.*, **54**, 818 (1938).
27. Hughes, A. L., and Rojansky, V., *Phys. Rev.*, **34**, 284 (1929); Hughes, A. L., and McMillen, J. H., *Phys. Rev.*, **34**, 291 (1929).
28. Blauth, E., *Z. Physik*, **147**, 228 (1951).
29. Batner, H., Simpson, J. A., and Kuyatt, C. E., *Rev. Sci. Instrum.*, **39**, 33 (1968).
30. Lee, J. D., *Rev. Sci. Instrum.*, **44**, 1291 (1972).
31. Golden, D. E., and Zecca, A., *Rev. Sci. Instrum.*, **42**, 210 (1971).
32. Hochital, D. A., and Ridgen, J. D., *Appl. Phys. Lett.*, **16**, 348 (1970).
33. Helmer, J. C., and Weichert, N. H., *Appl. Phys. Lett.*, **13**, 266 (1968).

Note added in proof: Vacuum Generators, Ltd. have provided the following data for their new ESCA 3: "Peak intensity on the Au 4f line of 107,000 counts per sec at FWHM of 4.3 eV (300,000 counts per sec at 2.0 eV) with a power of 300 watts, and a best reported resolution on Ag 3d of 0.87 eV."

2. Target Materials
 3. X-ray Window Filter
 4. Line Width Considerations
 - C. Analyzer Design
 1. Magnetic Deflection
 2. Spherical Capacitor
 3. Cylindrical Mirror
 4. Nondispersive Electrostatic Filter
 - D. Detectors
 1. Single Element Detectors
 2. Multi-element Detectors
 - E. Scanning Mode
 - F. Sample Considerations
 - G. Data Acquisition and Processing
- IV. Applications of ESCA to Surface Analysis
 - A. Organic Surface Analysis
 - B. Inorganic Surface Analysis
 - C. In-depth Analysis
 - V. Comparison with Other Surface Analysis Techniques
 - A. ESCA
 - B. AES
 - C. ISS
 - D. SIMS
 - E. Summary Comparison

References

I. INTRODUCTION

Since the discovery of the chemical shift phenomenon and the pioneering work by Siegbahn and co-workers in the mid-1950s,^{1,2} ESCA (Electron Spectroscopy for Chemical Analysis) has become a powerful tool for chemists and physicists. The technique has been used to study solid state band structure and atomic and molecular bonding in both the solid state and the gas phase. From the point of view of the analytical chemist, however, one of the most important uses of the technique has been in the analysis of solid surfaces. The ESCA technique is essentially nondestructive, universal for all elements except hydrogen, samples a layer less than ~30 Å in depth, and can be applied to any vacuum-worthy solid. Indeed, at this depth resolution, ESCA is the only spectroscopic technique which can be used to

the purpose of this article is not to survey the general field of electron spectroscopy or even the more specific area of X-ray photoelectron spectroscopy, as this would be redundant and hardly possible in the space available. The purpose of this article is to review X-ray photoelectron spectroscopy as presently applied to problems involving surface analysis. Section II.A gives a "broad brush" overview of the ESCA technique. Sections II.B and II.C contain more detailed discussions of reference levels, surface charging, chemical shifts, final state sources of structure, and quantitative analysis. These topics are important in a complete understanding of the ESCA method, and should be understood by those directly involved in spectral interpretation. However, some chemists may only be interested in understanding how ESCA can assist them in solving surface-related problems. These readers may wish to skip Sections II.B and II.C. In Section III, sample considerations and available commercial instrumentation are discussed, followed, in Section IV, by a review of selected applications of ESCA to surface analysis. Lastly, Section V compares ESCA with three other commercially available spectroscopic methods for surface analysis: Auger Electron Spectroscopy (AES), Ion Scattering Spectroscopy (ISS), and Secondary Ion Mass Spectrometry (SIMS).

As outlined, the general framework of this article necessitates that several important areas in the field (such as a quantitative treatment of the chemical shift phenomenon) be mentioned only briefly. References to key papers in the areas not emphasized are provided for the reader interested in more complete information.

II. PRINCIPLES OF ESCA

A. Technique Overview

The basic ESCA experiment involves exposure of the material to be studied to a flux of monochromatic X-rays of known energy. Absorption of these X-ray photons by atoms of the sample material results in the prompt emission of electrons, usually originating from the inner or core atomic orbitals. Since energy must be conserved in this photoemission process, the absorbed X-ray photon energy, $h\nu$, must be partitioned between the kinetic energy of the emitted electron, E_k , and the work expended in removing it from the atom, usually referred to as the electron

binding energy, E_b , $h\nu = E_k + E_b$. In practice, $h\nu$ is known, and E_k is measured by the spectrometer, allowing direct determination of the electron binding energy from the single difference between $h\nu$ and E_k . (In measurements conducted on solid materials, several other factors can influence the kinetic energy of emitted electrons. These factors and their significance are discussed in Section II.B.)

Since the atomic structure of each element is unique, measurement of the binding energies of one or two atomic orbitals for each element in a sample is usually sufficient to establish the qualitative elemental composition of the sample. All the elements of the periodic chart have electrons which can be detected in this way with the single exception of hydrogen. In addition, to qualitative elemental composition, information about the chemical environment and oxidation state of each element can frequently be extracted from a spectrum through precise measurement of electron-binding energies and peak shapes, and observation of multi-line structure.

The ability to obtain this information on solid materials is mainly significant in analytical chemistry because the spectrum is only characteristic of the outermost atomic layers of the sample, and provides a sensitive probe of surface composition and chemistry. The reason for this high degree of surface sensitivity is quite simple: the free photoelectrons traveling in solids are very easily scattered from the many bound electrons in the sample and lose some fraction of their kinetic energy in the process. Thus, only those photoelectrons generated within the top few atomic layers have any significant probability of escaping the sample with a kinetic energy given by $h\nu - E_b$. Electrons which have lost some portion of their kinetic energy may enter the spectrometer and be detected, but will normally contribute only to the spectrum background and will not distort the chemical information in the spectrum. The exact depth sampled by the ESCA technique depends upon a number of parameters, including the sample matrix composition and the kinetic energy of the electron of interest. (This is discussed in detail in Section II.C.) As a general rule, presently available data suggest the sampling depth of ESCA is ca. 30 to 100 Å for organic samples, ca. 10 to 30 Å for most inorganic compounds, and ca. 5 to 20 Å for metals. The matrix dependency of the sampling depth makes quantitative interpretation

ESC 4

Authors: Robert S. Swingle, II
Central Research and Development Department
E. I. du Pont de Nemours and Company
Experimental Station
Wilmington, Delaware

William M. Riggs
Physical Electronics Industries, Inc.
Eden Prairie, Minnesota

Referee: * Jon Amy
Department of Chemistry
Purdue University
West Lafayette, Indiana

TABLE OF CONTENTS

I.	Introduction and Scope
II.	Principles of ESCA
A.	Technique Overview
B.	Core Level Binding Energies
1.	Reference Levels in Conducting Solids
2.	Nonconductors and the Charging Effect
3.	Chemical Shifts in Solids/Photoelectrons
4.	Chemical Shifts in Solids/Auger Electrons
5.	Final State Sources of Multi-line Structure/Shake-up
6.	Final State Sources of Multi-line Structure/Exchange Splitting
C.	Quantitative Analysis
1.	Extrinsic Energy Loss Processes
2.	Intrinsic Processes
3.	Quantitative Theory
a.	Class 1 Samples
b.	Class 2 Samples
c.	Class 3 Samples
III.	Current ESCA Instrumentation
A.	Vacuum System
1.	Required Vacuum Level
2.	Design
B.	X-ray Source Design
1.	Generation of X-rays

of peak areas difficult, and generally precludes absolute quantitative analysis except in cases where rigorous calibration is possible. However, in most cases, relative atomic concentrations at a sample surface can be determined with an accuracy of about $\pm 10\%$.

B. Core Level Binding Energies

Reference Levels in Conducting Solids

Understanding reference levels for core electron binding energies in solids is an important consideration in spectra interpretation, and a short review of the subject seems appropriate.

For an isolated atom in the gas phase, each photoionization process can be described (neglecting recoil terms) by the simple conservation of energy equation:

$$E_{\text{ph}} = h\nu - E_{\text{K}} \quad (1)$$

where $h\nu$ is the energy of the X-ray photon, E_{K} is the kinetic energy of the photoelectron, and E_{B} is the binding energy of the electron referenced to the vacuum level. However, in the case of solid samples, additional terms must be considered in the energy equation. Figure 1 shows a typical energy diagram for an electrically conducting sample in contact with the spectrometer. The left and right sides of the figure refer to the sample and spectrometer energy levels, respectively. For the sample, the X-ray photon energy can be partitioned among: (1) E_{B} , the binding energy of the core level of interest referenced to the Fermi level, (2) ϕ_{SA} , the work function of the sample,

and (3) E_{K} , the kinetic energy of the photoelectron. During the experiment, the photoelectron will be accelerated from E_{K} to E_{K} (left side of Figure 1) by an amount equal to the so-called "contact potential" or the difference between the sample and the spectrometer work functions. Thus, E_{B} can be calculated from:

$$E_{\text{B}} = h\nu - E_{\text{K}} - \phi_{\text{SA}} \quad (2)$$

Note that the work function of the sample need not be known to determine E_{B} . As discussed below, this makes the Fermi level an experimentally convenient reference, and binding energies of core electrons in solids are normally referenced to the Fermi level.

Unfortunately, there is some controversy^{17,18} as to whether E_{B} is the best value to use for comparison with quantum calculations, or even with chemical parameters such as oxidation state. It has been suggested that better correlation of binding energies with these parameters may be possible when E_{B} is used in place of E_{B} . To determine E_{B} for core electrons in solids, however, the sample work function must be known and, except for metals and a few other pure materials, very little work function data exist in the literature. Consequently, in an analytical laboratory, ϕ_{SA} would need to be measured directly for most samples. Measurement of ϕ_{SA} is not an easy problem experimentally^{19,20} and would be impractical for routine analytical problems.

In addition, Citrin has noted that neither E_{B}

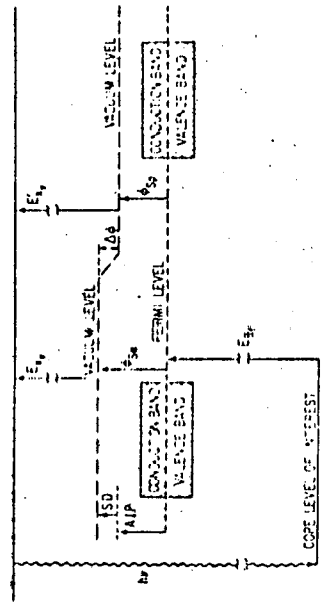


FIGURE 1. Energy level diagram for an electrically conducting solid in contact with a spectrometer.

nor E_{B} is the best value to use for comparison with theoretical calculations.²¹ Referring to Figure 1, the work function associated with a given sample can be thought of as being composed of two terms, one term a property of the surface being analyzed, and the other a property of the "bulk" material. The surface term, called the surface dipole or SD in Figure 1, arises from the interaction of the photoelectron with the orbitals which protrude beyond the nuclear surface plane. For crystalline materials, the magnitude of the surface dipole potential depends not only upon the sample itself, but also upon the crystal face being examined. The bulk term contributing to the work function is called the average internal electrostatic potential, or AIP, by Citrin, and is the average potential experienced by the electron as it travels in the solid. Binding energies referenced to the AIP level have the most meaning theoretically where $E_{\text{B AIP}}$ is defined as:

$$E_{\text{B AIP}} = E_{\text{B}} - \text{SD} \quad (3)$$

or

$$E_{\text{B AIP}} = E_{\text{B}} + \text{AIP} \quad (4)$$

Experimentally, however, it is not possible to separate the AIP and SD contributions to ϕ_{SA} and, unless one is dealing with a model system where either the SD or AIP terms can be calculated, the vacuum or Fermi reference levels are the only ones accessible. Thus, for each sample, the choice of vacuum or Fermi levels as a reference should be

dicated by which term, SD or AIP, is thought to be the bigger contributor to ϕ_{SA} for that sample. If SD is larger, E_{B} will be closer to $E_{\text{B AIP}}$ and, of course, the converse will be true if AIP is larger. As stated above, E_{B} is used almost exclusively because of convenience and is the only viable choice for an analytical laboratory.

2. Nonconductors and the Charging Effect

For the analytical chemist, the majority of the samples examined will not be electrically conducting and, in these cases, the reference level problem becomes more complex. The energy level diagram for a nonconductor in equilibrium with the spectrometer is shown in Figure 2. Nonconductors are characterized by a region between the top of the valence band and the bottom of the conduction band called the band-gap, whose magnitude (~ 1 to 4 eV) is much larger than kT at room temperature. For intrinsic semiconductors²² and insulators, where the band structure is known and no impurity states are present, the Fermi level is statistically well-defined as being at a position one half the magnitude of the band-gap above the top of the valence band. For most samples handled in an analytical laboratory, however, the band structure and even the magnitude of the gap are unknown. Thus, the position of the Fermi level is unknown, and using the Fermi level as a reference for core electron binding energies becomes somewhat arbitrary in these cases.²³

Complicating this picture for nonconducting samples is the problem of charging. During the ESCA experiment, the photoelectrons escaping the

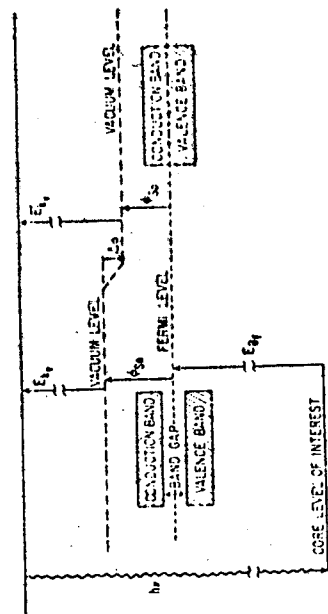


FIGURE 2. Energy level diagram for nonconductor in equilibrium with a spectrometer.

sample surface leave behind a positive charge and, because of the electrical properties of the sample, there may be no low resistance path available for electrons to flow from the spectrometer to the sample and neutralize the charge. Consequently, the sample charges positively, and the energy levels of the sample are shifted relative to the Fermi level of the spectrometer. In the absence of any electron return current, the sample would charge to some "breakdown" voltage, which might be as high as several hundred volts depending upon the sample. In an actual spectrometer, however, return current to the sample is supplied by photoelectrons generated from X-rays striking areas around the sample including, primarily, the metal foil window separating the X-ray tube from the sample. To a lesser degree, return current is also supplied by a conduction mechanism between the sample and spectrometer — possibly photoconduction across the surface of the sample. The net result of this charging current, i_c , and the sum of the discharging currents, i_d , is that a mean steady state potential, Q_{ch} , is rapidly established at the sample surface. Photoelectrons leaving the sample surface will then have a kinetic energy defined by:

$$E'_{k_v} = h\nu - E'_{F_s} - Q_{ch} \quad (5)$$

and the entire kinetic energy axis of the ESCA spectrum will be shifted from its true value. Although the magnitude of Q_{ch} will vary from sample to sample, for a constant X-ray tube current and anode voltage, Q_{ch} will be constant for a given sample during the ESCA analysis.

A number of methods are currently used to deal with the charging problem. These methods can be classified into two general types: (1) those which attempt to reduce Q_{ch} to a small value (<0.1 eV) — for example, by using extremely thin samples on a conducting substrate or by flooding the sample environment with low energy electrons; and (2) those methods which use an internal or external standard to measure the magnitude of Q_{ch} . Each of these is discussed separately below.

In the thin sample approach, ultrathin samples (one to several monolayers) are studied on a conducting support which is in electrical contact with the spectrometer. This method assumes that the resistance to bulk electrical conduction from the support to the sample surface will be sufficiently small to prevent charging. The validity of this assumption should be verified for each sample

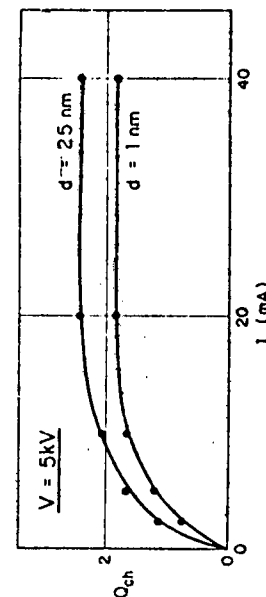


FIGURE 3. Sample charging vs. X-ray tube current at constant anode potential. [From Ebel, M. F. and Ebel, H. J. *Electron Spectrosc. Relat. Phenom.*, 3, 169 (1974). With permission.]

functions of the X-ray tube current, I . One would then expect that the difference between i_c and i_d , and thus Q_{ch} , would also be linear with I . In fact, another source of i_d , speculated to be photoconduction, adds to i_d from the window, with the result that Q_{ch} and I have the dependence shown in Figure 3. These authors give no experimental data for samples other than Teflon,* but they state that, for all cases studied, this Q_{ch} vs. I curve could be characterized by the equation:

$$Q_{ch} = A \frac{(BI)}{(1 + BI)} \quad (6)$$

where A and B are constants for a given sample. From Equation 5, since $h\nu$, E'_{F_s} , and ϕ_{sp} are independent of I , Q_{ch} in Equation 6 can be replaced by E'_{k_v} . A and B can then be determined for a given sample by fitting Equation 6 to a plot of E'_{k_v} vs. I and, in principle, a value of E'_{k_v} at $I = 0$ can be calculated which corresponds to zero surface charge. It is important to note, however, that Ebel and Ebel used external standards to determine the magnitude of Q_{ch} , and plotted Q_{ch} vs. I (rather than E'_{k_v} vs. I) because they found that negative sample charging was possible at low anode voltages. At a constant tube current, it was found that lowering the anode voltage by a factor of two decreased the total photoemission, and thus i_c , by much greater than a factor of two, while the contribution of i_d from the window remained essentially constant. At low anode voltages, i_d could be greater than i_c , and negative Q_{ch} was possible (see Figure 4). It is likely that

the value of anode voltage above which negative charging is not possible will depend upon both the sample and the instrument design. Until these variables are better characterized, the authors feel that this approach, like the flood-gun, should be used only in conjunction with an external standard. An additional consideration for an analytical laboratory is that this technique requires spectra to be run at a number of power settings for each sample, which may not be practical because of the time involved.

Before continuing to the internal and external methods of charge correction, a word about differential charging is in order. Thus far, charging has been discussed in terms of an average potential, Q_{ch} , at the sample surface. In fact, photoconductors have a small distribution of charge over their surfaces which broadens the measured photoelectron line width and can be the limiting factor in resolution.²⁸ In general, the higher the absolute value of Q_{ch} , the larger the charge distribution will be. For the limiting case of differential charging, where one portion of a sample is in good electrical contact with the spectrometer and the remainder is not, separate distinct peaks can be observed in the spectrum. An illuminating example of this latter effect can be found in Gruhn's study of vanadium dioxide.²⁹ Figures 5A and 6A show the B_{1s} and $V_{2p-O_{1s}}$ spectra, respectively, from a sample of VO_2 . These spectra were taken using a spectrometer which had no window between the sample and the X-ray source for supplying i_d to the sample. Note that two boron peaks and three O_{1s} peaks are evident when the sample is examined

*Teflon — duPont Trademark for TFE-Fluorocarbon Resin.

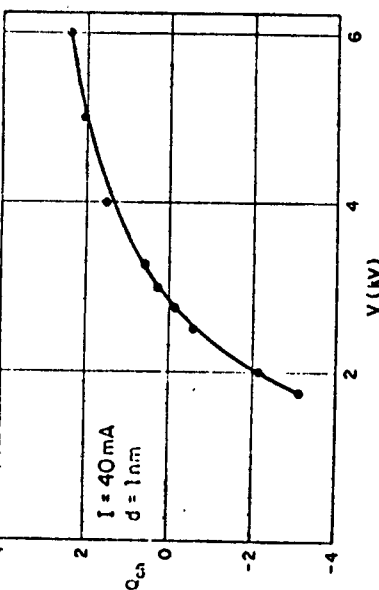


FIGURE 4. Sample charging vs. X-ray anode potential at constant tube current. [From Ebel, M. F. and Ebel, H., *J. Electron Spectrosc. Relat. Phenom.*, 3, 169 (1974). With permission.]

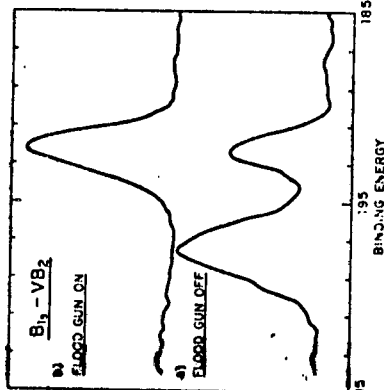


FIGURE 5. B_{1s} spectra from VB_2 with (a) flood gun off, and (b) flood gun on. (From Grunthaner, F. J., Ph.D. thesis, California Institute of Technology, Pasadena, 1974.)

under normal conditions. When an electron flood-gun was operated simultaneously with the photoemission experiment (Figures 5B and 6B), the two boron peaks and two of the three oxygen peaks coalesced into single lines. Even though VB_2 is a good conductor, the boron-oxide coating on some of the particles was evidently electrically insulated from the remainder of the sample. The same conclusion was reached when the VB_2 was

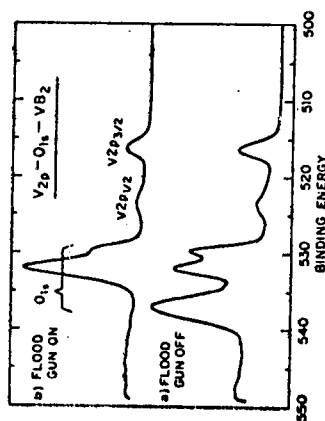


FIGURE 6. V_{2p} - O_{1s} spectra from VB_2 with (a) flood gun off, and (b) flood gun on. (From Grunthaner, F. J., Ph.D. thesis, California Institute of Technology, Pasadena, 1974.)

examined in a spectrometer which had an Al window between the X-ray source and the sample. Figure 7A shows the resulting V_{2p} - O_{1s} spectrum, which looks nearly identical to that in Figure 6b. Apparently, the i_d from the window is sufficient for charge neutralization of the nonconducting portion of the sample. When a DC potential is applied to the sample holder, photoelectrons originating from the conducting portion of the sample are shifted in the spectrum by an amount exactly equal to the applied potential as expected.

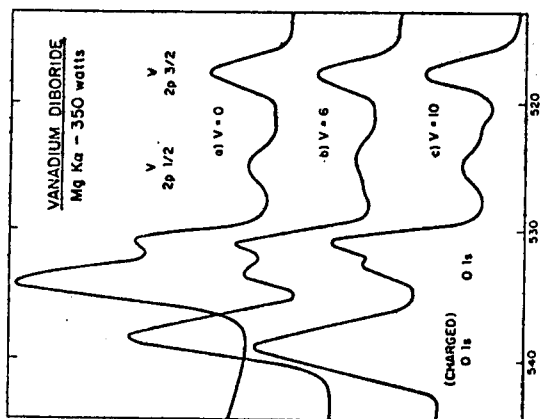


FIGURE 7. V_{2p} - O_{1s} from VB_2 with (a) zero applied potential, (b) 6 V applied potential, and (c) 10 V applied potential. (From Grunthaner, F. J., Ph.D. thesis, California Institute of Technology, Pasadena, 1974.)

Photoelectrons originating from the nonconducting portion, however, are shifted only slightly from their original kinetic energies. That they shift at all is due to a small effect which the applied potential has on the available i_d . Figures 7B and 7C show the resulting spectra for applied potentials of 6 and 10 V, respectively. These spectra have been normalized for the applied bias, and the differential charging noted previously in Figures 5A and 6A is again evident.

Clearly, care must be taken to insure that differential charging is not the source of multiple peaks in a spectrum. If the difference in binding energy between multiple peaks is constant with flood-gun current or with sample bias potential, the chemist can be reasonably sure that differential charging is not the cause of the multiple peaks. As mentioned previously, the general approach to charge correction using internal or external standards is to take all spectra for each sample under a given set of instrumental parameters and, by measuring the apparent binding energy of a "standard" photoelectron line with respect to its true binding energy, determine the amount of charge at the surface of the sample. The funda-

mental assumption of the standards method is that the reference photoelectron line arises from an element in electrical equilibrium with the sample which can "follow" exactly (within ± 0.1 eV) the charge on the sample surface.

In the internal standard method, the reference consists of an element that is part of the sample itself. In this case, the above assumption must be valid. The reference element, however, must be common to all the samples being analyzed and, most importantly, must not undergo a chemical shift from sample to sample. These latter two conditions are not always satisfied and greatly restrict the general applicability of the internal standard approach.

One good example of the internal standard approach can be found in the work by Ogilvie and Wolberg³⁰ on heterogeneous catalysts supported on alumina. These workers showed that for oxides of cobalt, nickel, copper, and zinc on α -alumina, a factor of ~ 3 to 10 more precision in binding energies was possible when the Al_{2p} photoelectron line was used as an internal standard for charge correction than when the external C_{1s} photoelectron line (see below) was used. The same improvement was even found in a number of spinels, where both tetrahedral and octahedral aluminum sites are present.

In the external standard approach, an element which is not common to the sample is used for charge correction. The C_{1s} hydrocarbon line at 285.0 eV, which is found on nearly all samples, has been used most commonly in the past.⁴ Sample bias experiments (similar to that described above for VB_2), in which a potential is applied between the sample and the spectrometer, have been applied to nonconducting samples such as $BaSO_4$,³¹ MoO_3 ,³² and $NaCl$.³³ For each sample, as a function of applied potential, the position of the impurity C_{1s} photoelectron peak was shifted by the same amount as the photoelectron peaks from sample. This is good evidence that the C_{1s} external standard is in electrical equilibrium with the sample and follows the surface charge. Because of convenience, this C_{1s} line is still being used as a standard in many laboratories. As pointed out by several authors,³² the problem with this standard is that one cannot always be certain of the origin of the carbon contamination and the same carbon species may not be present from sample to sample. Most commercial instruments today (see Section III) are pumped with "oil free" pumping systems, and the majority of carbon in these vacuum

bound only to hydrogen and other carbon atoms. The shoulder at ~287 eV on the large peak is due to the methylene carbons which are bound directly to 1 oxygen atom, and the highest binding energy peak at ~289 eV is due to the carbonyl carbon atoms. The O_{1s} spectrum from the polymer is also shown in Figure 9. Here, two peaks with ~1:1 relative intensities are evident and correspond to the two types of oxygen in the polymer.

Figure 10 shows a palladium spectrum from palladium black which illustrates the chemical shift in inorganic solids. The 3d level in palladium is split into a natural doublet (3d_{3/2} and 3d_{5/2}) due to spin-orbit coupling. Two peaks are found in each of these levels, with the higher E_B peaks being due to palladium oxide (PdO) on the surface of the palladium black, and the lower E_B peaks to the palladium metal (Pd) substrate.

The potential model equation for photoelectrons can be written as:

$$E_B = k Q_a + 1 + V_a \quad (7)$$

where E_B is the binding energy for a core electron in atom a, Q_a is the initial state charge on atom a, k is a constant for the core level of interest in atom a, and 1 is a constant determined by the reference level; V_a is given by:

$$V_a = \sum_b \frac{q_b}{r_{ab}} \quad (8)$$

where q_b is the initial state charge on atom b, r_{ab} is the distance between atoms a and b, and the summation is taken over all atoms in the sample except atom a. In practice, k and 1 are treated as adjustable parameters for a given core level electron and are determined from a least squares fit of calculated versus observed binding energies for a large number of compounds. V_a is a Madelung potential term and represents the potential found at atom a due to charges on all the other atoms surrounding atom a.

It is obvious from Equation 7 that the quantity (E_B - V_a), not E_B alone, should be linear with Q_a. Calculating V_a can be a problem in solids since, as opposed to the gas phase, all atoms, not just those in the molecule of interest, must be considered. For model solids of known structure, V_a can be calculated directly but, for most analytical samples, this will not be possible. Fortunately, studies in the literature for many core electrons

change relation could be quantized, photoelectron binding energies measured by ESCA could then be used as direct measures of atomic oxidation states and electron distributions in molecules. Since this chemical shift/atomic charge relationship was recognized, hundreds of atomic charge calculations on large numbers of chemical systems have been performed and compared with experimental binding energies. These calculations have ranged in complexity from simple Pauling electronegativity calculations³⁵ to *ab initio*³⁶ calculations using high quality wave functions. Many of these calculations have given excellent agreement with experiment, and many have not. It is not the purpose of this article to discuss these calculations in detail, and the reader is referred to the articles by Shirley³ and Gelius¹¹ for more information on this subject. Instead, in this section, we will first present several examples of the chemical shift in solids in order to illustrate its usefulness in structure and oxidation state determinations. Secondly, those factors other than initial state charge which affect electron binding energies in solids are described in a qualitative fashion to alert the reader to some of the problems in correlating E_B with atomic charge in solids, and to assist him in understanding the latest literature in this area.

The chemical shift effect in ESCA can be illustrated qualitatively by considering the carbon atoms in the organic polymers, polyethylene (PE) (CH₂-CH₂), in and polytetrafluoroethylene (PTFE) (CF₂-CF₂). In PTFE, the carbon atoms are bonded directly to two electronegative fluorine atoms which pull electron density away from the carbon atoms and toward the fluorine atoms. This creates a net positive charge on the carbon atoms in PTFE and, compared to the C_{1s} level in PE, the C_{1s} level in PTFE is deshielded from the carbon nuclear charge. Electrons in the C_{1s} level of PTFE are thus held more tightly by the nuclear charge, and exhibit a higher binding energy than electrons in the C_{1s} level of PE. Experimentally, the PTFE C_{1s} peak is found at ~8 eV higher binding energy than the C_{1s} peak for PE.³⁷ Another good example of chemical shifts in organic materials is found in Figure 9, which shows the C_{1s} and O_{1s} spectra from a commercial polyester film. Three peaks are evident in the C_{1s} spectrum. The origin of these peaks is easily discerned from polymer structure, relative peak intensities, and simple electronegativity considerations. The largest peak at ~285 eV is due to the ring carbons which are

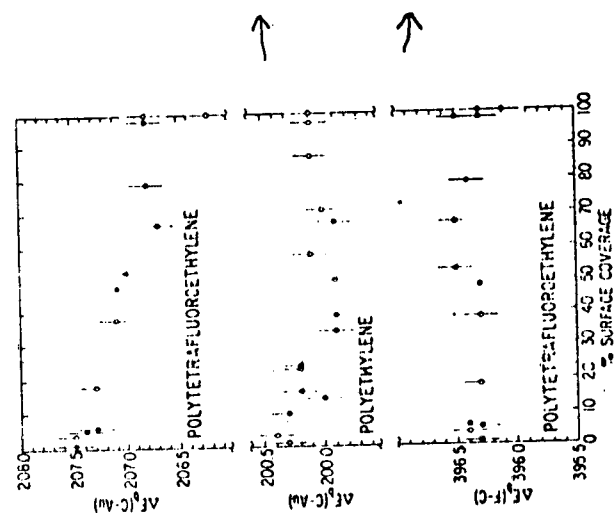


FIGURE 8. Differences in binding energies, ΔE_B , between selected peaks in PE and PTFE as a function of the amount of gold deposited on the polymer surfaces. [From Ginnard, C. R. and Riggs, W. M., *Anal. Chem.*, 46(9), 1306 (1974). With permission.]

represent data taken on three different samples of each polymer. As a function of gold coverage, the ΔE_B between the F_{1s} and C_{1s} peaks in PTFE remains constant within experimental error ($\sigma = \pm 0.2$ eV), as expected, since both peaks arise from the same molecular structure. The ΔE_B between the Au_{4f_{7/2}} and C_{1s} peaks changes as a function of gold coverage by as much as ~0.8 eV for PTFE and ~0.5 eV for PE. It is clear that when using Au as an external standard, care must be taken to insure approximately equivalent coverage among samples, preferably at the low to moderate coverages which do not significantly enhance surface charging.

3. Chemical Shifts in Solids/Photoelectrons

Most of the early research in ESCA was sparked by the recognition that the exact binding energy of a photoelectron was related to the magnitude of the charge on the atom originating the photoelectron. In principle, if this chemical shift/atomic

systems is usually due to CO and CO₂ slowly desorbing from the chamber walls. Only a small amount of carbon is present as hydrocarbon. Thus, it is likely that this so-called "pump-oil" carbon is detected by ESCA on many surfaces is not "pump-oil" at all, but arises from sorbed CO/CO₂ or from atmospheric contamination which occurred before the sample was placed in the spectrometer vacuum.

An alternate external standard approach to charge correction is to vacuum deposit a small amount of gold on each sample surface.³¹ The magnitude of Q_{ch} is calculated from the difference between the observed binding energy for the Au_{4f_{7/2}} peak and the commonly accepted value of 83.8 eV. Except in the case of ultraclean surfaces, gold vapor deposition proceeds initially by a nucleation process which results in the formation of electrically isolated islands of gold on the surface. The key assumptions in this charge correction method are (1) that the gold islands follow the surface charge, and (2) that the gold does not react with the sample. These two assumptions are generally valid since gold is relatively inert, and bias-potential experiments which alter Q_{ch} in the spectrometer have shown that the gold islands do follow the surface charge.^{31,32} at least at low gold concentrations. Exceptions to both assumptions have been pointed out in the literature, however. Betteridge, Carver, and Hercules³³ have shown that in some systems, the width and position of the gold peaks can change with sample, time of deposition, and probe temperature, indicating that the gold is reacting with the sample. In addition, Ginnard and Riggs³⁴ have shown that for gold deposited on polyethylene (PE) and polytetrafluoroethylene (PTFE) films, the magnitude of Q_{ch} increases as the amount of gold deposited on the polymer surfaces increases - probably because the higher total photoelectric yield of gold compared to that of the polymers results in larger i_c values with increasing gold coverage. An even more serious problem is that the electrical equilibrium between the gold and the polymers appears to shift significantly with increasing amounts of deposited gold. The ΔE_B between (1) the F_{1s} and C_{1s} peaks in PTFE, (2) the C_{1s} and Au_{4f_{7/2}} peaks in PE, and (3) the C_{1s} and Au_{4f_{7/2}} peaks in PTFE is plotted in Figure 8 as a function of the amount of gold on the two surfaces (expressed as % surface coverage). Open circles, filled circles, and triangles

POLYETHYLENE TEREPHTHALATE

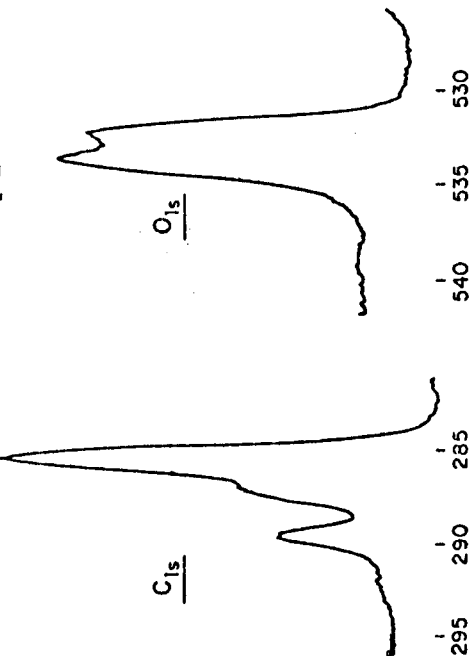
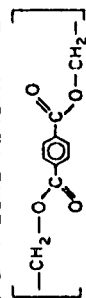


FIGURE 9. C_{1s} and O_{1s} spectra from polyethylene terephthalate.

PALLADIUM BLACK

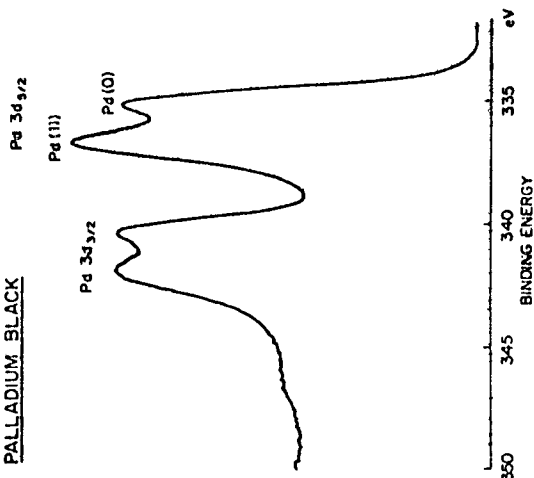


FIGURE 10. $Pd_{3d5/2-3/2}$ spectrum from palladium black.

have shown empirically that the V_a contribution in Equation 7 is either negligible or nearly constant since good linear fits between E_B and Q_a have been obtained. For some atoms where a plot of E_B vs. Q_a does not give a good fit, an assignment of oxidation state based on binding energies alone may not be unambiguous, and other characteristics in the spectrum must be used to obtain chemical information. In cases where the E_B/Q_a correlation is poor, significant variations in the V_a term from sample to sample may be one cause of the poor correlation.¹¹

Other reasons for a poor correlation of E_B with Q_a or oxidation state arise from so-called final state effects. Thus far, photoelectron binding energies have been discussed only in terms of initial state charges. However, as in all spectroscopic techniques, ESCA measures the energy difference between an initial and a final state, and observed chemical shifts are a measure of some average charge on the atom in the initial and final states, not of initial state charge alone. E_B can be written as:

$$E_B = E_i - E_f \quad (9)$$

where E_i and E_f are the total energies of the initial and final states, respectively. In early calculations of chemical shifts, it was assumed that a frozen-orbital approximation (Koopman's theorem)¹² could be used in describing the final state. This method assumes that the photoionization process is sufficiently fast that other electrons in the atom (or matrix) do not have time to relax toward the hole created in the electron shell by the ionization. Under this assumption, only initial state atomic charges are important in determining chemical shift since the final state energy can be given in terms of the initial state energy as:

$$E_f = E_i + \delta \quad (10)$$

where δ is the energy of the photoelectron in the initial state atom before ionization. As evident from Equation 9, δ must be equal to E_B . More recent work indicates that significant polarization or relaxation of electrons toward the photohole can occur,^{21,22} and that Equation 10 is not an adequate description of the final state. This relaxation can involve both other core electrons in the same atom and "extra atomic" electrons in the solid. The effect of this electron relaxation is to screen the photoelectron from the positive charge

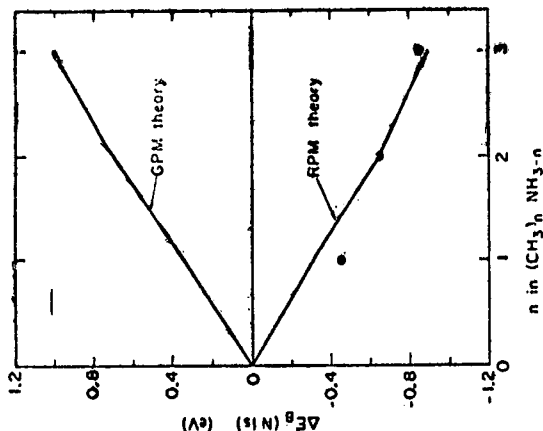


FIGURE 11. Calculated N_{1s} binding energies without (GPM) and with (RPM) relaxation terms for NH_3 , NH_4CH_3 , $NH(CH_3)_2$, and $N(CH_3)_3$. Experimental data shown as points. [From Davis, D. W., Banna, M. S., and Shirley, D. A., *J. Chem. Phys.*, 60(1), 237 (1974). With permission.]

at the nucleus. Thus, the photoelectron exhibits a higher kinetic energy (lower E_B) than it would have if no relaxation occurred. Calculated atomic charges which both include and exclude relaxation effects have been compared with experimental chemical shifts, and in most studies, those which include a relaxation term give better agreement with experiment. A striking example illustrating the effect of electron relaxation can be found in Shirley's study of N_{1s} binding energies in the series NH_3 , NH_4CH_3 , $NH(CH_3)_2$, $N(CH_3)_3$ (Figure 11).²³ Calculations using a ground state potential model (GPM - no relaxation) predict N_{1s} chemical shifts in a direction opposite to that predicted by calculations using a relaxation potential model (RPM). The experimental order of shifts agrees generally with the RPM calculations.

In summary, chemical shifts of photoelectrons in solids are related to initial state atomic charges and oxidation states, but reference level, and sample charging problems; Madelung terms, and electron relaxation can also be important in determining peak positions. For many atoms in

solids, chemical shifts determine oxidation states unambiguously. For other atoms, they do not. In these cases, other characteristics of the ESCA spectrum, such as Auger parameters, shake-up satellites, and multiplet structure due to exchange coupling, can often be used to obtain chemical information. Published photoelectron binding energies for a large number of solid compounds have been summarized in Reference 40.

4. Chemical Shifts in Solids: Auger Electrons

A core level ionized atom has two competing processes by which it can relax. The first step in the relaxation is the same for both processes: namely, an electron from a higher energy level (level 2) falls into the core level hole (level 1) created by the ionization. The energy released in this transition can be emitted by the atom either as an X-ray photon or as an Auger electron from a third atomic level (level 3). If a photon is emitted, its energy will be characteristic of the atom and approximately equal to the difference in binding energy between levels 1 and 2. Detection of these photons forms the basis of the X-ray fluorescence technique. If an Auger electron is emitted, its kinetic energy will also be characteristic of the atom and will be approximately given by:

$$E_K \approx E_{B1} - E_{B2} - E_{B3} \quad (11)$$

Auger electrons are usually described as a KLL, LMM, MNN, etc. Auger electrons, where the letters KLL, etc. refer to the principal atomic energy levels 1, 2, and 3, respectively, involved in producing the Auger electron. Because core ionized atoms are produced in the ESCA experiment, peaks due to Auger electrons are also detected in the ESCA spectrum. Auger peaks can be easily separated from photoelectron peaks because their kinetic energies do not depend on excitation energy. Thus, they exhibit no X-ray satellite structure and have the same kinetic energies when either Mg or Al K α radiation is used for photoexcitation. In addition, Auger peaks are broader in general than photoelectron peaks, particularly when levels 2 and 3 are valence band levels. For the remainder of this section, we will only be concerned with core-type Auger electrons, i.e., those in which levels 1 to 3 are all core levels.

Early observations of chemical shifts in Auger kinetic energies for a limited number of systems indicated that the magnitudes and directions of the Auger shifts were about the same as those

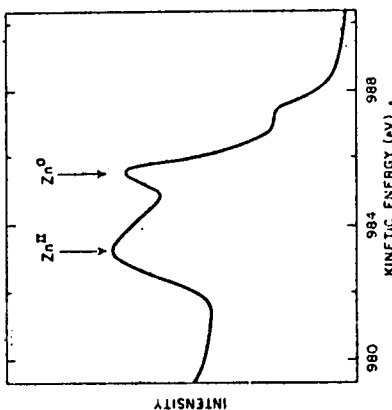


FIGURE 12. Portion of the Zn LMM Auger spectrum for a thin layer of ZnO on a ZnO substrate.

found for photoelectrons, and for some time, Auger peaks in the ESCA spectrum were regarded as more of a nuisance than anything else. However, more recent studies^{41,42} have found that Auger shifts are abnormally large for metal-metal oxide pairs. For example, although the Zn_{2p_{3/2}} binding energies are nearly identical for zinc metal and zinc oxide, the Zn LMM Auger spectrum exhibits a shift of ~4.6 eV between the two. Figure 12 shows a portion of the Zn LMM spectrum for a thin layer of ZnO on ZnO. Peaks due to both Zn⁰ and Zn^{II} are clearly evident. Wagner has summarized the Auger and photoelectron binding energies for 13 metal-metal oxide pairs (Table 1) and has illustrated the generality of the large relative Auger shifts in these systems. These Auger shifts have been investigated theoretically⁴³ and are ascribed almost entirely to much larger extra-atomic electron relaxation in the doubly charged final state for Auger emission compared to the singly charged final state for photoelectron emission. Large Auger shifts have also been found between nonconducting salts.^{44,45} Columns 2 and 3 of Table 2 list the Na_{1s} and sodium KLL Auger binding and kinetic energies, respectively, for sodium metal and 10 insulating sodium salts as determined by Wagner. Chemical shifts in the Na_{1s} binding energies for the insulating compounds vary only within a range of ~0.5 eV, while the corresponding Auger shifts vary over a range of ~3.5 eV and are nearly characteristic of the compound.

Wagner has proposed the "Auger parameter," α ,

which is defined as the difference in kinetic energy between the Auger and photoelectron peaks, as a useful measure for identifying chemical species. Values for α are listed in the fourth column of Table 2 for the sodium compounds and, although shifts in α ($\Delta\alpha$) are nearly the same as the Auger shifts (ΔE , Auger), $\Delta\alpha$ has an important practical advantage over ΔE , Auger. Because α is calculated from a difference in peak positions, there are no reference level or sample charging problems to be

concerned with, and α can be easily measured with ± 0.1 -eV accuracy. Wagner has demonstrated that the Auger parameter has a large range for all elements which give sharp core-type Auger peaks and which are accessible with Al K α radiation. These elements include Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Cu, Zn, Ga, Ge, As, Se, Te, Br, Cd, In, Sn, Sb, Te, and Xe (MNN). With higher energy incident radiation, the Auger parameter might be extended to Al, Si, P, S, Cl (KLL), Br,

TABLE 2

Chemical Shifts and the Auger Parameter for Sodium Compounds (Al K α Radiation)

Chemical form	N _{1s} E _B	K _{L₂₃} E _{K(Auger)}	α	$\Delta E_B(PE)$	$\Delta E(Auger)$	$-\Delta\alpha$
Na(S)	1071.7	994.2	579.3			
NaI	1071.4	991.4	576.2	-0.3	2.8	3.1
NaBr	1071.5	990.8	575.7	-0.2	3.4	3.6
NaCl	1071.4	990.5	575.3	-0.3	3.7	4.0
NaSCN	1071.1	990.7	575.2	-0.6	3.5	4.1
N ₂ SO	1071.1	990.6	575.1	-0.6	3.6	4.2
NaNO ₂	1071.4	990.0	574.8	-0.3	4.2	4.5
N ₂ SO	1071.0	990.0	574.4	-0.7	4.2	4.9
NaNO ₃	1071.2	989.8	574.4	-0.5	4.4	4.9
NaF	1071.0	988.8	573.2	-0.7	5.4	6.1
N ₂ Sif ₆	1071.5	987.9	572.8	-0.2	6.3	6.5

Kr, Pb, Sr, Y, Zr, Nb, Mo (LMM), and all heavy metals (MNN).

5. Final State Sources of Multi-line Structure/ Shake-up

Core electron chemical shifts from an element in two or more oxidation states are not the only possible sources of multi-line structure in an ESCA spectrum. Substituting Equation 9 into Equation 1 and solving for kinetic energy gives:

$$E_K = h\nu - (E_f - E_f') \quad (12)$$

From this equation it becomes obvious that even when all atoms of a particular element in a sample have the same oxidation states and initial state energies, if more than one discrete final state is possible, more than one photoelectron kinetic energy will be possible, and more than one peak will be observed in the spectrum. Electron shake-up transitions and exchange splitting due to unpaired electrons are the two main phenomena in photoionization responsible for multiple final states. Peaks due to shake-up or exchange splitting are usually referred to as "intrinsic" peaks because they arise from the photoionization process itself. [This is opposed to "extrinsic" energy loss peaks (see Section 1B) which arise from discrete, inelastic electron scattering processes occurring after photoionization has taken place and the electron is moving through the solid.] The physical bases of shake-up and exchange splitting and their analytical usefulness for oxidation state measurements in solids are discussed below.

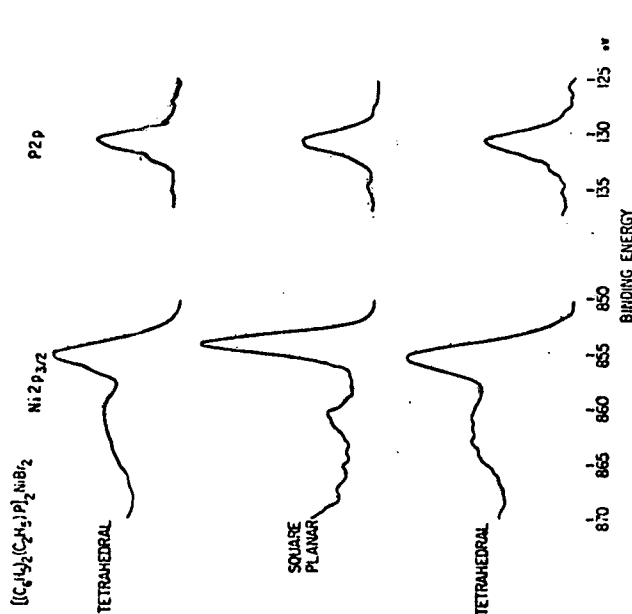


FIGURE 13. Ni_{2p3/2} - P_{2p} spectra for [C₆H₅(C₂H₅)₂PI]₂NiBr₂ in square planar (low spin) and tetrahedral (high spin) configurations.

Warming causes a solid state isomerization to the tetrahedral form and the reappearance of the shake-up satellite structure. Similar studies on a large number of copper compounds have shown that shake-up satellites occur in the 2p_{1/2-3/2} spectra of all Cu^I species, but are absent in the spectra of Cu^I and Cu⁰ compounds.⁵¹ In addition, for both nickel and copper, the shape of the satellite structure differs somewhat among different compounds and appears to be characteristic of the ligand or anion bound to the metal. (This fact has been used as evidence that at least a portion of the shake-up satellite structure is due to a ligand to metal charge transfer excitation.⁵²) Figure 14 compares the Ni_{2p1/2-3/2} spectra from NiCl₂ and NiO. Both compounds are high spin Ni^{II} and exhibit shake-up satellites in their spectra. The satellite structure is sufficiently different in the two spectra, however, that it can easily be used to distinguish one compound from the other.

6. Final State Sources of Multi-line Structure/ Exchange Splitting

When unpaired electrons are localized on an

atom being studied by ESCA, each core level spectrum from that atom can exhibit multiple peaks due to exchange coupling of the unpaired electrons with the photohole.⁵³ Consider the Mn_{2s} spectrum from MnF₂ shown in Figure 15 as an example.⁵⁴ The Mn^{II} ion has 5 unpaired d electrons, and the final state for 3s photoemission (3s¹ 3p⁵ 3d⁵) can be either a ⁷S or ⁵S state, depending upon whether the 3s electron remaining after photoionization has its spin parallel to (⁷S) or antiparallel to (⁵S) the d electrons. The ⁷S state is slightly lower in energy than the ⁵S state because exchange interaction between electrons with parallel spins reduces the electron-electron coulomb repulsion. The two large peaks observed in the Mn_{2s} spectrum of MnF₂ correspond to the two final states, with the higher intensity ⁷S peak found at lower binding energy as expected. (The two small peaks are due to ⁵S states with other electron configurations.) The separation between the ⁷S and ⁵S peaks is equal to the energy difference between the 2 final states and is proportional to the quantity (2S + 1), where S is the total spin on the metal atom in the final state.

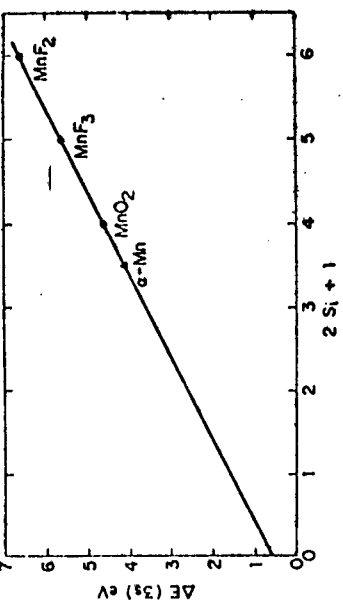


FIGURE 16. Mn_{3s} $2s$ separation, ΔE , vs. $2Si + 1$ for Mn^{2+} , MnF_2 , MnO_2 , and α -Mn. [From McCreely, F. R., Kowalczyk, S. P., Ley, L., and Shirley, D. A., *Solid State Commun.*, 15, 1051 (1974). With permission.]

If it can be assumed that the spin density on the atom is the same in the initial and final states, then for a series of compounds of a particular paramagnetic metal, the splitting of the peaks in the ESCA spectrum should be related to the total spin on the metal or to the covalent character of the metal-ligand bond.

Qualitative trends of the magnitude of the $3s$ splitting with total spin and metal-ligand covalent character have been reported in the literature for Cr, Fe, and Mn.⁵⁵ Kowalczyk et al.⁵⁶ have used the Mn_{3s} splitting found for α -Mn metal, compared with those found for MnF_2 (Mn^{II}, d^5), MnF_3 (Mn^{III}, d^4), and MnO_2 (Mn^{IV}, d^3), as evidence of a localized magnetic moment in α -Mn metal (see Figure 16). The reader is cautioned, however, that the relationship of total spin with core level splitting may not be characteristic of all paramagnetic metals. For example, no correlation of Cu_{3s} splitting with the covalent character of Cu^{II} ligand bonds has yet been found.⁵¹ Additional research on standard compounds is needed in this area.

B. Quantitative Analysis

In order to solve many problems related to surface chemistry, it is necessary to determine only qualitatively the major elements present on the surface and, in some cases, the oxidation states of these elements. Other problems require that relative or even absolute atomic concentrations be determined. A number of successful studies have appeared in the literature which use the ESCA technique for quantitative analysis. These studies

include measurements of both surface and bulk compositions in such diverse areas as chemically treated polymer surfaces,⁵⁷ fluorochromicals sorbed on polymer fibers and films,⁵⁸ aluminum oxide films on aluminum foil,⁵⁹ electrodeposited metals,⁶⁰ metals chelated to fiberglass surfaces,⁶¹ structural groupings in nitroso rubbers,⁶² molybdenum oxidation states,⁶³ and gold-silver alloys.⁶⁴ These examples, as well as applications in our own laboratories, have shown that ESCA can be used routinely as a semiquantitative ($< \pm 50\%$ relative error) tool when relative atomic concentrations are compared among samples. Quantitative ($< \pm 10\%$ relative error) comparisons are also possible within a series of closely related samples.

This section of the paper discusses extrinsic and intrinsic energy loss processes⁶⁵ and demonstrates how differences in these processes from sample to sample can affect the accuracy of quantitative analysis. A simple model which can be used to obtain relative atomic concentrations at a sample surface is presented. The assumptions inherent in this model are critically examined, and some general guides for the analyst are suggested to aid in the quantitative interpretation of ESCA spectra.

1. Extrinsic Energy Loss Processes

In order to discuss quantitative surface analysis, it is necessary to have an understanding of the inelastic electron scattering processes which determine the effective sampling depth of the ESCA technique in solid samples. These inelastic electron scattering events are commonly referred to as

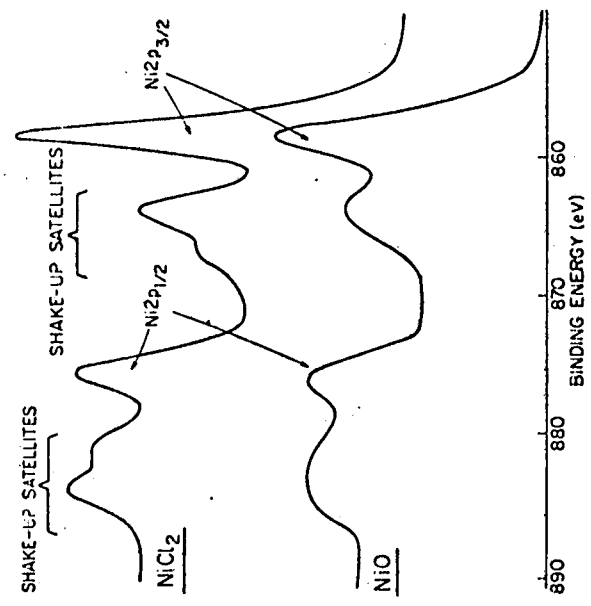


FIGURE 14. $Ni_{2p_{3/2}}$ spectra for $NiCl_2$ and NiO .

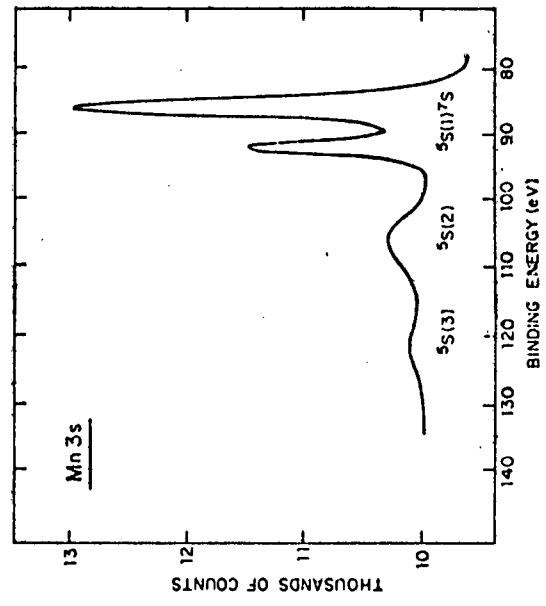


FIGURE 15. Mn_{3s} spectrum from MnF_2 . [From Kowalczyk, S. P., Ley, L., Poliak, R. A., McCreely, F. R., and Shirley, D. A., *Phys. Rev. B*, 7, 4009 (1973). With permission.]

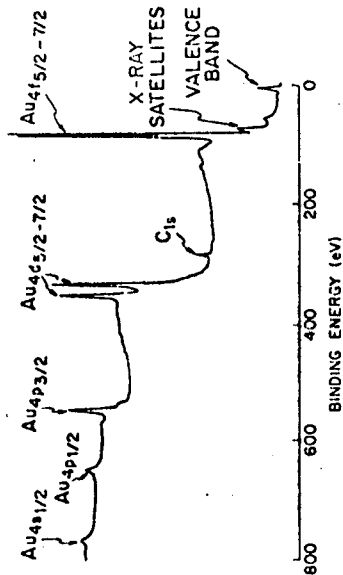


FIGURE 17. Partial survey scan from gold foil.

extrinsic events, as they occur after photoionization has taken place and the photoelectron is moving through the solid. Consider the broad "survey scan" of gold foil shown in Figure 17. Discrete photoelectron peaks are found in the spectrum for the valence band at near zero binding energy and, progressing toward higher binding energy, for each successive electronic level in the gold atom. A small amount of carbon contaminant is also present at the gold surface. Note, however, that these discrete peaks actually account for less than 1% of the total number of electrons detected. There is a large increase in background to the left (lower kinetic energy) of each peak that is due to photoelectrons which, before escaping from the sample surface, have lost a portion of their kinetic energy by undergoing one or more inelastic scattering processes. This high probability for inelastic electron scattering is the property of electrons in solids that makes ESCA a surface-sensitive technique. Only those photoelectrons generated within the top few atomic layers of the sample have a significant probability of escaping the sample without losing a portion of their kinetic energy. Qualitatively, one can think of a number of inelastic events which can take place as a photoelectron (or any free electron) moves through a solid.⁶⁶ For example, the electron may scatter inelastically from a bound electron in the matrix by exciting it to some bound but normally unfilled state in the conduction band (e.g., interband transition) or to an unbound state (ionization). The free electron can also inelastically scatter from collective modes of electron (plasmon) or lattice (phonon) oscillations. Finally, inelastic interaction with other quantized particles

(excitons, etc.) in solids may also be possible, but little is known about these interactions at present. It is important to note that each solid matrix will have a different ability to inelastically scatter electrons, depending upon the number and energies of the available transitions in that matrix. Thus, the inelastic mean free paths of photoelectrons in solids and, consequently, the sampling depth of the ESCA technique will vary from sample to sample.

Experimentally, it can be shown that the relative importance of different inelastic scattering mechanisms can change with different matrices. Figure 18 shows two 200-eV scans of aluminum encompassing both the Al_{2s} and Al_{2p} photoelectron lines. The lower spectrum is labeled "oxidized" and was taken using a sample of aluminum foil that had been exposed to the atmosphere. Both aluminum core levels are doublets with, in each case, the higher binding energy peak being due to the aluminum oxide layer on the surface of the foil, and the lower binding energy peak being due to the metal substrate. The upper spectrum is labeled "clean" and was taken on the same piece of aluminum foil after mechanically abrading the surface under a flowing stream of dry nitrogen. Although the oxide/metal doublets are still evident in the "clean" spectrum, substantially less oxide is present on this abraded surface when compared to the "oxidized" surface. Note the differences in the general shapes of the background for the two samples. First, the background in the "oxidized" sample is still rising at 250-eV binding energy, while it is falling in the "clean" sample. Even more striking, however, is the discrete structure evident in the "clean" foil spec-

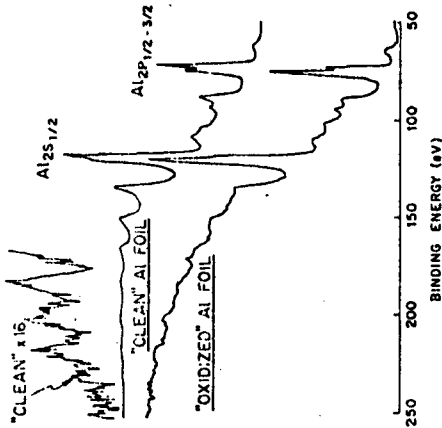


FIGURE 18. Al_{2s} - Al_{2p} and energy loss spectra for "clean" and "oxidized" aluminum foil.

trum. At least six discrete peaks at kinetic energies lower than the Al_{2s} line can be identified. Going towards lower kinetic energies, these peaks have successively lower intensities and are separated from one another by ~17.5 eV, the energy of the bulk plasma oscillation in aluminum. These peaks arise from Al_{2s} photoelectrons which, on escaping from the sample, have lost a discrete amount of energy (from 1 to 6 times ~17.5 eV) in scattering from the bulk plasmon in aluminum. The remaining structure in the "clean" spectrum can be assigned either to X-ray satellites or to surface or bulk plasmon loss structure associated with the Al_{2p} photoelectrons. Some of this plasmon structure can also be seen in a careful inspection of the "oxidized" spectrum, but it is clear from the general lack of discrete structure that a different inelastic electron scattering mechanism, probably electron-electron scattering, is important in the oxide layer. Different inelastic scattering processes will usually involve different excitation energies and a different number of total possible excitations. As will be shown below, the energy and number of possible excitations in a solid matrix determine the total probability for inelastic electron scattering in that matrix, and thus it is likely that the inelastic mean free paths of the Al_{2p} and Al_{2s} electrons are different in aluminum metal than in aluminum oxide.

For an electron moving in a solid, we can define a total inelastic scattering coefficient, S_i , which is related to the probability of that electron under-

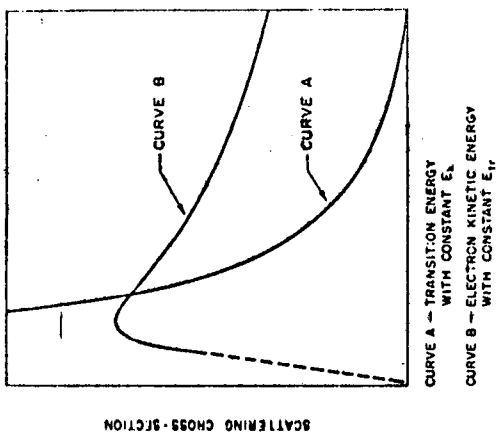


FIGURE 19. Dependence of inelastic electron scattering cross-section on (a) transition energy at constant electron kinetic energy, and (b) electron kinetic energy at constant transition energy.

going an inelastic event. S_i is usually given in units of $(\text{length})^{-1}$ and by definition is equal to $1/\lambda$, where λ is the inelastic mean free path of the electron in the solid. Wendt,⁶⁷ Wheeler,⁶⁸ and Powell⁶⁹ have separately derived equations relating the inelastic electron scattering coefficient to the kinetic energy of the photoelectron, E_K , and the electronic transition energy, E_{Tr} . These equations are generally similar in form and can be expressed by:

$$S_i = \frac{C}{E_K} \frac{Z_{Tr}}{E_{Tr}} \left(\frac{4E_K}{E_{Tr}} \right) \quad (13)$$

where C is a normalization constant. Z_{Tr} is the number of electrons in the matrix which are available for some excitation of energy E_{Tr} , and the summation is carried out over all possible electronic excitations (where E_{Tr} is less than E_K) in the solid. Unfortunately, unless the complete filled and unfilled density of electronic states is known for a given sample, allowed values of E_{Tr} (and Z_{Tr}) will not be known, and Equation 13 cannot be solved exactly. Calculations using various approximations for Z_{Tr} and E_{Tr} have been attempted,⁷¹ but none of these calculations can be applied presently to analytical samples. Even so, an inspection of Equation 13 gives us some qualitative information of value. Curve A of Figure 19 shows, from Equation 13, the general form of

the inelastic electron scattering coefficient versus the transition energy involved in a single inelastic event for a photoelectron with some known kinetic energy. It can be seen that the probability for inelastic electron scattering increases dramatically as the energy of the excitation gets smaller. Consequently, the number and energy of the unfilled states closest to the filled states, and the valence rather than the core electrons, will be important in determining the inelastic mean free path of a photoelectron in a solid. Curve B in Figure 19 plots the general form of the inelastic electron scattering coefficient versus the photoelectron kinetic energy for some known excitation in the matrix by the photoelectron. This curve rises from zero at some threshold corresponding to the excitation energy to a maximum at about three times the threshold energy, and then decreases with electron kinetic energy. (A dotted line is shown for the beginning of the curve and as this portion is derived from experiment and is not well-described by Equation 13. According to Powell,⁶⁹ structure may be observed in this region.) Recalling from Equation 13 that the total inelastic scattering coefficient is composed of a sum of the individual coefficients for each possible inelastic event, the total inelastic electron scattering coefficient for a particular solid matrix will not be a smoothly varying function of the photoelectron kinetic energy. As the kinetic energy of the photoelectron increases, additional thresholds will be crossed, and the total probability for inelastic scattering will be increased by the addition of the new possible excitations. From Curve A, however, the probability of these additional excitations occurring, relative to the low energy transitions, becomes small very quickly as the threshold energy increases. This is the "saving grace" for quantitative surface analysis by ESCA. In the kinetic energy region of interest (~200 to 1500 eV), the additional excitations which become possible with higher and higher E_k result in very small perturbations to the total S_i vs. E_k curve, and in this kinetic energy region of the curve, S_i can be approximated by a smoothly varying function of $1/E_k$. Although the absolute magnitude of S_i can change dramatically from sample to sample, the E_k dependence remains approximately the same and, as pointed out below, relative photoelectron intensities can be compared from sample to sample.

2. Intrinsic Processes

Thus far, we have only considered extrinsic

energy loss processes or those which occur after photoionization has taken place and the photoelectron is moving through the solid matrix. Intrinsic processes can also affect the number of photoelectrons from a core level detected at a particular kinetic energy. Intrinsic processes are those which occur during the ionization process, such as shake-up and multiplet structure due to unpaired electrons (discussed in Section II.A). These processes can partition the photoelectrons from a given core level into two or more kinetic energies. The intensity (and position) of a shake-up satellite relative to the main line can be very sensitive to local electronic effects and may change from sample to sample.⁵⁰ Thus, for quantitative analysis, it is necessary to sum the areas of all the peaks resulting from a single core level. In some cases, the distribution of final states is large enough that the resulting multiplet structure is broad and ill-defined, and measurements of the total area of the multiplet structure become difficult or impossible. Thus, core levels which are known from the literature to exhibit shake-up satellites (e.g., 2p levels in some first row transition metals) or multiplet effects with large energy separation (e.g., 2p and 3s levels in some first-row transition metals) should not generally be used for quantitative analysis even though they may be the most sensitive core levels for the atoms of interest. Less sensitive lines (e.g., 3p in some first row transition metals) which do not exhibit these effects are a better choice even though more time may be necessary to acquire a spectrum of good quality. If one is forced to use a core level that does exhibit intrinsic structure, summing the areas of all peaks appears to be the only present solution for quantitative analysis since the theory of shake-up and multiplet splitting cannot be applied routinely to most samples of analytical interest.

The effect of intrinsic processes on relative intensity ratios can be significant even when large intrinsic satellites are not immediately apparent in the spectrum. Table 3 lists the Na_{1s}/F_{1s} intensity ratios, corrected for stoichiometry, for seven different sodium and fluorine containing compounds. The ratios were determined both by Wagner⁷⁰ and by Swingle.⁷¹ Swingle's ratios are somewhat higher than those measured by Wagner, possibly because of surface contamination effects. However, the same order of intensities is observed from compound to compound, and the amount of variance in the ratios is very large (~100%). The energy loss regions for the Na_{1s} , F_{1s} , and Na_{2s} levels were examined by Swingle to determine if

TABLE 3

Compound	Na_{1s}/F_{1s} Intensity Ratios from Wagner ⁷⁰	Swingle ⁷¹
NaF	2.00	2.24
NaBF ₄	2.59	3.43
Na ₂ FeF ₆	1.48	1.86
Na ₂ SiF ₆	2.14	2.26
Na ₂ GeF ₆	2.33	2.70

⁷⁰Data from Reference 70.

⁷¹Data from Reference 71.

differences in the discrete energy loss structure associated with the photoelectrons of each compound could account for these intensity ratio variations. Figure 20 shows the energy loss spectra for these electrons in NaF normalized for kinetic energy. The sodium 2s peak is included for kinetic reference purposes. A striking similarity in the loss regions of all 3 electrons is noted, with the first major energy loss occurring at approximately -11.0 eV. A comparison between these data and the 50-keV electron transmission experiments on NaF by Creuzberg⁷² indicates that this is a plasmon loss. At 22.0 eV, sufficient structure for the harmonic process is also present for all 3 photoelectrons, but the remaining structure of each loss region is not solely accounted for by extrinsic energy loss processes. While there is qualitative agreement between the shapes of the sodium 1s and sodium 2s spectra, the fluorine 1s spectrum shows significantly more structure, including a large peak at 27.0 eV which is not visible in either sodium spectrum. Consequently, this peak must be due to one or more intrinsic processes, possibly shake-up, which are characteristic of the fluoride ion in NaF.

Figure 21 compares the F_{1s} energy loss spectra from NaBF₄ with NaF. The portion of the loss region exhibiting identifiable structure in NaBF₄ has been shaded to emphasize its approximate area relative to the area of the main photoelectron peak. It is apparent that any change in the intensity of the discrete energy loss structure from compound to compound can have considerable effect on the area of the photoelectron peak. For example, in Figure 21, note the large loss at 32.5 eV in the NaBF₄ spectrum which does not occur in NaF. This peak is likely due to some intrinsic process as it is not present with the same

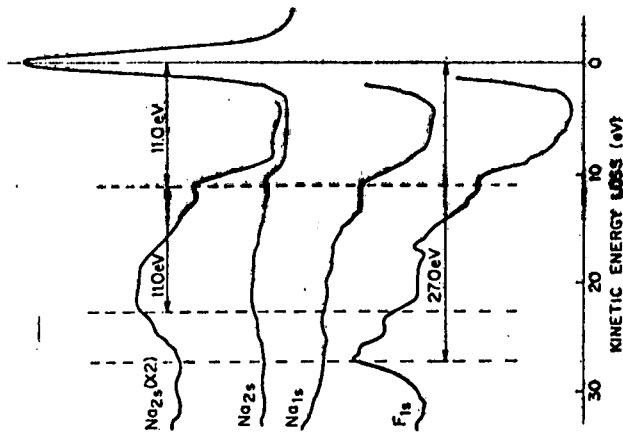


FIGURE 20. Energy loss spectra for Na_{1s} , Na_{2s} , and F_{1s} photoelectrons from NaF. [From Swingle, R. S., II, *Anal. Chem.*, 47(1), 21, (1975). With permission.]

relative intensity in the Na_{1s} spectrum of NaBF₄. The area of this satellite is ~25% of the area of the F_{1s} line, and its presence could account for the high Na_{1s}/F_{1s} ratio noted in Table 3 for NaBF₄.

Generally, in solids, the energy loss structure is not well-defined, and it is not realistic to try to include selected areas of the loss structure in a measurement of the photoelectron peak intensity. Each photoelectron can have a different total probability for extrinsic plus intrinsic energy loss, and this fact will be reflected in an increase or decrease of the photoelectron peak area. Any model for quantitative surface analysis using ESCA must take this fact into account, and attempt to minimize its effect on quantitative accuracy.

3. Quantitative Theory

In the previous sections, we have discussed extrinsic and intrinsic energy loss processes for

atom, however, can be substantially ($>20\%$) larger for those orbitals with lower angular momenta compared to the values calculated for 125-eV radiation. This effect has been confirmed experimentally by Wagner.^{7,8} and Table 5 lists some measured relative intensities for different levels in the same atoms taken using both Mg K α and Al K α radiation.

The relative photoelectric cross-sections shown in Table 4 compare favorably with the experimentally determined atomic sensitivities published by Wagner for the Varian IEE-15 spectrometer.^{7,9} Figure 22 plots atomic number versus Wagner's relative sensitivities using the 1s, 2p $_{3/2}$, 2s $_{1/2}$, and 4f $_{7/2}$ levels where appropriate. (Note that Wagner's sensitivities are referenced to the F $_{1s}$ level vs. the C $_{1s}$ reference level in Table 4.) Because of the energy-loss problems discussed in the previous two subsections, it is difficult to accurately determine relative atomic sensitivities using solid standards. Until comprehensive measurements of photoelectric cross-sections have been made on gas phase systems, the calculated cross-sections are probably more accurate than relative sensitivities based on experimental measurement of photoelectron intensities from solids.

In summary, the simple treatment outlined above says that for spectrometers using a retarding field to sweep the kinetic energy spectrum, the area of a photoelectron line divided by its respective sensitivity factor (photoelectric cross-section) gives a "corrected intensity" which is related to the number of atoms of that element on the sample surface. Ratios of these corrected intensities for different elements detected on the same sample surface give a good estimate of the relative atomic concentrations at that surface, particularly if the photoelectron kinetic energies are similar. It is not possible at present to calculate absolute atomic concentrations (e.g., atoms/cm 2) at a surface from these corrected intensities unless critical assumptions are made concerning surface morphology, atomic density, and the magnitude of S_j in the solid of interest, or unless carefully selected standards with known surface compositions are available.

The experimentalist must exercise caution when using a material of known bulk stoichiometry as a "standard" for ESCA. One must know whether the surface of the standard is truly representative of the bulk stoichiometry, and this may not be easy to determine. Nearly all materials

intensities to N_j . However, in spectrometers which use a retarding field to sweep the ESCA spectrum, it has been shown empirically that, to a large extent, the kinetic energy dependences of the K_j and S_j terms in Equation 14 cancel one another, and that Equation 14 can be approximated by:

$$I_j(\infty) = A \alpha_j N_j \quad (15)$$

where A is constant for a given sample. (The magnitude of A will change from sample to sample since, as noted previously, the magnitude of S_j varies with the sample. However, the kinetic energy dependence of S_j can be approximated by a smoothly varying function of $1/E_k$ in the 200- to 1500-eV range.) Relative atomic concentrations for elements on the same surface can then be calculated from:

$$N_j/N_i = \frac{I_j(\infty) (\alpha_i)}{I_i(\infty) (\alpha_j)} \quad (16)$$

Note that if the kinetic energies of the i and j photoelectrons are nearly the same, it is not necessary to assume that the kinetic energy dependences of the K_j and S_j terms in Equation 14 cancel one another. In this case, Equation 16 follows directly from Equation 14 since $S_i = S_j$ and $K_i = K_j$. Consequently, if possible, it is generally advisable to use photoelectrons of about the same kinetic energies for the best quantitative results.

Atomic emissivities, α_j , which correlate directly with relative elemental sensitivities in the Varian IEE-15 spectrometer have been calculated by Wendt from known values of X-ray mass absorption coefficients. α_j can also be estimated from the more recent mass absorption coefficients tabulated by Henke and Ebisu or from calculated photoelectric cross-sections. Table 4 lists Swingle's compilation^{7,8} of the Mg K α (1254-eV) photoelectric cross-sections relative to the C $_{1s}$ level for each element in the periodic table. Values in this table were taken from J. H. Scofield's absolute cross-sections calculated using Hartree-Slater orbitals.^{7,6,7,7} Al K α (1487-eV) photoelectric cross-sections have also been calculated by Scofield and, relative to the C $_{1s}$ level, the most sensitive level for each element agrees within $\sim 10\%$ with those values shown in Table 4 for Mg K α radiation. The 1487-eV photoelectric cross-sections for different atomic levels within the same

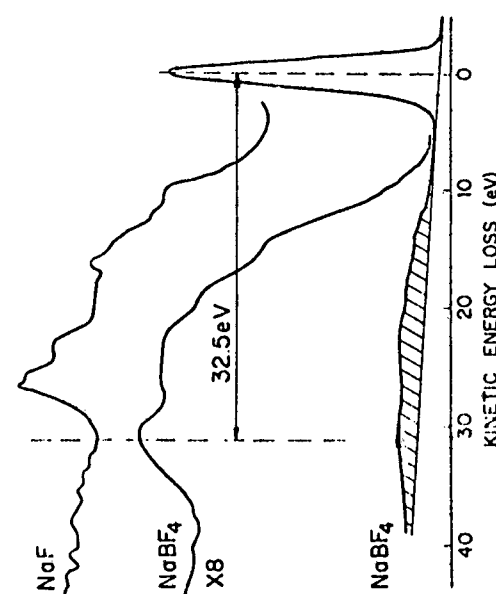


FIGURE 21. F $_{1s}$ energy loss spectral regions for NaF 8 and NaF. [From Swingle, R. S., II, *Anal. Chem.*, 47(1), 21 (1975). With permission.]

thick layer as far as the ESCA technique is concerned.

Several expressions have been developed which relate the photoelectron intensity from an infinitely thick sample to fundamental parameters. These expressions are more or less complex depending upon which variables (sample density, photon flux, source-sample-analyzer angular geometry, surface "shading" effects, instrument kinetic energy response function, etc.) are taken into account. For this discussion, the simplified expression first proposed by Wendt and Riggs^{4,9,6,7} will be used.

For an infinitely thick sample, the intensity for photoelectron j , $I_j(\infty)$, can be written as:

$$I_j(\infty) = K_j \alpha_j N_j / S_j \quad (14)$$

where α_j is the emissivity of the core shell of interest in atom j , N_j is the number of such atoms per cubic centimeter, K_j is the instrument response function dependent upon the kinetic energy of the photoelectron, and S_j is the total inelastic electron scattering coefficient in cm $^{-1}$ for photoelectron j in the sample of interest. For many spectrometers, accurate instrument response functions are not known at present, and Equation 14 cannot be used in its absolute sense to relate photoelectron

photoelectrons in solids and have demonstrated in a qualitative fashion how differences in these processes from sample to sample affect the accuracy of quantitative analysis. In this section, a method is presented which can be used to determine semiquantitative relative atomic concentrations at a sample surface. Because photoelectron intensities depend upon the inelastic mean free path of the photoelectron as well as the atomic concentration, it is convenient for purposes of discussion to divide solid samples into categories dependent upon the homogeneity of the sample in the surface (XY) plane and depth (Z) directions. Application of the quantitative theory to each class of compounds can then be discussed separately. The reader is cautioned to use the material presented in this subsection as a guide, only. Other, more detailed, quantitative models are possible,^{7,5,7,6} and not all the conclusions presented here are universally accepted.

a. Class I Samples

Samples falling in this class are homogeneous in the XY plane as well as in the Z direction over a range greater than three to five times the inelastic mean free path of the highest kinetic energy photoelectron of interest. Consequently, the sample is fully homogeneous throughout an infinitely

257

TABLE 4

Photoelectric Cross Sections Relative to Cls Level for Mg K α (1254eV) Radiation

	1s _{1/2}	2s _{1/2}	2p _{1/2}	2p _{3/2}	3s _{1/2}	3p _{1/2}	3p _{3/2}	3d _{3/2}	3d _{5/2}	4s _{1/2}	4p _{1/2}	4p _{3/2}	4d _{3/2}	4d _{5/2}	4f _{5/2}	4f _{7/2}	5s _{1/2}	5p _{1/2}	5p _{3/2}	5d _{3/2}	5d _{5/2}	5f _{5/2}	5f _{7/2}	6s _{1/2}	6p _{1/2}	6p _{3/2}	6d _{3/2}	6d _{5/2}	6f _{5/2}
1	0.0002																												
2	0.0019																												
3	0.019																												
4	0.019																												
5	0.0008																												
6	0.0008																												
7	0.0008																												
8	0.0008																												
9	0.0008																												
10	0.0008																												
11	0.0008																												
12	0.0008																												
13	0.0008																												
14	0.0008																												
15	0.0008																												
16	0.0008																												
17	0.0008																												
18	0.0008																												
19	0.0008																												
20	0.0008																												
21	0.0008																												
22	0.0008																												
23	0.0008																												
24	0.0008																												
25	0.0008																												
26	0.0008																												
27	0.0008																												
28	0.0008																												
29	0.0008																												
30	0.0008																												
31	0.0008																												
32	0.0008																												
33	0.0008																												
34	0.0008																												
35	0.0008																												
36	0.0008																												
37	0.0008																												
38	0.0008																												
39	0.0008																												
40	0.0008																												
41	0.0008																												
42	0.0008																												
43	0.0008																												
44	0.0008																												
45	0.0008																												
46	0.0008																												
47	0.0008																												
48	0.0008																												
49	0.0008																												
50	0.0008																												
51	0.0008																												
52	0.0008																												
53	0.0008																												
54	0.0008																												
55	0.0008																												
56	0.0008																												
57	0.0008																												
58	0.0008																												
59	0.0008																												
60	0.0008																												
61	0.0008																												
62	0.0008																												
63	0.0008																												
64	0.0008																												
65	0.0008																												
66	0.0008																												
67	0.0008																												
68	0.0008																												
69	0.0008																												
70	0.0008																												
71	0.0008																												
72	0.0008																												
73	0.0008																												
74	0.0008																												
75	0.0008																												
76	0.0008																												
77	0.0008																												
78	0.0008																												

258

TABLE 5

Effect of Photon Energy on Measured Relative Intensities

Sample	Element	Orbitals	Intensity Ratios	
			Mg Ka (1254 eV)	Al Ka (1487 eV)
MgF ₂ 4A SiCve	Mg	2 ¹ /2s	0.83	0.70
	Al	2p/2s	1.04	0.82
	Si	2p/2s	1.59	1.23
GeO ₂ NaAlO ₂	Ge	3d/3p _{3/2}	1.29	1.08
	Al	3d/3p _{3/2}	1.19	1.15
	Se	3d/3p _{3/2}	1.36	0.92
Na ₂ SeO ₄ NaB:	B:	3d/3p _{3/2}	1.45	1.15

are subject to some degree to surface contamination by H₂O, CO, CO₂, or hydrocarbon. Most metal alloys exhibit preferential surface segregation of one element relative to another, and oxygen enrichment or deficiency at many metal oxide surfaces appears to be the rule rather than the exception.

Grating angle ESCA^{10,11} described in Section IV, may be useful in determining whether the surface of a "standard" is representative of bulk stoichiometry. Ion sputtering can also be useful in generating surfaces of known stoichiometry, but this technique must be used with great care since preferential sputtering of one element relative to another is a well-documented phenomenon^{11,12} and can lead to a surface which does not consist of the "standard" stoichiometry. For problems in which they are applicable, organic homopolymers are good standards because they are not generally subject to surface oxidation, adsorption, or segregation problems. For other problems, the only general guide is to use a standard as nearly like the sample of interest as possible. When possible, it is best to compare relative atomic concentrations among samples. If absolute concentrations are necessary, the pitfalls mentioned above must be considered.

Note that the quantitative model presented here does not deal with the effects of intrinsic processes on photoelectron peak intensities. As discussed previously, it is not possible to do this for most analytical samples, and peaks exhibiting obvious intrinsic satellites should not be used for quantitative analysis if alternative peaks are available. When comparing intensity ratios from a

closely related series of samples, intrinsic processes will not usually present a problem but, to be sure, the corrected intensities of more than one photoelectron peak from each of the elements of interest can be measured and compared.

b. Class 2 Samples

Samples falling in this class are layered samples that are homogeneous in the XY plane but not homogeneous over the sampling depth of the ESCA technique. If the element of interest is in the top layer and the layer has a thickness X , then the intensity of photoelectron j from that element is given by:

$$I_j(X) = I_j(\infty) [1 - e^{-S_j X}] \quad (17)$$

where $I_j(\infty)$ is the intensity that would be observed if the layer were infinitely thick. For two photoelectrons arising from elements in the top layer, the relative concentrations are given from Equations 14 and 17 as:

$$N_i/N_j = \left(\frac{I_i(X)}{I_j(X)} \right) \left(\frac{1 - e^{-X S_j}}{1 - e^{-X S_i}} \right) \quad (18)$$

Note that this expression has a ratio of exponential terms involving both the layer thickness and the inelastic scattering coefficients of the two photoelectrons. The relative atomic concentrations cannot be calculated directly from Equation 18 unless the kinetic energies of the two photoelectrons are nearly the same (in which case it can be assumed that $S_i = S_j$ and Equation 18 reduces to

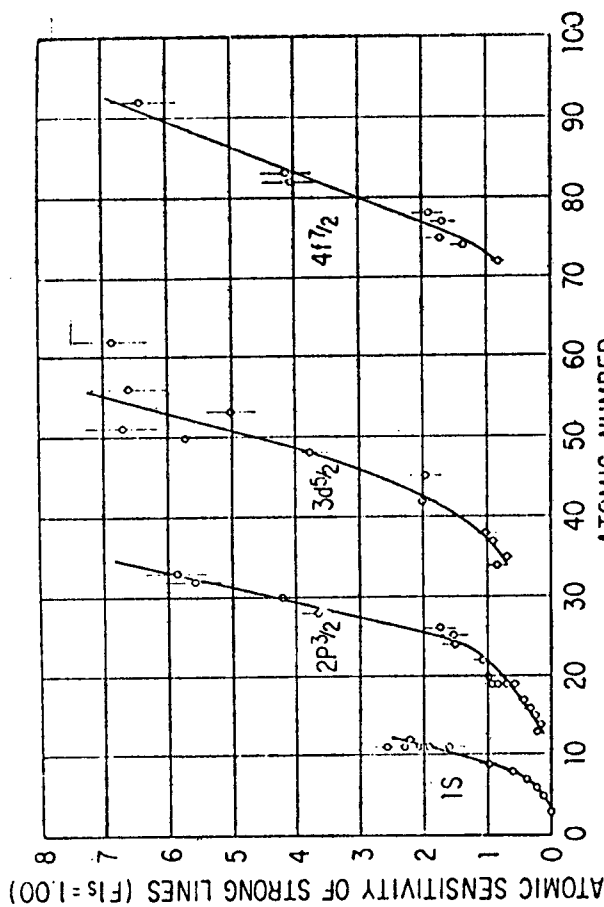


FIGURE 22. Experimental atomic sensitivities relative to F_{1s} level determined on Varian IEE-15 spectrometer. [From Wagner, C. D., *Anal. Chem.*, 44(6), 1050 (1972). With permission.]

Equation 16) or unless the layer thickness is known and absolute values of S_i and S_j in the layer are known or can be estimated (Equation 18 cannot be solved knowing only the relative magnitudes of S_i and S_j). If neither of these conditions can be met, then intensity ratios can be used among similar samples with the same layer thicknesses as a measure of relative concentrations in the surface layers of the samples. However, each corrected intensity ratio will not represent the relative atomic concentration of the two elements at that surface. If the layer thickness cannot be assumed constant from sample to sample, then corrected intensity ratios are not even useful for relative comparison among samples. In these cases, it may be helpful to use grazing angle ESCA in order to reduce the sampling depth of the technique to less than the layer thickness. This effectively changes a Class 2 into a Class 1 sample.

The photoelectron intensity from an element in

a substrate layer covered by a layer of thickness Y is given by:

$$I_j(Y) = I_j(0) [e^{-S_j Y}] \quad (19)$$

where $I_j(0)$ is the intensity that would be observed if the covering layer were of zero thickness, and S_j is the inelastic scattering coefficient of the photoelectron in the covering layer matrix. The same considerations are important in determining relative atomic concentrations for elements in the substrate layer that are mentioned above for the top layer and, consequently, this case will not be treated further. It should be mentioned that, subject to the limitations discussed earlier, ion sputtering may be useful in this case to remove the covering layer, thus changing the substrate into a Class 1 sample.

Comparing photoelectron intensities from elements localized in different layers becomes an

even more complex problem. The special case of an ultrathin surface layer (less than one monolayer) on an infinitely thick substrate is of interest, however, since many samples of practical interest can be treated using this model. Supported metal catalysts with single metal atoms or small metal atom clusters on a substrate and partly exchanged ion exchange resins are two examples of this type of sample. If the substrate is only slightly covered by the surface atoms (1 to 5% coverage), it can be assumed that the intensity of the photoelectrons from atoms in the surface layer is not attenuated at all by inelastic scattering and that the intensity of the photoelectrons from the substrate is not attenuated by the surface layer. Thus, the substrate intensity can be used as an internal standard, and the intensity ratio of the surface atom peak divided by the substrate peak will be directly related to the number of surface atoms on a given sample. Although these intensity ratios are not easily converted to either absolute or relative atomic concentrations at the surface of a single sample, they are useful in direct comparison with intensity ratios from other similar samples as a measure of the relative amounts of the surface-localized element.

C. Class 3 Samples

Samples in this class are not homogeneous in either the XY plane or the Z direction. While the sampling depth depends on the inelastic mean free path of the photoelectron in the solid, there is no X-Y resolution in the ESCA technique, and the spectrum consists of an integral signal from all irradiated portions of the sample surface. In general, only qualitative analysis is possible with Class 3 samples. In certain situations, special sample preparation techniques such as masking portions of the sample surface can be useful. Otherwise, surface analysis techniques with better XY resolution should be used for quantitative analysis.

III. CURRENT ESCA INSTRUMENTATION

Although commercial ESCA instrumentation has only been available for a relatively short time (since about 1970), at least eight different commercial instruments have been available during that period, and they have been characterized by great diversity of design. As with any complex

instrumentation, the design of a commercial electron spectrometer involves a number of trade-offs. We will discuss the important considerations making these trade-offs in ESCA instrumentation. For convenience, this discussion will be organized by instrument component and function, including discussions of vacuum system design, X-ray source design, analyzer design, detectors, modes of scanning, sample considerations, and various means of data output.

A. Vacuum System

1. Required Vacuum Level

There are two basic requirements imposed upon the design of vacuum systems for ESCA measurements. The first is that the analyzer vacuum be sufficient for the mean free path of an electron in the vacuum environment to be long compared to the distance it must travel between sample and detector. This requires vacuum levels on the order of 10^{-6} torr. Most commercial instruments also operate the X-ray source directly in the analyzer vacuum. The vacuum level required for X-ray source operation is similar to that dictated by electron mean free path considerations. The second and more rigorous vacuum requirement is that the vacuum level be sufficient that the sample surface is not altered significantly by the vacuum atmosphere during the measurement. One can show by simple calculation that at a vacuum level of 1×10^{-6} torr, approximately 1 monolayer of molecules per second will accumulate on a surface if the sticking coefficient of the gas molecules is unity on that surface. If sticking coefficients near unity were common, this would mean that vacuum in the 10^{-6} -torr range would be required to maintain a surface in clean condition for a measurement requiring on the order of 1 hr. However, as Tracy²³ has recently pointed out, it is rare for the sticking coefficient of gases on surfaces to be near unity. In fact, for most gases on most materials, the sticking coefficient is less than 10^{-3} , which means that a 10^{-7} -torr vacuum is adequate for most ESCA measurements. Furthermore, the sticking coefficient usually drops drastically after one monolayer of material is adsorbed on the surface; the sticking coefficient of a gaseous molecule on a layer of similar molecules is normally far smaller than the sticking coefficient of the molecule on the bare surface of a material such as a metal. Since the vast majority of samples which one wishes to examine for analytical pur-

poses have been handled in a laboratory atmosphere, their surfaces are already saturated with adsorbed gas when one introduces them into the spectrometer. The likelihood of further gas adsorption as a result of vacuum atmosphere is small. Vacuum requirements are more rigorous for Auger measurements due to phenomena such as electron beam induced adsorption. This has occasionally led, through inappropriate analogy, to the erroneous conclusion that vacuum requirements for ESCA are more stringent than they actually are.

For operation at the relatively moderate vacuum levels that are adequate for ESCA, on the order of 10^{-6} to 10^{-9} torr, the absolute vacuum level is less important than the composition of the vacuum atmosphere. Materials with generally high sticking coefficients or those which, if adsorbed on a sample would interfere with data interpretation (such as hydrocarbons and water) are to be avoided if possible; on the other hand, relatively inert gases such as argon, neon, and nitrogen can be tolerated at relatively high levels during ESCA measurement.

2. Design

The details of the design of the vacuum system for ESCA hardware will depend upon considerations of cost, utility, and intended application of the equipment. The major areas of consideration are discussed below.

Some instruments have sample introduction chambers, and others do not. There are two major advantages to using a vacuum interlock sample introduction system. The first is that the analyzer high vacuum can be maintained at all times and need not be broken for sample interchange. It is possible in some instruments of this design to change samples in as little as 2 to 3 min without significant degradation of the analyzer vacuum. This capability is particularly advantageous in an analytical or other laboratory where sample throughput is an important consideration. Instruments with sample introduction chambers tend to have significantly higher throughput than those which do not, even if only one sample is introduced at a time. A second advantage of the introduction chamber is that with proper design, it can also be used as a reaction or sample preparation chamber. In this chamber, one can conduct experiments such as ion etching the sample, vacuum evaporating metals onto the sample either for calibration purposes or for study of the metals

themselves, and conducting gas-solid reactions which may be of interest in corrosion and heterogeneous catalysis.

The major disadvantage of the sample introduction chamber is that it typically necessitates the use of some sort of sliding vacuum seal. It is relatively difficult to maintain true ultrahigh vacuum conditions when a sliding seal is used to introduce samples, although commercial instruments are available with introduction chambers and sliding seals which operate routinely in the 10^{-9} -torr range. The sample is also exposed to contamination as it slides through the seal chambers during sample introduction. Since the sliding action wipes the probe, this can become a dirty area. Further, traces of water will be carried into the analyzer vacuum probe rod unless a dry box is used around the introduction chamber area.

When rigorous ultrahigh vacuum conditions are desired, sample introduction chambers are normally not used. In these cases, the sample chamber is designed so that a number of samples can be introduced at once, since the pump-down times may be on the order of 12 hr or more, and multiple samples are therefore a requirement in order that sample throughput not suffer to an intolerable extent.

The choice of vacuum pumps for an ESCA vacuum system is one which has been made in a number of different ways by commercial manufacturers. A popular combination of "dry" pumps is a molecular sieve sorption pump for rough pumping in combination with a differential ion pump for producing high vacuum. Advantages of this system include the total absence of pumping fluids, which avoids the possibility of contamination of the sample or vacuum system by these fluids. The pumps are reliable and based on well-known technology. A characteristic of ion pumps is that not all gases are pumped with equal speed. Fortunately, however, the gases which are not pumped well by ion pumps, such as argon, are almost totally innocuous in the ESCA experiment. Therefore, ion pumps are generally a good choice. A second combination which is of value is the use of a cryosorption pump for rough pumping, with both ion pumping and sublimation pumping in the high vacuum section. An ion pump and sublimation pump in close proximity to one another produce synergistic pumping effects since the ion pump pumps material which the sorption pump or sublimation pump does not pump well, and vice

versu. Again, this is a totally dry pumping system capable of producing ultrahigh vacuum. A further advantage of systems utilizing ion pumps is that power failures or pump shutdowns rarely damage ion pumps and the ion current readout serves as a pressure gauge. A third possibility is that of a turbomolecular pump backed by a large mechanical pump. Advantages of this kind of pump are that all gases are pumped with essentially equal efficiency and high gas loads can be tolerated. If the turbomolecular pump is sufficiently large in size, it can also produce ultrahigh vacuum conditions. Disadvantages of this kind of pumping system are that fluid is present in the mechanical pump and lubricating fluids are necessary for the bearings of the pump turbine. In the event of a vacuum accident, the vacuum system can become contaminated with organic fluids from these sources. A further disadvantage is that turbomolecular pumps are relatively expensive. A fourth possibility is the combination of a diffusion pump backed by a mechanical roughing pump. The advantages of this kind of system are that it is based on familiar and thoroughly developed technology and is relatively inexpensive and rugged. The disadvantages, however, lie in the presence of organic pumping fluids in both the diffusion pump and the mechanical pump, necessitating the use of very efficient cryogenic trapping to prevent oil vapors from entering the analyzer and contaminating the sample. In the event of a vacuum accident, the analyzer and sample areas can quite easily become contaminated with organic pumping fluids.

The incorporation of bakeout facilities and the ultimate temperature of bakeout available are other variables in vacuum system design for ESCA. If ultrahigh vacuum is desired, bakeout capability to a temperature of 250°C is typically required. In a system of this kind, bakeout heaters will typically be permanently installed, and flanges and all other materials of construction will be designed to easily withstand the rigors of 250°C at ultrahigh vacuum. A more moderate bakeout in the temperature range of 125 to 150°C is also useful for producing favorable vacuum conditions, especially for reducing the background of water desorbing from the vacuum system walls.

Metal flanges using copper gaskets as sealing materials are normally used in UHV systems. The advantage of this kind of flange design is that it can be baked to 250°C or more without degrading

its performance as a vacuum seal. The disadvantages are that it is relatively expensive and that it is more difficult to work with than alternatives. The major alternative in use in ESCA vacuum flange design is the use of flanges incorporating Viton® fluoroelastomer seals. These seals can readily withstand moderate bakeout conditions and are relatively inexpensive to fabricate and easy to assemble free of leaks. The possibility that the elastomer material will desorb undesirable hydrocarbon material in the vacuum system, however, frequently discourages the use of this type of seal in ultrahigh vacuum systems. With appropriate flange design, however, Viton® can be used effectively in UHV systems. Other gasket materials which are sometimes used include tin and gold. The advantage of these soft metals is that gaskets can be formed to provide bakeable seals on flanges of relatively inexpensive design.

B. X-ray Source Design

1. Generation of X-rays

Generation of X-rays for an ESCA experiment is accomplished by imposing a potential of 10 to 12 kV between a hot filament emitting electrons and the X-ray anode. Electrons are accelerated to the anode material, and the ensuing collisions create inner level vacancies in the atoms of the target material. Subsequent relaxation then produces the characteristic X-rays of the anode material which are used in the ESCA experiment. Bremsstrahlung,⁶⁴ a background of continuous radiation extending to the maximum energy of the excited electrons, is also generated as the high energy electrons decelerate rapidly in the target material. This is illustrated in Figure 23 for both aluminum and magnesium anodes.

2. Target Materials

For purposes of ESCA measurements, aluminum and magnesium are the most useful target materials. Aluminum K α radiation has an energy of 1486.6 eV and an energy distribution (full width at half maximum of the overlapped K $\alpha_{1,2}$ doublet) of approximately 0.9 eV. The magnesium K α line has an energy of 1253.6 eV and an energy width of approximately 0.7 eV. Thus, a somewhat narrower electron kinetic energy distribution and a correspondingly higher ESCA resolution are obtained with a magnesium anode. The slightly lower magnesium X-ray photon energy means that certain otherwise useful ESCA lines, especially

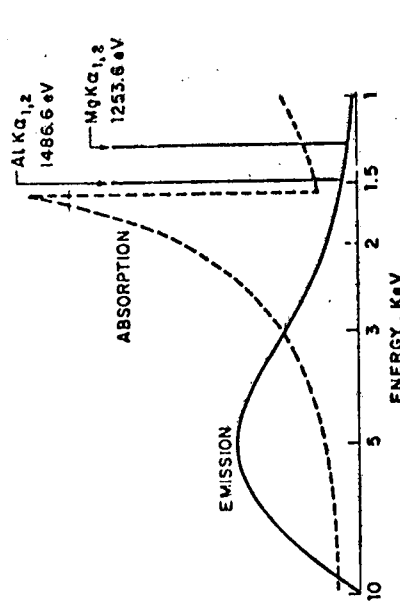


FIGURE 23. Mass absorption coefficient of aluminum as a function of energy (---), and intensity distribution of magnesium or aluminum anode X-ray tubes operated at 10 kV (—).

magnesium L_s are not accessible with this anode, and anode cooling is somewhat more critical. Nevertheless, magnesium is normally the anode of choice for ESCA experiments because of the higher resolution available. Aluminum is used occasionally when it is necessary to observe the magnesium L_s line or to avoid interferences from X-ray generated Auger electrons.

3. X-ray Window/Filter

A thin window is normally interposed between the X-ray source and the sample in an ESCA experiment, primarily to prevent electrons from the X-ray source from entering the kinetic energy analyzer and contributing to the spectral background. For this purpose, thin metal foils, normally aluminum or beryllium, are used. If aluminum is used as the X-ray window, it serves the secondary function of a wavelength filter to improve the signal-to-background ratio observed in the spectra, since the aluminum X-ray absorption spectrum exhibits a K absorption edge at an energy just above that of the aluminum K emission line. Figure 23 illustrates this effect with the aluminum absorption spectrum in the 1 to 10 kV energy range shown superimposed upon the emission spectrum. Inspection of this figure shows that X-rays of energy significantly higher than the K α emission are very strongly absorbed, whereas the K α emission line itself is only weakly absorbed. Even though the effect is not quite so dramatic,

the same filtering of magnesium radiation by the aluminum window material occurs.

4. Line Width Considerations

Minimizing the width of the exciting X-ray line is desirable since the width of this line appears directly in the width of the observed photoelectron peak; the wider the X-ray line, the more resolution suffers. As previously stated, narrow lines are normally obtained through the selection of magnesium as the source of X-rays for ESCA. However, there is commercial instrumentation available wherein crystal dispersion techniques are used to disperse and partially monochromatize the X-rays which fall on the sample. The best known of these schemes⁶⁵ utilizes a technique known as dispersion compensation wherein the X-ray line is dispersed across the sample as a function of energy and the photoemitted electrons are spatially correlated with the point from which they originate on the sample. This dispersion compensation scheme allows the observation of electrons of a range of energy focused as if they were all of the same energy. The advantage of this approach over direct monochromatization using narrow slits is the conservation of the small amount of X-ray energy which is available, producing higher signal strengths than would otherwise be achieved. The use of X-ray source monochromatization allows the observation of ESCA lines approximately 0.4 eV (20 to 40%) narrower than those achievable on

instruments not utilizing X-ray monochromatization. Another important feature of monochromatized systems is the very low background achieved due to elimination of the bremsstrahlung portion of the X-ray spectrum. This is especially significant in the valence band region.

C. Analyzer Design

Numerous schemes have been utilized for measurement of electron kinetic energy distributions. Included here will be only those designs which are presently being utilized in commercial instrumentation or which are significant for historical reasons. More thorough and detailed reviews are available in the literature.^{7,8}

1. Magnetic Deflection

The earliest electron spectrometers for ESCA utilized a magnetic field to sort electrons from one another on the basis of kinetic energy.¹ The magnetic field was scanned by varying the current to coils which produced the field. This type of spectrometer never achieved commercial use, primarily because of its extreme sensitivity to ambient magnetic fields and the need for cancellation of these fields at the spectrometer through the use of surrounding Helmholtz coils. They were also very insensitive and difficult to operate. In spite of their disadvantages, much pioneering ESCA research was carried out with magnetic instruments, and several are still in operation.

2. Spherical Capacitor

The spherical capacitor analyzer⁶ consists of sections of two concentric spheres of different radii. This type of analyzer functions in a manner analogous to a prism and lens system. Electrons having different energies are separated from one another as they traverse the electric field established between the two spherical sectors. Electrons having the same energy and diverging from each other as they enter the analyzer will be brought to a focus at the exit slit. Because of this characteristic, the spherical sector is space focusing; that is, a point source is imaged as a point. Because this analyzer has a well-defined focal plane, it can be utilized with multi-element detectors, which are discussed later.

3. Cylindrical Mirror

The cylindrical mirror or cylindrical capacitor analyzer is another type currently in use in

commercial instrumentation.^{8,9} This analyzer consists of two coaxial cylinders, with the outer cylinder at a potential which is negative relative to the inner cylinder. The sample and detector are located at opposite ends of the cylinders along the common axis. An optical baffle is located inside the inner cylinder to prevent electrons from moving in a straight line from the sample to the detector. The potential difference between the inner and outer cylinders creates a cylindrical electrostatic field. Entrance and exit slots are cut around the circumference of the inner cylinder, with the planes of these slots parallel to each other and normal to the coaxis of the cylinders. The axial symmetry of this analyzer produces space focusing. In contrast to the spherical capacitor analyzer, no focal plane exists with this device. The intrinsic resolution capability of this type of analyzer is apparently not especially high. The commercial adaptation of the analyzer utilizes tandem cylindrical capacitors to improve resolution by causing electrons to traverse two analyzing fields before being detected.

4. Nondispersive Electrostatic Filter

The third type of analyzer currently available commercially utilizes two spherically symmetric retarding fields.^{8,9} A simplified diagram of this analyzer is shown in Figure 24. The first retarding field encountered by the photoelectrons is used in the reflection mode and functions as a low energy pass filter. The second field is used in the transmission mode as a high pass filter. The first filter rejects high energy electrons by scattering from the solid plate which is the second field defining element of this filter; the second filter rejects low energy electrons by simple reflection. There is a small energy overlap between these two filters which yields a narrow transmission function as illustrated. The resolution of this analyzer is dependent only upon the energy overlap of the two filters and the sharpness of their cutoff characteristics and not on acceptance angle or aperture size. Thus, it has the advantage of simultaneous achievement of high resolution and high sensitivity. This analyzer is not space focusing, nor does it have a focal plane.

D. Detectors

1. Single Element Detectors

Most electron spectrometers which are currently available commercially utilize single element

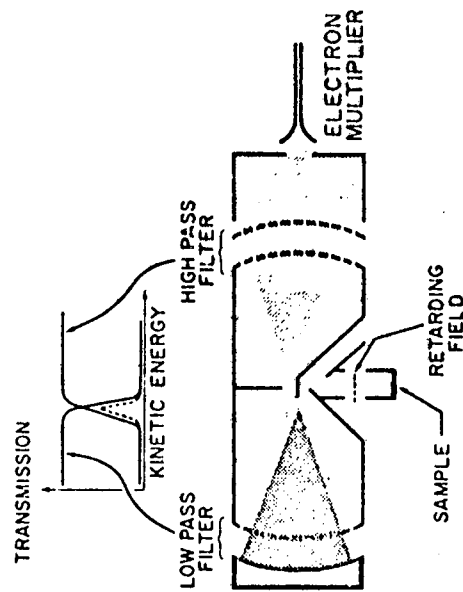


FIGURE 24. Simplified schematic diagram of a nondispersive electron kinetic energy analyzer. (Courtesy of Du Pont Instrument Products Division)

detectors positioned at the exit aperture. By far the more common type of detector in use is the continuous dynode type. Their advantages are relatively high gain, the ability to operate in either a pulse counting or a current mode, and the ability to withstand repeated exposure to air when the instrument is vented without degrading performance. The more conventional multiple stage copper/beryllium type electron multiplier is also usable in ESCA applications, but is much less common.

2. Multi-element Detectors

Electron spectrometers utilizing analyzers which have a focal plane can, in principle, make use of multi-element detectors. These detectors consist of an array of linear multiplier surfaces arranged side-by-side. This array can be placed on the focal plane of the spectrometer, and electrons of a range of energies may be collected across it. By simultaneously examining a large number of resolution elements, multi-element detectors currently in use can produce in excess of 100 X improvement in signal-to-noise ratio per unit data acquisition time.⁹ In the most widely used configuration, a phosphor screen is placed directly behind the array. When an electron strikes a particular element of the array, it creates an electron pulse at the phosphor screen, in turn

generating a pulse of light. A vidicon camera scans the phosphor screen and detectors and transmits the light pulses to the pulse counting equipment of the spectrometer.^{8,9} Since currently it is not technologically feasible to fabricate multi-element detectors such that the gain and noise of all elements is identical, an incident electron will produce a different light pulse intensity on different detector elements, thus distorting the spectral information. In order to circumvent this problem, the spectrum is normally scanned back and forth across the detector array so that each spectral element will be detected for an equal period of time by each detector element, thus averaging out differences in gain and noise from element to element in the detector. The result is true Poisson statistics, which give an improvement in signal-to-noise ratio proportional to the square root of the number of scans. The advantage of these detectors is the dramatic improvement in the amount of time required to take data. An additional potentially useful characteristic of this arrangement is that some spatial resolution (ca 1 mm²) can be obtained by means of electronic slits. The disadvantages include the requirement for a focal plane spectrometer, the cost, and the relatively complicated ancillary equipment such as the phosphor screen, the vidicon camera, and data handling equipment. At the present time, multi-

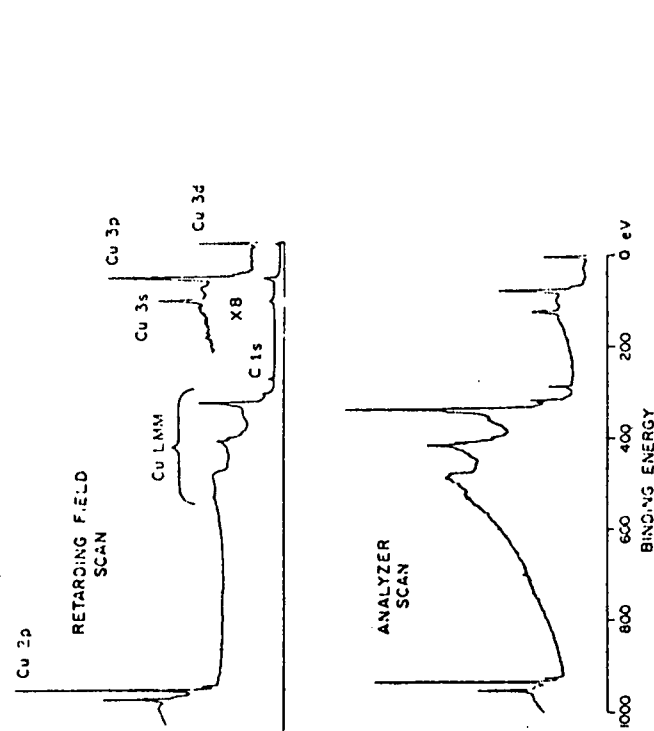


FIGURE 25. Survey spectra of copper metal comparing spectral background and peak intensity ratios from retarding field scanning (top) and an analyzer scanning modes (bottom).

element detectors are used only in instruments utilizing X-ray monochrometers because of the low signals achieved from such instruments and the corresponding need to enhance them by every means available.

E. Scanning Mode

There are two fundamental ways in which an ESCA spectrum may be scanned. The first is to scan the electron kinetic energy analyzer so that the electron energy which will pass through it to the detector is continuously varied. In the case of the spherical capacitor or the cylindrical mirror analyzer, this is done by varying the electrostatic field between the spherical or cylindrical electrostatic elements of the analyzer. In the case of the nondispersive analyzer, the energy of the filter functions would be continuously varied. There is one commercial spectrometer currently available which scans exclusively in this mode, and another is available which can scan in either mode. The

appears to be more intense in the analyzer scanning mode than does the copper 2p 3/2 photoelectron line. This is anomalous, for the number of emitted LMM Auger electrons cannot exceed the number of emitted Cu 2p electrons since the Auger transition begins with a 2p vacancy. In the retarding field scan mode, the Cu 2p_{3/2} line is approximately 3 times as intense as the Auger line, which is qualitatively in agreement with expectation. This reflects the basic difference between the two scanning modes: the analyzer scanning mode tends to distort the spectrum in favor of electrons at high kinetic energy, whereas the retarding field mode does not. This is due to the fact that with retardation, the spectrometer sensitivity variation with kinetic energy tends to cancel the effect of changing electron escape depth with kinetic energy. The discussion in Section II.C clarifies this further. From an analytical point of view, it appears on empirical grounds that the retarding field mode is more convenient because of the agreement of peak intensity ratios observed between spectra obtained in this mode and the relative sensitivities derived from the calculated photoelectric cross-sections (Table 4). Samantiallative estimation of sample composition is therefore more straightforward using spectrometers scanned by retardation.

F. Sample Considerations

Some of the most important instrumental design considerations are centered on the size, shape, and other characteristics of the sample, as well as the facilities for preparing, manipulating, and pretreating the sample. Some of these are discussed briefly below.

The sample phase is obviously a primary consideration. Spectrometers are available which can accept both solid and gas phase samples. To date, gas phase X-ray photoelectron spectroscopy research has revealed little direct analytical application. Therefore, at the present time, the ability to handle solid samples is the only important consideration for spectrometers intended for analytical measurements.

Spectrometers vary in their ability to accept samples of different sizes and shapes since this is a design compromise involving other factors. With any present available sample configuration, one must occasionally use his ingenuity to get his sample into the instrument. In most spectrometers, a sample with a rough surface will give a lower signal

intensity than a sample of the same composition with a smooth surface. In spectrometers using X-ray monochromators and dispersing optics, resolution also degrades with sample roughness. In these instruments, the depth of field of the entrance lens is very small and the sample must be positioned within a few thousandths of an inch to optimize resolution and sensitivity.

Some spectrometers maintain the sample in a horizontal configuration at all times, while others either do not mount the sample horizontally or require that it be rotated through a nonhorizontal configuration for insertion into the spectrometer. Obviously, if a horizontal configuration is maintained throughout, this is an advantage for operating with powdered samples which then need not be held in place with an adhesive or other special arrangement.

If liquids or other volatile materials are to be examined, the ability to lower the sample temperature in order to reduce the vapor pressure sufficiently so that it may be examined in the vacuum environment may be required. Conversely, the ability to increase sample temperature above ambient can be important if phase transitions are to be studied or gas-solid reactions at the sample surface are to be conducted.

The availability of a sample reaction chamber is an important instrumental consideration. Conducting gas-solid reactions is best done in a special chamber in order to avoid exposure of the spectrometer to corrosive or otherwise damaging environments. Other kinds of sample pretreatment such as ion etching, scraping, vapor deposition of metals, and fracturing to expose fresh surface are also best done in a chamber connected to, but isolated from, the analyzer chamber.

The ability to ion etch samples is a further useful capability. Ideally, the angle between the sample and the ion beam will be between 25 and 40° in order to maximize the etching rate.^{91,92} The ion beam energy should be relatively low—normally below about 2000 eV in order to minimize the amount of damage done to the surface by the ion beam.

The ability to do angular dependence measurements in the spectrometer can be important both for quantitative work (see Section II.C) and in order to obtain in-depth information nondestructively (Section IV.C).

It is sometimes important to be able to transfer samples into the spectrometer while maintaining

them under an inert atmosphere. Although no commercial spectrometers have attachments available for this procedure, some are more easily adaptable to transfer of samples under inert atmosphere than are others.

G. Data Acquisition and Processing

In current ESCA instrumentation, the data obtained are inherently digital, with electron counting being the normal detection mode. Thus, digital data accumulation systems, such as multichannel analyzers and computers operating in multichannel data acquisition modes, are common. At least two commercially available ESCA instruments also have analog data collection modes. When the signal is sufficiently strong, it is convenient to convert the digital signal to analog with an appropriate ratemeter. The ratemeter output is then used to drive an XY recorder, thereby allowing the data to be plotted in real time. When applicable, analog data acquisition is more convenient and often faster than corresponding digital data acquisition and is a useful option to have available. By appropriate choice of scanning speeds and ratemeter time constant, the signal/noise ratios which are achievable with analog scanning are equivalent to those obtainable with equal data acquisition time in a digital scanning mode.

Digital data acquisition and the corresponding ability to signal average repetitive scans over a spectral region are an important capability in ESCA because of the widespread occurrence of relatively weak signals. These signals may be enhanced by long-term signal averaging in order to extract weak signals from background noise. Multichannel analyzers, commercially available from several manufacturers, are the simplest and least expensive means of obtaining this capability. Most multichannel analyzers which are currently available are sufficiently flexible for data acquisition over narrow spectral regions for obtaining high resolution data as well as for obtaining survey scan data over wide spectral regions. Furthermore, these instruments usually have useful data manipulating capabilities. For example, digital smoothing of data, background slope correction, and subtraction of background, as well as differentiation and integration of data, are all possible with most commercial multichannel analyzers. Figure 26 shows the application of the multichannel analyzer capability to background

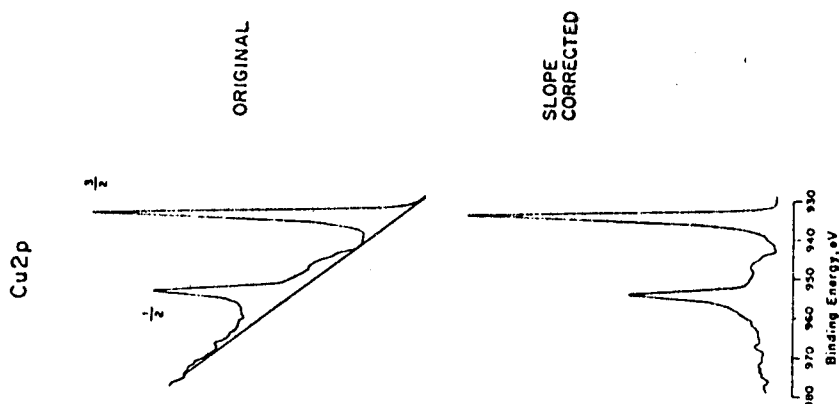


FIGURE 26. Correction of steeply sloping background.

correction of the steeply sloped background from a copper spectrum.

A form of resolution enhancement is also possible with the use of multichannel analyzers, as illustrated by the spectra in Figure 27. The resolution enhanced spectrum shown in Figure 27 is obtained by a simple manipulation of data in the commercial multichannel analyzer available with an electron spectrometer.^{9,3}

The use of a computer for digital data acquisition allows signal averaging of weak signals with a greater degree of flexibility than does the hardwired multichannel analyzer since the number of data points obtainable in a given spectral region is typically variable over a wider range than that

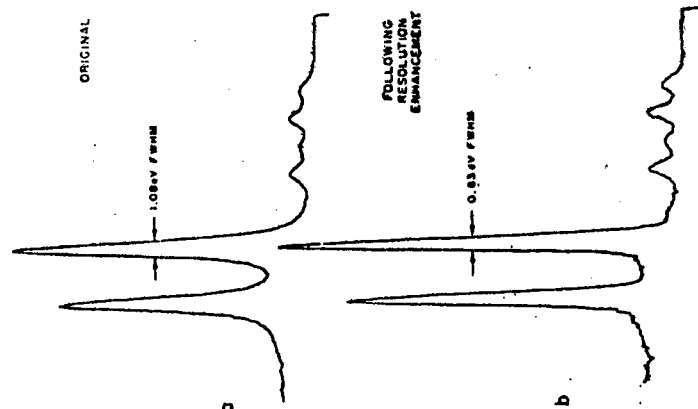


FIGURE 27. Resolution enhancement using multichannel analyzer. (From Du Pont Instruments Tech. Product Bull. #650-1010, June, 1975.)

available with a multichannel analyzer. Strictly for data acquisition, however, the signal averaging capability of a computer is roughly equivalent to that of a multichannel analyzer. The real advantage of a computer is that it can also be utilized to control the spectrometer. Data acquisition can be programmed in a number of spectral regions, and control can be transferred to the computer for unattended operation. The importance of this capability is inversely proportional to the intrinsic speed and sensitivity of the spectrometer. Highly sensitive spectrometers obtain data quickly enough that this ability becomes relatively unimportant. Conversely, a spectrometer with inherently slow data acquisition capabilities can make better use of computer control capability to conserve operator time.

Once data have been obtained in digital form, whether in a multichannel analyzer or in a computer, further data processing can produce

important and useful results. If the data are obtained in a multichannel analyzer, means must be available to transfer them to an appropriate computer by punched paper tape, magnetic tape, or a direct MCA/computer interface. If the spectrometer is equipped with a sufficiently powerful computer, data processing can be accomplished directly with the dedicated computer. With many instruments, however, this prevents simultaneous operation of the spectrometer.

ESCA data lend themselves to data processing techniques for several reasons. Spectrometer functions are often known or can be determined or approximated. The inherent resolution of the technique is not great; therefore, the need exists for mathematical methods for deconvoluting closely overlapped spectra. Finally, peak shapes and widths are often known or constant.

The literature contains procedures for correction of background and curve fitting^{9,4} as well as sophisticated techniques for data smoothing and deconvolution of the spectrometer function and Fourier-type resolution enhancement.^{9,5,6} An example of the results which are obtainable using a variation of Van Cittert's method^{9,7} due to Jansson and co-workers^{9,8,9} is shown in Figure 28. In this case, polynomial filtering and physical constraints such as the prohibition of negative solutions are applied. When properly used, techniques of this sort have yielded results which are in satisfying agreement with theory. In general, the use of computer data manipulation techniques should grow in importance in ESCA in the future.

IV. APPLICATIONS OF ESCA TO SURFACE ANALYSIS

In this section of the paper, applications of ESCA to surface related problems are presented. This section is not intended to be a comprehensive review of the published applications. Rather, some selected studies are presented in order to demonstrate the broad utility of the ESCA technique to problems in both organic and inorganic surface chemistry. In the last part of this section, some principles and examples of in-depth analysis by ESCA using grazing angle and ion sputtering techniques are presented.

A. Organic Surface Analysis

One of the first applications of ESCA to surface analysis of organic materials was published by

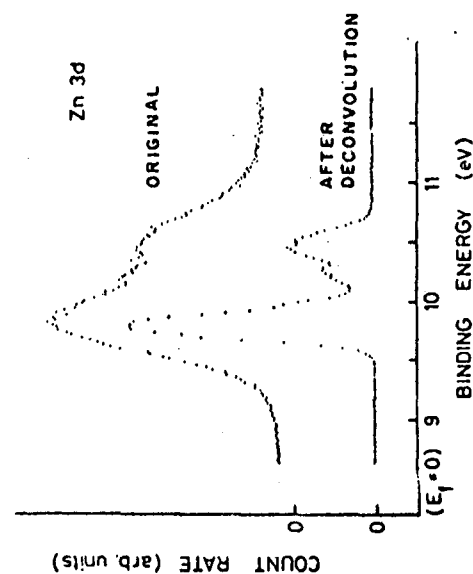


FIGURE 28. Resolution enhancement using a computer technique. [From McLachlan, A. D., Jenkin, J. G., Liesegang, J., and Leckey, R. C. G., *J. Electron Spectrosc. Relat. Phenom.*, 3, 207 (1974). With permission.]

Millard¹⁰⁰ and concerned the effects of corona discharge and low temperature discharge treatments on the surface chemistry of wool fibers. Millard studied the sulfur, nitrogen, carbon, and oxygen spectra of the wool fibers before and after the discharge treatments. The most significant changes were noted in the S_{2p} spectra, which are shown in Figure 29. The top spectrum was taken from untreated wool, while the middle and bottom spectra were taken from wool fibers which had been exposed, respectively, to a corona discharge and to a low temperature plasma in air. The top spectrum exhibits a large peak at ~ 163.5 eV due to the $\sim 3.7\%$ sulfur present in the wool as part of the amino acid cystine. A smaller peak at higher binding energy is also evident in this spectrum. The intensity of the small peak relative to that of the cystine sulfur peak increases substantially after exposure to both the corona discharge and the low temperature plasma. Its binding energy is characteristic of sulfur in the +6 oxidation state, and apparently the cystine sulfur is oxidized by the treatment to a sulfate ion or to some organic compound containing S^{+6} . The sulfur in the wool appears to be much more susceptible to oxidation than is nitrogen under the treatment conditions studied since no oxidized forms of nitrogen were detected in the N_{1s} spectra taken after the surface treatments.

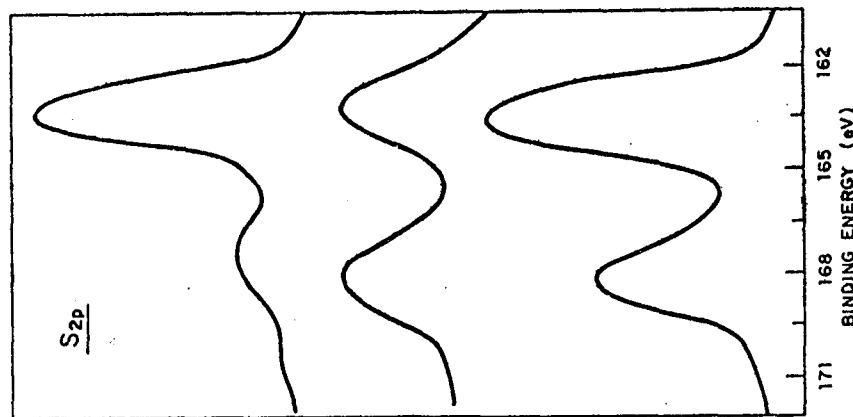


FIGURE 29. S_{2p} spectra from untreated wool fibers (top), corona discharge treated wool fibers (middle), and low temperature plasma discharge treated wool fibers (bottom). [From Millard, M. M., *Anal. Chem.*, 44(4), 828 (1972). With permission.]

resemblance to those from the control. The carbon peak is now centered at a lower binding energy of ~ 285 eV and exhibits a high binding energy tail extending to ~ 289 eV. Using an analog curve resolver, this carbon peak was fitted to three overlapping Gaussian curves, with the results shown in Figure 31. The binding energies of the three peaks are typical of hydrocarbon (saturated or unsaturated), carbonyl-, and carboxyl-type carbon atoms. A large oxygen peak is also evident on the etched surface, and the fluorine intensity

has been reduced compared to the control by more than an order of magnitude. To determine if the large hydrocarbon peak was due to saturated or unsaturated hydrocarbon, the etched film was subsequently submerged in bromine-in-carbon tetrachloride solution, the classical test for unsaturation. The spectra in lines 2 and 3 of Figure 30 indicate that no bromine was detected on an FEP control subjected to the same treatment, but that bromine was detected on the etched surface. In addition, compared to line 1, the central component of the C_{1s} spectrum in line 3 has increased in intensity relative to the hydrocarbon peak. Brominated carbon atoms are expected to exhibit a higher binding energy than hydrocarbon, and the central component of this group of peaks is probably a sum of the intensities from brominated and carbonyl carbon. Since the oxygen spectrum is essentially unchanged, the difference between the carbon spectra in lines 1 and 3 must be due to the introduction of bromine-carbon bonding, and at least some unsaturation is present on the surface of the etched film. By comparing these ESCA results with electron micrographs, the authors conclude that the solvated electrons in the Na/NH_3 etching solutions combine with and remove fluorine from the polymer surface. A condensed, highly reactive, sponge-like carbon network remains which reacts with the etching solvent and with atmospheric oxygen and moisture when it is removed from the solution. The result is a rough, porous hydrocarbon surface layer containing unsaturated and carbonyl and carboxyl groups.

B. Inorganic Surface Analysis

Hercules et al.⁶¹ have devised a method for trace analysis of metals which utilizes the surface sensitivity of the ESCA technique. By flowing a solution containing the metal of interest through a glass fiber disk that had been silylized with dithiocarbamate functional groups, the authors were able to concentrate trace quantities of the metal on the surface of the glass disk by ion exchange. Figure 32 shows a spectrum from 1 of these glass fiber disks after flowing through a 100-ml solution containing 20 ppm of lead. The large peak at ~ 152 eV is due to silicon in the glass substrate, while the other 2 peaks at ~ 143 and 148 eV are due to lead $4f_{5/2}$ and $4f_{7/2}$ core levels from the lead concentrated on the glass surface. Using this method, the authors reported detection levels of ~ 10 ppb for Pb, Ca, Ti, and Hg, and they

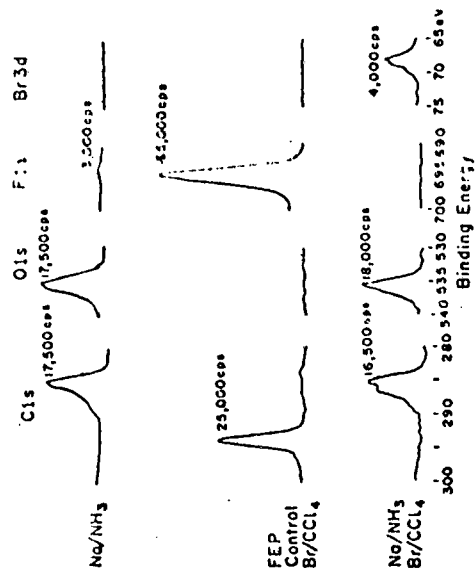


FIGURE 30. C_{1s} , O_{1s} , F_{1s} , and Br_{3d} spectra from Na/NH_3 etched FEP film (top), FEP control film (middle), and etched film (bottom) after immersion in bromine-in-carbon tetrachloride solutions. [From Dwight, D. W., and Riggs, W. M., *J. Colloid Interface Sci.*, 47(3), 670 (1974). With permission.]

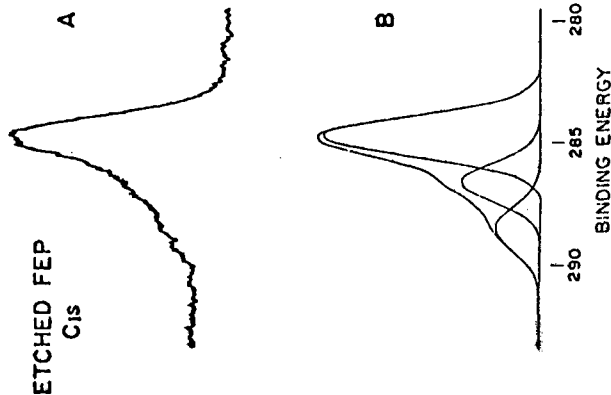


FIGURE 31. (a) Experimental and (b) Deconvoluted C_{1s} spectrum from Na/NH_3 etched FEP film. [From Dwight, D. W., and Riggs, W. M., *J. Colloid Interface Sci.*, 47(3), 650 (1974). With permission.]

estimate that under certain conditions, this could be extended to the parts per trillion range for the heavy metals.

Swingle, Ginnard, and Madden¹⁰¹ have studied electroless nickel-boron coatings with ESCA in order to correlate the physical properties of the Ni-B system with changes in surface chemistry as the coating is heated in vacuum and heated in air. Such heat treated Ni-B coatings are very hard and are more wear resistant than tool steels, hard chromium, and a variety of other metallic coatings. In addition, the coatings are electrically conducting, resistant to air oxidation, and readily braised and soldered. ESCA spectra were taken after each of a series of sequential heat treatments. Only a portion of the data presented by the authors will be discussed here. Figures 33 and 34 compare the B_{1s} , S_{2p} and N_{1s} spectra, respectively, from the coating as plated, after heating at 260°C for 90 min in vacuum, and after heating at 460°C for 90 min in vacuum. At least 3 distinct boron peaks at approximately 192, 188, and 182 eV are evident in Figure 33. Comparing the binding energies of these peaks with those of selected standards indicates that the high E_B peak at 192 eV is due to an oxide or mixed oxide of boron. The peak at 188.0 to 188.5 eV could be due to a number of boron containing species,

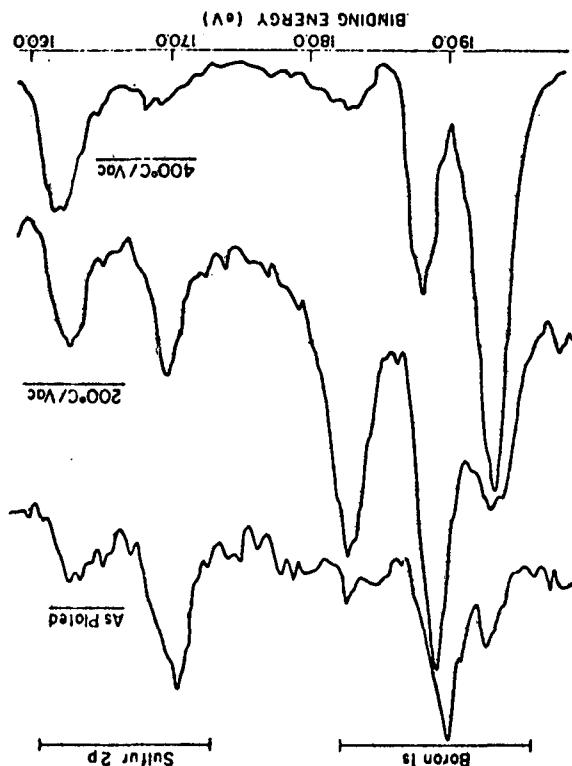


FIGURE 32. Si_{2p} , S_{2p} spectrum from glass fiber disk after flowing 100 ml solution of 20 ppm lead through the disk. [From Carlson, S. A., and Hercules, D. M., *Anal. Chem.*, 45(11), 1794 (1973). With permission.]

FIGURE 33. B_{1s} , S_{2p} spectra from Ni-B electroless plate as plated (top) after heating at 200°C in vacuum for 90 min (middle), and after heating 400°C in vacuum for 90 min (bottom). [From Swingle, R. B., Ginnard, C. B., and Madden, D. W., *J. Colloid Interface Sci.*, 47(3), 670 (1974). With permission.]

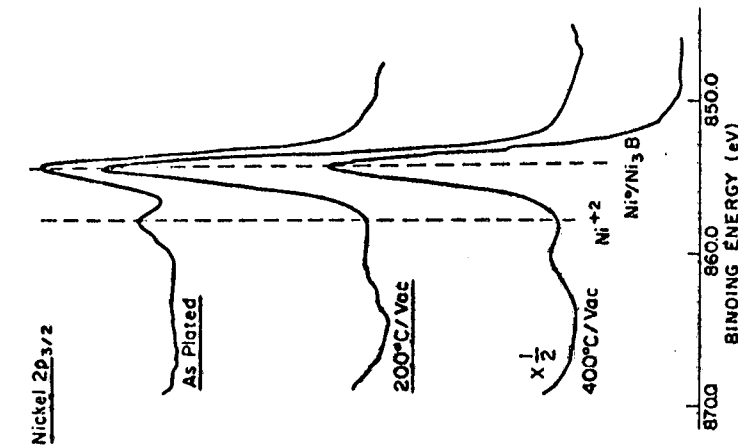


FIGURE 34. $Ni_{2p_{3/2}}$ spectra from Ni-B electroless plate as plated (top), after heating at 200°C in vacuum for 90 min (middle), and after heating 400°C in vacuum for 90 min. (From Swingle, R. S., II, Ginnard, C. R., and Madden, G. I., ESCA Studies of Nickel-Boron Electroless Coatings, presented at the Pittsburgh Conference on Analytical Chemistry, Cleveland, March, 1975.)

including the intermetallic Ni_3B phase believed to be present in the coating.¹⁰² Note that both the 192- and 188-eV peaks show small changes in peak width and relative binding energies from treatment to treatment, indicating that more than 1 distinct species contributes to each of the peaks. The third peak at 182 eV presents a problem in interpretation since, to the authors' knowledge, no B_{1s} binding energies this low have been reported in the literature. At present, the authors feel that this species is due to boron, or possibly borohydride, which is randomly distributed in the Ni-B solid solution, and that extra-atomic relaxation accounts for the very low binding energy. Two sulfur

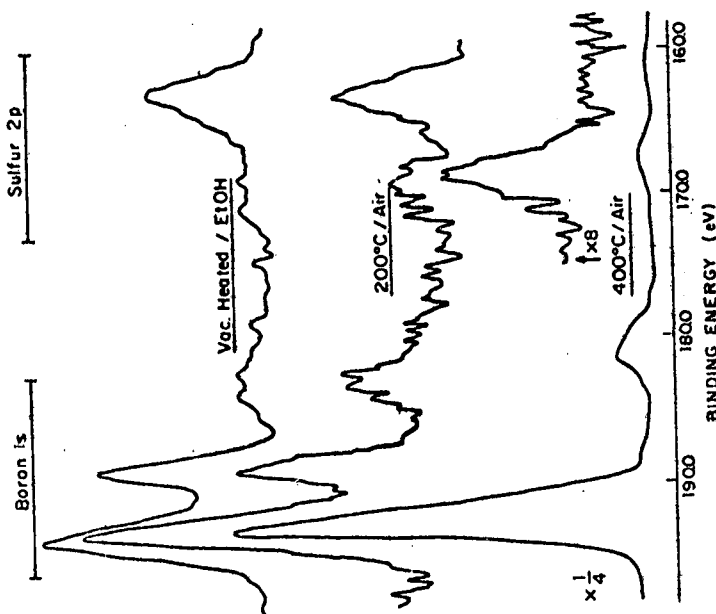


FIGURE 35. B_{1s} - S_{2p} spectra from Ni-B electroless plate after vacuum/heat treatments (top), after heating at 200°C in air for 90 min (middle), and after heating at 400°C in air for 30 min. (From Swingle, R. S., II, Ginnard, C. R., and Madden, G. I., ESCA Studies of Nickel-Boron Electroless Coatings, presented at the Pittsburgh Conference on Analytical Chemistry, Cleveland, March, 1975.)

however, several important conclusions concerning its nature are evident. First, the $Ni^{2+}p_{3/2}$ binding energy of the Ni^{+2} species is consistently 0.5 to 0.9 eV higher than that for simple NiO , suggesting that nickel oxidation products other than NiO must be present. Second, large amounts of other elements present in the coating bath, including carbon and thallium, are detected in the coating and must be codeposited with the nickel and boron in the coating process. (The authors show Ti_{2p} spectra which indicate substantial Ti enhancement of the surface after heating at 400°C in air.) Last, in contrast to nickel, all the boron detected after heating at 400°C in air has been oxidized. Because λB_{1s} is greater than λNi_{2p} , this result suggests that the oxide layer is not homogeneous

with depth and that boron is preferentially oxidized toward the bottom of the coating. This conclusion is in agreement with the preferential boron oxidation noted in the vacuum heat treatments and probably accounts for the oxidation resistance of the Ni-B coating.

Heterogeneous catalysis is another field where the characterization of solid surfaces is of great importance. Applications of ESCA in this area have been recently reviewed by Riggs and Parker¹⁰³ and by Brinen¹⁰⁴ and, except for the brief example below, will not be discussed in detail. Figure 37 shows the X-ray photoelectron spectra taken from a charcoal supported palladium catalyst used in the reduction of a nitrogen containing organic compound.¹⁰⁵ The purpose of

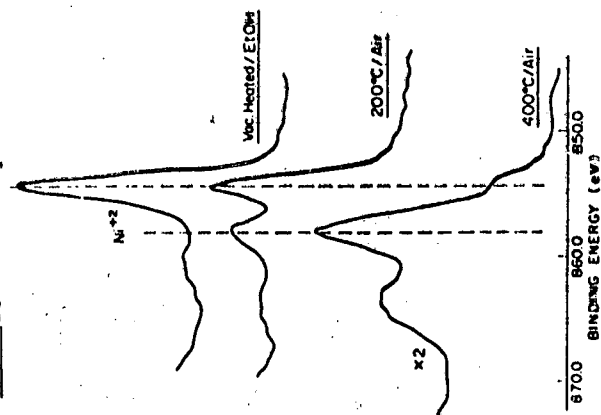


FIGURE 36. $\text{Ni}_{2p_{3/2}}$ spectra from Ni-B electroless plate after vacuum heat treatments (top), after heating at 200°C in air for 90 min (middle), and after heating at 400°C in air for 30 min (from Spring, R. S., H. Ginnard, C. R., and Madden, G. L., ESCA Studies of Nickel-Boron Electroless Coatings, presented at the Pittsburgh Conference on Analytical Chemistry, Cleveland, March, 1975.)

the study was to determine the cause of catalyst deactivation. Poisoning of the catalyst surface by either sulfide or chloride compounds was suspected as the cause of the deactivation since X-ray fluorescence indicated no difference in the total palladium content between active and inactive catalyst samples. The ESCA spectra, however, show that both sulfur and chlorine are absent on the spent catalysts and that, compared to the active catalyst, a large amount of nitrogen is present. In addition, the inactive catalyst exhibits a much lower palladium intensity, indicating that some nitrogen-containing by-product of the reaction is coating the surface of the catalyst and blocking the active palladium sites. This hypothesis is supported by the large increase in palladium intensity and reduction in nitrogen intensity (Figure 38) found after ion sputtering the spent catalyst.

C. In-Depth Analysis

In solving many chemical problems, it is useful to determine atomic composition and oxidation state information as a function of depth into the sample. Using ESCA, this "depth profiling" can be accomplished with either grazing angle 79.30° or ion sputtering²¹ techniques. Some principles, relative advantages, and examples of each technique are presented below.

Figure 39 illustrates the general principle of grazing angle ESCA for a specular surface. The effective sampling depth of the ESCA technique is related to $\lambda \sin \theta$, where λ is the inelastic mean free path of the photoelectron in a solid (see Section II.C), and θ is the take-off angle of the photoelectron with respect to the plane of the sample surface. In the grazing angle experiment, spectra are taken as a function of θ , and at $\theta = 15^\circ$, for example, the sampling depth is about $\frac{1}{4}$ ($\sin 15^\circ \approx 0.25$) of that for $\theta = 90^\circ$. Grazing angle has two important advantages compared to ion sputtering. First, it is nondestructive in nature and permits oxidation states to be measured as a function of depth. (The latter may not be possible with ion sputtering due to the preferential sputtering effects mentioned below.) Second, for most spectrometers, grazing angle is inexpensive to implement since only the geometry of the sample-to-analyzer entrance need be altered. Expensive accessories are not generally required. The most important disadvantage of grazing angle compared to ion sputtering is that samples can only be profiled over a depth equal to two or three times λ . For most samples, λ lies in the range of 10 to 30 Å, and ion sputtering is necessary for profiles beyond 50 to 100 Å in depth.

The usefulness of grazing angle for enhancing the surface sensitivity of ESCA has been illustrated by M. W. Duch²⁶ using a model system consisting of an adsorbed monolayer of perfluorodecanoic acid on glass. Figure 40 shows the C_{1s} spectra from this system taken at $\theta = 90^\circ$ and $\theta = 15^\circ$. At $\theta = 90^\circ$, a large C_{1s} peak is seen at 285.0 eV due to the hydrocarbon contaminant. The higher binding energy structure at 290 to 300 eV is difficult to interpret due to the overlap of the chemically shifted C_{1s} peaks from the fluorocarbon and carboxyl carbon atoms with the $\text{K}_{2p_{3/2}}$ doublet from potassium in the glass substrate. At $\theta = 15^\circ$, the $\text{K}_{2p_{3/2}}$ peaks are almost completely removed from the spectrum, and 3 peaks are seen at ~ 289 , 292, and 294 eV due to the $-\text{CO}_2^-$, $-\text{CF}_2^-$, and CF_3^- groups,

FIGURE 38. $\text{Pd}_{3d_{5/2}}$ and N_{1s} spectra from spent charcoal supported palladium catalyst before (top) and after (bottom) ion sputtering. (from Ginnard, C. R., Du Pont Applications Data, Bull. ES-0007, February, 1974.)

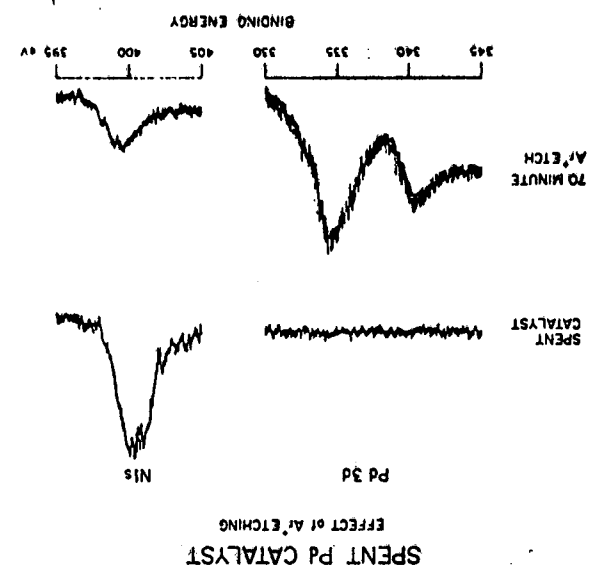
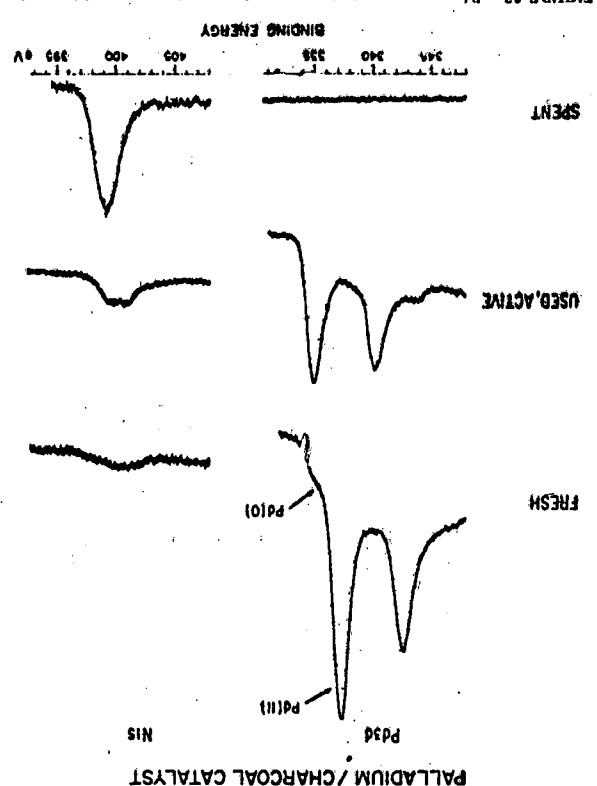


FIGURE 37. $\text{Pd}_{3d_{5/2}}$ and N_{1s} spectra from fresh (top), used but active (middle), and used but inactive (bottom) charcoal supported palladium catalyst. (from Ginnard, C. R., Du Pont Applications Data, Bull. ES-0007, February, 1974.)



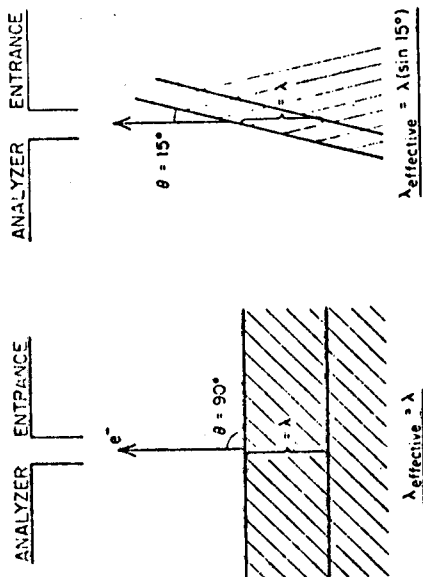
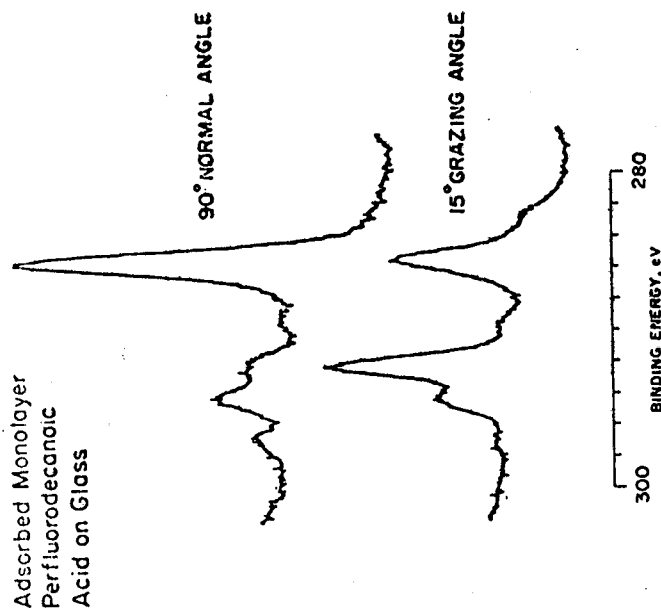


FIGURE 19. Principles of grazing-angle ESCA for specular surfaces.

respectively, in the adsorbed molecule. Note the increased intensity of the CF_3 -peak relative to that of the $-\text{CO}_2$ -peak, even though the same number of CF_3 - and $-\text{CO}_2$ -carbon atoms are present in the adsorbed molecule. This is probably due to the orientation of the adsorbed perfluorodecanoic acid molecules, with the polar $-\text{CO}_2$ -group localized primarily at the glass-adsorbate interface and the $-\text{CF}_2$ -group localized primarily at the adsorbate-vacuum interface.

Grazing angle ESCA has been used by Swingle, Groff, and Monroe¹⁰⁷ to study the surface of single crystals of the organic charge-transfer complex, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ). The complex is of interest because of its one-dimensional metallic character and reported superconductivity fluctuations at 60K.^{108,109} Unusual structure in both the N_{1s} and the S_{2p} spectra of this complex had been reported,^{110,111} and the study was undertaken to determine if this multiplex structure resulted from shake-up or from chemical shift due to different amounts of electron transfer at the surface of the crystals compared to the bulk. Figure 41 compares typical background corrected N_{1s} spectra from TTF-TCNQ taken at $\theta = 90^\circ$ and $\theta = 15^\circ$. The $\theta = 90^\circ$ spectrum exhibits the multiplex structure characteristic of TTF-TCNQ, while the $\theta = 15^\circ$ spectrum is dominated by a single peak at 399.0 eV. Similar changes with θ are

Carbon 1s ESCA Spectrum

FIGURE 40. $\text{K}_{2\text{P}}/\text{I}_{2-3}/\text{I}_{1s} - \text{C}_{1s}$ spectra at $\theta = 90^\circ$ (top) and $\theta = 15^\circ$ (bottom) for a monolayer of perfluorodecanoic acid adsorbed on glass. (From Duch, M. W., personal communication, 1975.)

For example, it is now known that many metal oxides are reduced to the corresponding metal or to lower oxides by Ar^+ sputtering because oxygen, with its high sputtering yield and high volatility, is more likely to escape the sample than is the metal. This fact has even been used by Yin, Ghose, and Adler⁹¹ to generate FeO from Fe_2O_3 *in situ* and to study changes in iron core electron binding energies with iron oxidation states. Kim et al.⁸² have studied 26 metal oxides with ESCA before and after ion sputtering, and they found a direct correlation between the free energy of formation of the metal oxide and the tendency of the oxide to be reduced by an Ar^+ ion beam.

V. COMPARISON WITH OTHER SURFACE ANALYSIS TECHNIQUES

In this section, ESCA is briefly compared with

three other modern, high vacuum, spectroscopic techniques for solid surface analysis. These techniques are Auger Electron Spectroscopy (AES),⁹³ Ion Scattering Spectroscopy (ISS),¹¹³ and Secondary Ion-Mass Spectrometry (SIMS).¹¹⁴ Many other techniques for surface analysis have been discussed in the literature, but they will not be mentioned here because they (1) are concerned with the physical rather than the chemical nature of surface (e.g., Scanning Electron Microscopy), (2) are only applicable to well-defined surfaces under ultrahigh vacuum (e.g., Low Energy Electron Diffraction and UV Photoelectron Spectrometry), (3) probe too deeply into a sample (e.g., Attenuated Total Reflectance Infrared and Soft X-ray Fluorescence), or (4) have not yet been developed to a point where they can be routinely applied to analytical samples (e.g., Ion Neutralization Spectrometry and Inelastic Electron Back-

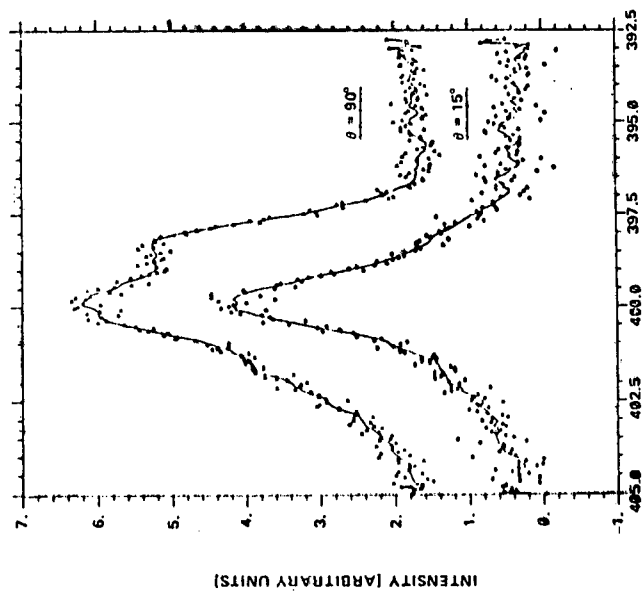


FIGURE 41. Background corrected N_{1s} spectra from single crystals of TTF-TCNQ taken at $\theta = 90^\circ$ (top) and $\theta = 15^\circ$ (bottom). [From Swingle, R. S., II, Groff, R. P. and Monroe, B. M., *Phys. Rev. Lett.*, 35(7), 452 (1975). With permission.]

scattering Spectrometry). ESCA, AES, ISS, and SIMS are all commercially available and well established in the literature. A brief description of the basic principles of each of these techniques is given separately below. This is followed by some general remarks concerning the relative strengths and weaknesses of the techniques.

A. ESCA

In the ESCA experiment, a solid surface is exposed to X-rays of energy $h\nu$, and the kinetic energy distribution of the ejected photoelectrons is measured. The resulting spectrum is usually plotted as intensity versus E_B , the electron binding energy, where E_B is given approximately by:

$$E_B = h\nu - E_K \quad (20)$$

Each core level of every atom in the periodic table

has a characteristic range of binding energies. The exact binding energy of a photoelectron line can often be used as a measure of element oxidation state.

B. AES

Auger electrons result from relaxation of a core level (level 1) ionized atom. In the first step of this relaxation process, an electron from a level of higher energy (level 2) falls into the level 1 vacancy. The difference in energy between the two levels ($E_B - E_{B_2}$) is then emitted either as an X-ray photon, which is the basis of X-ray fluorescence, or as an Auger electron from level 3, leaving a doubly ionized atom. The Auger electrons have kinetic energies characteristic of the atom and given approximately by:

$$E_K = E_{B_1} - E_{B_2} - E_{B_3} \quad (21)$$

Unlike the ESCA technique, the Auger electron kinetic energy is independent of the energy used for primary ionization. In the commercial spectrometers, the initial ionization of the atoms in the sample is accomplished with an electron beam. The Auger spectrum is usually plotted as the first derivative of the intensity with respect to kinetic energy, dN/dE_K , versus kinetic energy in order to eliminate the high background in the spectrum from the large number of backscattered primary electrons.

C. ISS

In this technique, a solid surface is bombarded with a collimated beam of monoenergetic noble gas ions, usually $^4\text{He}^+$, $^3\text{He}^+$, $^{20}\text{Ne}^+$, or $^{40}\text{Ar}^+$. A small fraction of these ions will undergo binary elastic collisions with atoms in the first monolayer of the sample and will be reflected from the surface. For a 90° scattering angle, classical collision theory shows that the mass, M_1 , of the reflecting atom at the sample surface can be calculated from:

$$E_i/E_0 = \frac{M_1 - M_0}{M_1 + M_0} \quad (22)$$

where E_0 and M_0 are the energy and mass of the incident ion, respectively, and E_i is the energy of the reflected ion. In the commercial spectrometer, the ions scattered at 90° are energy analyzed, and a spectrum of intensity versus E_i/E_0 is produced.

D. SIMS

In this method, a solid surface is bombarded with an ion beam, and the secondary or sputtered ions ejected from the surface by the action of the beam are mass analyzed with a mass spectrometer. Conventional mass spectra are produced and, with the appropriate electronics, both positive and negative ion SIMS are possible.

E. Summary Comparison

Table 6 compares these four techniques in nine important categories. Depth resolution is about the same in ESCA and AES since the sampling depths of both techniques are governed by the inelastic mean free path, λ , of the electrons in solids. Experimentally, λ has been shown to vary from 5 to ~ 100 Å depending upon the matrix and the exact kinetic energy of the electron being considered. Most λ values fall in a range of 10 to

30 Å, however, and for specular surfaces, the effective sampling depth can be reduced to 1 to 2 atomic layers using grazing angle techniques. The sampling depth in the ion techniques (ISS and SIMS) depends upon the sputtering rate of the sample relative to the scan time necessary to collect a spectrum. The sputtering rate, in turn, depends upon the mass of the incident ions and the current density of the incident ion beam. When a beam current of 1 μA is defocused over 1 cm^2 of the sample surface, the beam current density of 1 $\mu\text{A}/\text{cm}^2$ will result in a SIMS depth resolution of ~ 1 to 5 atomic layers depending upon the matrix, the scan time, and whether or not cratering or edge effects are important. If the same 1 μA ion beam is then focused to a spot ~ 30 μm in diameter, the beam current density is increased by greater than 4 orders of magnitude to ~ 50 mA/cm^2 . The sputtering rate is increased and the depth resolution is decreased proportionately (for constant scan time). Rastering the ion beam across the sample surface can improve the depth resolution significantly and is an important feature for secondary ion mass spectrometers which employ large current densities. The sampling depth for ISS is a single monolayer. Incident ions that penetrate past the first monolayer have a high probability of being neutralized by the matrix, and neutrals are not detected by the ion scattering spectrometer even if they are elastically reflected at a 90° scattering angle.

The ESCA technique has no spatial resolution, and the signal is an integral of photoelectrons from all irradiated portions of the sample. A sample can be as small as ~ 1 mm^2 . The electron beam diameter in commercial AES instruments may be as small ~ 5 to 10 μm , and spectrometers with imaging capability are commercially available. The ion beam diameter in the commercial ISS instrument ranges from several millimeters to ~ 250 μm in diameter, and at present, the technique has little or no spatial resolution compared to some commercial AES instruments.

The range of costs for present commercial spectrometers is given in column 3 of Table 6. The exact price depends greatly upon the data acquisition system and the number of accessories purchased with each basic spectrometer. For a simple SIMS attachment to an existing vacuum system, an ion gun and mass spectrometer can be purchased for approximately \$25,000. A complex ESCA system can cost over \$200,000, while ion

TABLE 6

Modern Vacuum Techniques for Surface Analysis

	Depth resolution	Spatial resolution	Cost (\$)	Qualitative analysis	Quantitative analysis	Chemical information	Surface damage	Monolayer sensitivity
ESCA	10-30 Å	N/A	60-200K	Good	Good	Yes	1	10^{-1} to 10^{-3}
AES	10-30 Å	As small as 5-10 µm	60-150K	Good	Fair	Limited at present	2	10^{-1} to 10^{-3}
ISS	1 monolayer	N/A to 250 µm depending upon beam diameter	45-75K	Fair	Fair	Not generally available	3	10^{-1} to 10^{-3}
SIMS	1 monolayer	N/A to 2 µm depending upon beam diameter	25K without vacuum system	Good	Poor	Very limited	3	Extremely variable

microprobes with imaging capabilities can exceed \$500,000.

The ability of the techniques to qualitatively analyze a surface is shown in column 4. Both ESCA and AES easily detect all elements in the periodic table, with the notable exception of hydrogen. Some overlapping of peaks is found in ESCA and AES spectra, but this is generally not a problem for qualitative analysis because most elements exhibit more than one peak. ESCA and AES do not distinguish between different isotopes of the same element. ISS is rated fair in this category because of its poor sensitivity for elements with atomic numbers below oxygen and the poor mass resolution of the technique at high mass. The latter problem is partly overcome by using noble gases of high mass (e.g., ^{40}Ar) as the probe, but then elements with masses less than the probe mass are not detected. ISS can resolve some isotopes, notably ^{16}O and ^{18}O . All modern mass spectrometers have sufficiently high resolution to resolve nominal masses to ~500 and, consequently, SIMS resolves all isotopes in the periodic table. Overlap between ions of the same mass is often a problem since both monatomic and polyatomic clusters are sputtered as ions from solid surfaces. Relative natural abundances of different isotopes and higher mass resolution can aid in qualitative peak identification. SIMS has a unique and important advantage over all three of the other techniques in that it can detect hydrogen.

parameters, shake-up satellites, and multiplet effects can all be used to obtain oxidation state or electronic environment information from ESCA. This potential is also present in AES, but generally has not been explored. AES spectra interpretation is more complex in this regard, and most commercial instruments with single-pass cylindrical mirror analyzers (CMA) do not have sufficient resolution to detect small chemical shifts in Auger lines. ISS has not been used to extract chemical information, but recent work indicates this may be possible in the future for a limited number of cases.¹¹⁷ In general, for the ion techniques, chemical information below the first atomic layer is lost due to preferential sputtering. SIMS gives very limited chemical information. Interpretation of cracking patterns and cluster ions arising from the sputtering of solid surfaces has not yet advanced to the state-of-the-art found for ions produced in the gas phase.

Column 7 lists the relative order of surface damage produced by the four techniques. ESCA is the only one which readily lends itself to the

analysis of organic materials. The electron beam excitation used in AES severely damages (or even destroys) organic materials. ISS and SIMS, because they are ion techniques, are not "nondestructive" in nature. In these cases, the surface is slowly removed by sputtering during the measurement.

Column 8 lists the approximate sensitivities in monolayers for ESCA, AES, and ISS. These numbers are variable depending upon the element under consideration and the surface morphology of the sample. Sensitivity for the SIMS technique is extremely variable, as pointed out in the discussion on quantitative analysis.

It should be clear from this discussion that each of the techniques has its strengths and weaknesses. No single technique is a panacea for all surface analysis problems, and the one most applicable to a particular laboratory will depend upon the type of problems encountered in that laboratory. In many cases, a combination of two or more of these techniques may be more useful than one alone.

REFERENCES

1. Siegbahn, K., Nordling, C., Fahlman, A., Nordberg, R., Hamrin, K., Hedman, J., Johansson, G., Bergmark, T., Karlsson, S., Lindgren, I., and Lindberg, B., *ESCA-Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy*, Almqvist and Wiksell, Uppsala, Sweden, 1967.
2. Siegbahn, K., Nordling, C., Johansson, G., Hedman, J., Hedén, P. F., Hamrin, K., Gelius, U., Bergmark, T., Wenner, L. O., Manne, R., and Baer, Y., *ESCA Applied to Free Molecules*, American Elsevier, New York, 1969.
3. Bettridge, D. and Williams, M. A., *Anal. Chem.*, 46(5), 125R (1974).
4. Herricks, D. M. and Carver, J. C., *Anal. Chem.*, 46(5), 133R (1974).
5. Hammett, A. and Orchard, A. F., *Electron. Struct. Magn. Inorg. Compd.*, 1, 1 (1972).
6. Evans, S. and Orchard, A. F., *Electron. Struct. Magn. Inorg. Compd.*, 2, 1 (1973).
7. Hammett, A. and Orchard, A. F., *Electron. Struct. Magn. Inorg. Compd.*, 3, 218 (1974).
8. Baker, W. E., Jr., Brundie, C. R., and Thompson, M., *Chem. Soc. Rev.*, 1(3), 355 (1972).
9. Swartz, W. E., Jr., *Anal. Chem.*, 45(9), 788A (1973).
10. Brundie, C. R., *Surf. Defect Prop. Solids*, 1, 171, 1972.
11. Gidycz, U., *Phys. Scr.*, 9(3), 133 (1974).
12. Shirley, D. A., *Adv. Chem. Phys.*, 23, 85 (1973).
13. Dekeyser, W., Fiermans, L., Vandertelen G., and Vennik, J., *Electron Emission Spectroscopy*, D. Reidel Publishing, Boston 1973.
14. Shirley, D. A., Ed., *Electron Spectroscopy*, American Elsevier, New York, 1972.
15. Baker, W. E. and Brundie, C. R., *Photoelectron Spectroscopy - Chemical and Analytical Aspects*, Pergamon Press, New York, 1972.
16. Seiser, K. A., *Low Energy Electron Spectrometry*, Interscience, New York, 1972.
17. Garm, P. H., Shaw, R. W., Jr., Packer, A., and Thomas T. D., in *Electron Spectroscopy*, Shirley, D. A., Ed., American Elsevier, New York, 1972, 691-702.
18. Gadey, A. F., Joyner, R. W., and Roberts, M. W., *Chem. Phys. Lett.*, 27(4), 580 (1974).
19. Nathan, R. and Hopkins, B. J., *J. Phys. E.*, 7(10), 851 (1974).

20. Accrelli, P. and Missoni, G., *J. Electron Spectrosc. Relat. Phenom.*, **5**, 417 (1974).
21. Citra, P. H. and Harman, D. R., *Phys. Rev. B*, **10**(12), 4948 (1974).
22. Waugh, J. L. T., *The Constitution of Inorganic Compounds*, Interscience, New York, 1972, 607.
23. Hollander, J. M. and Shirley, D. A., *Ann. Rev. Nucl. Sci.*, **20**, 435 (1970).
24. Johansson, G., Holman, J., Berndtson, A., Nilsson, M., and Nilsson, R., *J. Electron Spectrosc. Relat. Phenom.*, **2**, 293 (1973).
25. Kim, K. S., O'Leary, T. J., and Winograd, N., *Anal. Chem.*, **45**(13), 2214 (1973).
26. Hochstetler, D. A. and McKoon, R. T., *Appl. Phys. Lett.*, **20**, 158 (1972).
27. Ebel, H. F. and Ebel, H., *J. Electron Spectrosc. Relat. Phenom.*, **3**, 169 (1974).
28. Dickinson, T., Povey, A. F., and Sherwood, P. M. A., *J. Electron Spectrosc. Relat. Phenom.*, **2**, 441 (1973).
29. Guntharner, F. J., Ph. D. thesis California Institute of Technology, Pasadena, 1974.
30. Ogilvie, J. L. and Wolberg, A., *Appl. Spectrosc.*, **26**(3), 401 (1972).
31. Hnatowich, D. J., Hadis, J., Perlman, M. L., and Ragani, R. C., *J. Appl. Phys.*, **42**(12), 4883 (1971).
32. Dumas, W. P. and Lester, J. E., *Anal. Chem.*, **45**(8), 1416 (1973).
33. Betteridge, D., Carst, J. C., and Hercules, D. M., *J. Electron Spectrosc. Relat. Phenom.*, **2**, 337 (1973).
34. Ginnard, C. R. and Riggs, W. M., *Anal. Chem.*, **46**(9), 1306 (1974).
35. Ginnard, C. R. and Riggs, W. M., *Anal. Chem.*, **44**(7), 1310 (1972).
36. Bagus, P. S., The role of Ab initio molecular orbital calculations in the analysis and interpretations of X-ray photoelectron spectra, in *Proceeding of the International Symposium on X-Ray Spectra and Electronic Structure of Matter*, Facsler, A. and Weich, G., Eds., Fotodruck Frank OHG, München, 1972, 256.
37. Clark, D. T., Feast, W. J., Kileast, D., and Musgrave, W. K., *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 21, 389 (1973).
38. Koopmans, T. C., *Physica*, **12**, 104 (1933).
39. Davis, D. W., Banna, M. S., and Shirley, D. A., *J. Chem. Phys.*, **60**(1), 237 (1974).
40. *Handbook of Spectroscopy*, Vol. 1, Robinson, J. W., Ed., CRC Press, Cleveland, 1974, 517, 752.
41. Wagner, C. D. and Bilen, P., *Surf. Sci.*, **35**, 82 (1973).
42. Wagner, C. D., *Anal. Chem.*, **47**(7), 1201 (1975).
43. Kowalczyk, S. P., Ley, L., McFeely, F. R., Pollak, R. A., and Shirley, D. A., *Phys. Rev. B*, **9**(2), 351 (1974).
44. Wagner, C. D., *Anal. Chem.*, **44**(6), 967 (1972).
45. Wagner, C. D., Chemical Shifts of Auger Lines, and the Auger Parameter, presented at Discussions of the Faraday Society, Vancouver, Canada, July, 1975.
46. Carlson, T. A., Carver, J. C., and Vemon, G. A., *J. Chem. Phys.*, **62**(3), 932 (1975).
47. Wertheim, G. K., Cohen, R. L., Rosencwaig, A., and Guenther, H. J., in *Electron Spectroscopy*, Shirley, D. A., Ed., American Elsevier, New York, 1972, 813.
48. Ikemoto, I., Thomas, J. M., and Kuroda, H., *J. Chem. Soc. Faraday Discuss.*, **54**, 208 (1972); Ikemoto, I., Thomas, J. M., and Kuroda, H., *Bull. Chem. Soc. Jap.*, **46**, 2237 (1973); L. J. Aarons et al., *J. Chem. Soc. Faraday II*, **69**(2), 279 (1973).
49. Tolman, C. A., Riggs, W. M., Linn, W. J., King, C. M., and Wendi, R. C., *Inorg. Chem.*, **12**(12), 2756 (1973).
50. Matienzo, L. J., Yin, L. F., Grim, S. O., and Swartz, W. E., Jr., *Inorg. Chem.*, **12**(12), 2762 (1973).
51. Frost, D. C., Ishizani, A., and McDowell, C. A., *Vol. Phys.*, **24**(4), 861, 1972.
52. Kim, K. S., *J. Electron Spectrosc. Relat. Phenom.*, **3**, 217 (1974).
53. Shirley, D. A., Carver, J. C., and McFeely, F. R., *Phys. Rev. A*, **2**(4), 1109 (1970).
54. Kowalczyk, S. P., Ley, L., Pollak, R. A., McFeely, F. R., and Shirley, D. A., *Phys. Rev. B*, **7**, 4009 (1973).
55. Carver, J. C., Schweizer, G. K., and Carlson, T. A., *J. Chem. Phys.*, **57**(2), 973 (1972).
56. McFeely, F. R., Kowalczyk, S. P., Ley, L., and Shirley, D. A., *Solid State Commun.*, **15**, 1051 (1974).
57. Dwight, D. W. and Riggs, W. M., *J. Colloid Interface Sci.*, **47**(3), 650 (1974).
58. Phillips, R. W., *J. Colloid Interface Sci.*, **47**(3), 687 (1974).
59. Clark, D. T. and Tripathi, K. C., *Nucl. Phys. Sci.*, **244**, 77 (1973).
60. Binen, J. S. and McClure, J. E., *Anal. Lett.*, **5**(10), 737 (1973).
61. Carlson, S. A. and Hercules, D. M., *Anal. Chem.*, **45**(11), 1794 (1973).
62. Kileast, D., Feast, W. J., Musgrave, W. K. R., and Clark, D. T., *J. Polym. Sci. A-1*, **10**, 1637 (1972).
63. Swartz, W. E. Jr. and Hercules, D. M., *Anal. Chem.*, **43**(15), 1774 (1971).
64. Larson, P. E., *Anal. Chem.*, **44**(9), 1678 (1972).
65. Wertheim, G. K. and Rosencwaig, A., *Phys. Rev. Lett.*, **26**(19), 1179 (1971).
66. Pines, D., *Elementary Excitations in Solids*, W. A. Benjamin Publishing, New York, 1963.
67. Wendi, R. C. and Riggs, W. M., Surface Analysis by X-ray Photoelectron Spectroscopy, presented at Eastern Analytical Symposium, New York, Nov. 1971.
68. Wheeler, J. A., personal communication, 1973.
69. Powell, C. J., *Surf. Sci.*, **44**(1), 29 (1974).
70. Wagner, C. D., *Anal. Chem.*, **44**(6), 1050 (1972).
71. Swingle, R. S., II, *Anal. Chem.*, **47**(1), 21 (1975).
72. Kreuzburg, M., *Z. Phys.*, **196**, 433 (1966).
73. Ebel, H. and Ebel, M. F., *X-Ray Spectrom.*, **2**(1), 19 (1973).

74. Carter, W. J., Schweizer, G. K., and Carlson, T. A., *J. Electron Spectrosc. Relat. Phenom.*, **5**, 827 (1974).
75. Du Pont Tech. Product Bull., #68, 1007, September, 1974.
76. Scofield, J. H., Tech. Report No. 51326, University of California Radiation Lab., 1973.
77. Scofield, J. H., personal communication, 1973.
78. Wagner, C. D., personal communication, 1975.
79. Fraser, W. A., Florio, J. V., DeGass, W. N., and Robertson, W. D., *Surf. Sci.*, **36**, 661 (1973).
80. Fadley, C. S., Baird, R. J., Siekhaus, W., Novak, T., and Bergstrom, S. A. L., *J. Electron Spectrosc. Relat. Phenom.*, **4**, 93 (1974).
81. Yin, L. F., Ghose, S., and Aulic, L., *Appl. Spectrosc.*, **26**(3), 355 (1972).
82. Kim, K. S., Baidiger, W. E., Amy, J. W., and Winograd, N., *J. Electron Spectrosc. Relat. Phenom.*, **5**, 351 (1974).
83. Tracy, J. C., in *Electron Emission Spectroscopy*, Dekeyser, W., Fiermans, L., Vanderhulst, G., and Vennik, J., Eds., Reidel Publishing, Boston, 1973, 295-329.
84. Jenkins, R. and de Vries, J. L., *Practical X-Ray Spectrometry*, 2nd ed., Springer-Verlag, New York, 1969.
85. Siegbahn, K., Hamond, D., Fellner-Feldgel, H., and Barnett, E. F., *Science*, **176**, 245 (1972).
86. Wannberg, B., Gelius, U., and Siegbahn, K., *J. Phys. E*, **7**(3), 149 (1974).
87. Sard, H. Z., *Rev. Sci. Instrum.*, **38**(9), 1210 (1967).
88. Lee, J. D., *Rev. Sci. Instrum.*, **44**(7), 893 (1973).
89. Gellender, M. F. and Baker, A. D., *J. Electron Spectrosc. Relat. Phenom.*, in press, 1975.
90. Helmer, J. C. and Weichert, N. H., *Appl. Phys. Lett.*, **13**(8), 266 (1968).
91. Carter, G. and Colligon, J. S., *Ion Bombardment of Solids*, American Elsevier, New York, 1968.
92. Kaminsky, M., *Atomic and Ionic Impact Phenomena on Metal Surfaces*, Academic Press, New York, 1965.
93. Du Pont Instruments Tech. Product Bull., #650-1010, June, 1975.
94. Fadley, C. S., Ph. D. dissertation, University of California at Berkeley, 1970.
95. Wertheim, G. K., *J. Electron Spectrosc. Relat. Phenom.*, **6**, 239 (1975).
96. McLachlan, A. D., Jenkins, J. G., Liesegang, J., and Lockey, R. C. G., *J. Electron Spectrosc. Relat. Phenom.*, **3**, 207 (1974).
97. Van Cittert, P. H., *Phys.*, **69**(5-6), 298 (1931).
98. Jansson, P. A., Hunt, R. H., and Plyter, E. K., *J. Opt. Soc. Am.*, **58**(12), 1665 (1968).
99. Jansson, P. A., Hunt, R. H., and Plyter, E. K., *J. Opt. Soc. Am.*, **60**(5), 596 (1970).
100. Millard, M. M., *Anal. Chem.*, **44**(4), 828 (1972).
101. Swingle, R. S., II, Ginnard, C. R., and Madden, G. L., ESCA Studies of Nickel-Boon Electroless Coatings, presented at the Pittsburgh Conference on Analytical Chemistry, Cleveland, March, 1975.
102. Portnoy, K. I., Romashov, V. M., Chubakov, V. M., Lentskaya, N. Kh., Salibetov, S. E., Parozhik, M., 50(2), 15 (1967).
103. Riggs, W. M. and Parker, J. L., in *Modern Methods of Surface Analysis*, Candenna, A. W. and Wolberg, S. P., Eds., American Elsevier, New York, 1975.
104. Binen, J. S., *J. Electron Spectrosc. Relat. Phenom.*, **5**, 377 (1974).
105. Ginnard, C. R., Du Pont Applications Data, Bull. ES-0007, February, 1974.
106. Duch, M. W., personal communication, 1975.
107. Swingle, R. S., II, Groff, R. P., and Monroe, B. M., *Phys. Rev. Lett.*, **35**(7), 452 (1975).
108. Coleman, L. B., Cohen, M. J., Sandman, D. J., Yamagishi, F. G., Carito, A. F., and Heeger, A. L., *Solid State Commun.*, **12**(11), 1125 (1973).
109. Ferrara, J., Cowan, D. O., Wadzka, V., Jr., and Perlstein, I. H., *J. Am. Chem. Soc.*, **95**, 948 (1973).
110. Ginnard, C. R., Swingle, R. S., II, and Monroe, B. M., *J. Electron Spectrosc. Relat. Phenom.*, **6**(1), 77 (1975).
111. Grobman, W. D., Pollak, R. A., Eastman, D. E., Niass, E. T., Jr., and Scott, B. A., *Phys. Rev. Lett.*, **32**(10), 534 (1974).
112. Coad, J. P. and Cunningham, I. G., *J. Electron Spectrosc. Relat. Phenom.*, **3**, 435 (1974).
113. Brongersma, H. H. and Mul, P. N., *Surf. Sci.*, **35**, 393 (1973).
114. Benninghoven, A., *Surf. Sci.*, **35**, 427 (1973).
115. Palmberg, P. W., *Anal. Chem.*, **45**(6), 549A (1973).
116. Shimizu, R., Ishitani, T., Kondo, T., and Tamura, H., *Anal. Chem.*, **47**(7), 1020 (1975).
117. Erickson, R. L. and Smith, D. P., *Phys. Rev. Lett.*, **34**(6), 297 (1975).

ABSTRACT

Core line x-ray photoelectron spectra are reported for the iron compounds $\alpha\text{Fe}_2\text{O}_3$, $\gamma\text{Fe}_2\text{O}_3$, αFeOOH , NiFe_2O_4 , CoFe_2O_4 , Fe_3O_4 and FeO . Such XP spectra are of particular value in characterizing surface films containing iron corrosion products. For the oxides and hydroxides FeOOH , FeO and Fe_3O_4 , the observed chemical shift is sufficiently large to permit these species to be uniquely distinguished from the other ferric oxides. In Fe_3O_4 , both ferrous and ferric oxidation states are observed and their relative concentrations can be determined using spectral line fitting procedures. The oxides $\alpha\text{Fe}_2\text{O}_3$, $\gamma\text{Fe}_2\text{O}_3$, NiFe_2O_4 and CoFe_2O_4 have almost identical core binding energies, but the multiplet splitting patterns observed in their $\text{Fe}(2p)$ core levels are sufficiently different to permit their use for characterization. The $\text{Fe}(2p)$ multiplet pattern observed for $\alpha\text{Fe}_2\text{O}_3$ agrees well with splitting previously calculated for the free Fe^{+3} ion. Valence band spectra for $\gamma\text{Fe}_2\text{O}_3$, $\alpha\text{Fe}_2\text{O}_3$, Fe_3O_4 and FeO are reported and band assignments are made. The effect of ion bombardment of iron oxide surfaces has been studied and evidence for the reduction of ferric oxides to FeO is presented.

INTRODUCTION

The formation of a variety of ferrous and ferric oxides and hydroxides is possible during the aqueous corrosion of iron metal surfaces under alkaline conditions. At low temperatures ($<100^{\circ}\text{C}$) in high-oxygen environments, a number of forms of ferric hydroxide result, which, on further heating gradually transform to αFeOOH (goethite) and $\alpha\text{Fe}_2\text{O}_3$ (hematite). At similar temperatures but under reducing conditions, Fe_3O_4 (magnetite) is a major corrosion product⁽¹⁾. At high temperatures (300°C), ion exchange occurs rapidly between Fe_3O_4 surfaces and other ions such as Ni^{+2} or Co^{+2} leading to the formation of the mixed spinels NiFe_2O_4 and CoFe_2O_4 ⁽²⁾. Electrochemical studies of magnetite oxidation show that $\gamma\text{Fe}_2\text{O}_3$ (maghemite) is formed by hydrolysis as a passivating layer on the Fe_3O_4 surface⁽³⁾. In corrosion studies in this laboratory, it is of interest to identify these and other oxide species in thin films grown on iron and iron alloy surfaces. X-ray Photoelectron Spectroscopy (XPS or ESCA) is being developed as a surface analytical tool to determine such chemical structures.

This paper reports a study of the XPS spectra of the simple and mixed iron oxides $\alpha\text{Fe}_2\text{O}_3$, $\gamma\text{Fe}_2\text{O}_3$, Fe_3O_4 , FeO , NiFe_2O_4 and CoFe_2O_4 and the hydroxide αFeOOH . The details of core line spectra ($\text{Fe}(2p)$, $\text{Fe}(3s)$, $\text{Fe}(3p)$ and $\text{O}(1s)$), valence band spectra, and Auger line spectra ($\text{L}_{3\text{M}_4,5}\text{M}_{4,5}$) are discussed with the particular view to identifying features which allow identification of each species in corrosion systems.

In addition, the effect of ion bombardment on a number of iron oxide systems has been studied to determine the chemical effects of depth profiling in an iron oxide film.

One other comparative study of iron oxide XP spectra has been made by Allen et al ⁽⁴⁾ who obtained Fe(2p) and O(1s) spectra of $\alpha\text{Fe}_2\text{O}_3$, Fe_3O_4 , FeO, αFeOOH and several ferrates. They found that the Fe(2p) spectra were particularly difficult to analyze, because of a steeply rising background and broadened line-widths. They attributed such broadening to multiplet splitting and shape-up phenomena. In this work, the spectra of some of these and other oxides have been obtained under higher resolution and distinct structure within the peak envelopes can be identified in most cases. The resolved structure is found generally to agree with multiplet splitting parameters calculated for free ferric and ferrous ions, but the structure of the surrounding environment also has some effect on the splitting of the Fe(2p) line. The resultant shape of the Fe(2p) line is useful for characterizing some of the ferric oxides where chemical shifts are minimal. Using both chemical shift and multiplet splitting effects, distinct spectral characteristics can be described for each oxide studied.

Several previous XPS studies have been concerned with the analysis of $\text{Fe}_3\text{O}_4^{(4-9)}$. This inverse spinel oxide is of particular interest because it contains both ferric and ferrous ions in a 2:1 ratio and these should be distinguishable by their differing chemical shifts.

Previous XPS investigations of Fe_3O_4 have shown that the core line shapes are skewed on their low binding energy side, compared to spectra of pure ferric oxides, particularly after ion bombardment of the Fe_3O_4 surface (6). This suggests the presence under the envelope of a ferrous ion component of low binding energy. Asami et al (9) have recently attempted to isolate a component due to ferrous iron by subtraction of the $\text{Fe}(2p\ 3/2)$ spectrum of Fe_2O_3 from that for Fe_3O_4 . A major problem confronting XPS investigations of Fe_3O_4 , FeO and NiFe_2O_4 is the tendency of these surfaces to react rapidly with oxygen to yield an overlayer of Fe_2O_3 (10). In this present work, spectral characterization of these oxides has been improved considerably by taking account of this during sample handling. The Fe_3O_4 spectra are analyzed by a novel process of least squares spectral line fitting in which the line shape contribution from ferric ion is restrained during the computer assisted resolution of the envelope. This method can be used to estimate $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratios on magnetite surfaces.

EXPERIMENTAL

Spectroscopic Procedure - The photoelectron spectrometer used was a McPherson ESCA-36 with a cryogenically pumped sample chamber whose operating pressure is 5×10^{-7} Pa. Primary energy calibration is based on values of 84.0 eV for the $\text{Au}\ 4f(7/2)$ line for metallic gold and 1253.6 eV energy difference between the $\text{Mg}(2p)$ and $\text{Mg}(1s)$ lines for

magnesium metal. Appropriate relativistic corrections were made to the energy values⁽¹¹⁾. During operation, copper metal is used as a secondary energy standard in the spectrometer. The values of Cu(2p 3/2) and Cu(3p 3/2) lines used were $932.45 \text{ eV} \pm 0.1$ and $75.02 \pm 0.1 \text{ eV}$ respectively. Al K α exciting radiation was used, except where the higher resolution Mg K α radiation was required for improved definition of a complex peak shape.

Surface charging was not detected on any sample except αFeOOH . This observation is based on the invariance of the background hydrocarbon C(1s) binding energy ($285.0 \pm 0.15 \text{ eV}$) as well as the reproducibility of sample binding energies to better than $\pm 0.2 \text{ eV}$ for at least three independently prepared specimens. The surface charging on αFeOOH was measured using the C(1s) line and ranged from 0.9 - 2.3 eV.

Ion bombardment of sample surfaces was carried out with a Varian ion gun. With this gun, it is possible to raster the ion beam evenly over an area $7 \times 7 \text{ mm}$. Argon ions of 3 KeV energy were used with a flux density of 20 ma/m^2 . The beam intersected the surface at a glancing angle of 50° .

Sample Preparation - All powder specimens were mounted by smearing them onto a grooved copper flat. $\alpha\text{Fe}_2\text{O}_3$ (hematite) was examined as a powder (Fisher Reagent) and as a thin film grown on iron metal in oxygenated water. They gave identical spectra. $\gamma\text{Fe}_2\text{O}_3$

(maghemite) was prepared by reaction of iron (II) sulphate and iron (III) ammonium sulphate in boiling 1M NaOH, followed by autoclaving under oxygen in 1M NaOH at 130°C for 4 days. X-ray diffraction showed that the tetragonal system of $\gamma\text{Fe}_2\text{O}_3$ was the only form present. The powder was crushed under argon immediately before examination to open surfaces not previously exposed to air. XPS spectra were identical to those for uncrushed powder showing that no decomposition product such as hematite formed on the outside surface. CoFe_2O_4 was obtained from Cerac Inc., Butler, Wisc. and its structure was confirmed by x-ray diffraction. NiFe_2O_4 was made by coprecipitation of the oxalates of nickel and iron followed by heating at 600°C for several days. Although the bulk composition was confirmed to be NiFe_2O_4 by x-ray diffraction, changes in the Ni(3p)/Fe(3p) intensity ratio with time showed that the surface of NiFe_2O_4 was air sensitive, often forming iron rich oxide phases on the surface. Samples were considered acceptable only where the sensitivity corrected intensity ratio⁽¹²⁾ approached that expected from stoichiometry.

High purity Fe_3O_4 was prepared in a quartz tube furnace by reacting $\alpha\text{Fe}_2\text{O}_3$ at 700 - 1000°C under a mixture of CO and CO_2 , calculated⁽¹³⁾ to give stoichiometric Fe_3O_4 at that temperature. The sintered product was rapidly quenched to room temperature and immediately transferred to the spectrometer sample chamber, always under a nitrogen atmosphere. X-ray diffraction analysis showed only lines attributable to Fe_3O_4 . The $\text{Fe}^{+2}/\text{Fe}^{+3}$ concentration ratio was determined

to be 0.50 ± 0.02 by redox titration of a sample immediately following its dissolution in dilute sulphuric acid. Fe_3O_4 spectra with ferrous/ferric ion concentrations lower than normal were obtained from samples prepared using iron metal as a starting material rather than Fe_2O_3 ⁽¹⁴⁾. Ferrous oxide (Wustite) was also prepared by reducing Fe_2O_3 at 600°C in a CO/CO_2 mixture whose ratio was adjusted⁽¹³⁾ to give $\text{FeO}_{0.95}$. This sample was also handled completely under nitrogen. αFeOOH (Goethite) was prepared by dehydration of gelatinous $\text{Fe}(\text{OH})_3$, which was precipitated from a 1M $\text{Fe}(\text{NO}_3)_3$ solution by 0.1N NH_4OH ⁽¹⁵⁾. The precipitate was dried in a vacuum furnace for four days and was confirmed to be pure $\alpha\text{FeO}(\text{OH})$ by x-ray diffraction.

Spectrum Analysis - To reduce distortion caused by the sharply rising backgrounds in the $\text{Fe}(2p)$ and $\text{Fe}(3p)$ spectra, a baseline correction function of the type suggested by Barrie and Street⁽¹⁶⁾ was subtracted. The form of this function is shown in Figure 1(a). The magnitude of the correction at any point is proportional to the integrated spectral intensity on the low binding energy side of the point. Fitting of the low binding energy onset region with Gauss-Lorentzian peak shapes is found to be substantially better when using this function, instead of the more common linear approximation which over-estimates the background contribution in this region.

The peak fitting routine used in this work has been described previously by Bancroft et al⁽¹⁷⁾. The bands used in fitting a peak

envelope are defined according to their centroid position, half-width, shape (usually equal combination of Gaussian and Lorentzian distributions) and intensity. These parameters are then varied to obtain a minimum error sum of squares between the values for the experimental curve and the trial combination of bands. A quantitative measure of the "goodness" of the final fit is provided. An important feature of this program is its ability to constrain certain parameters of selected bands within set limits, while allowing others to vary freely. This permits known contributions to the band envelope to be fixed, while a best fit is established for the remaining portion of the envelope.

RESULTS

(A) CORE LINE SPECTRA

(1) $\alpha\text{Fe}_2\text{O}_3$, $\gamma\text{Fe}_2\text{O}_3$ and αFeOOH

These compounds are grouped together because of certain basic similarities in their Fe(2p) spectra which will be discussed below. The iron core line spectra of $\alpha\text{Fe}_2\text{O}_3$ are shown in Figure 1, while high resolution Fe(2p 3/2) spectra of α and γ forms of Fe_2O_3 are compared in Figure 2. Although the main Fe(2p 3/2) line is broad (FWHM $\approx$ 3 eV), considerable structure which is quite reproducible, is seen as part of the asymmetric peak envelope (see Figures 1(a) & 2(b)). Prominent also

in the $\alpha\text{Fe}_2\text{O}_3$ Fe(2p) spectrum is a satellite band about 8 eV above the Fe(2p 3/2) line (see Figure 1(a)). For $\gamma\text{Fe}_2\text{O}_3$, the shape of the main Fe(2p 3/2) line is clearly narrower. The spectrum of the α form has two distinct peaks separated by 1.0 eV while that for the γ form has only one slightly broadened maximum. Further weak structure is found on the high binding energy side of both peaks, which are asymmetric on the high binding energy side.

The structure in the Fe(2p) spectra was fitted by least squares routine following subtraction of the background. The steep leading edge and double maximum in the $\alpha\text{Fe}_2\text{O}_3$ Fe2p 3/2 spectrum was found to be well fitted by two narrow (FWHM = 1.4 eV) peaks of approximately equal intensity, separated by 1.2 eV. The remainder of the envelope was fitted by a series of peaks constrained to similar width and shape of decreasing intensity (see Figure 3). Any other attempted combination of fewer peaks and greater half-width could not reproduce the structure in the envelope.

The intensity distribution of these peaks can be rationalized on the basis of multiplet splitting of the Fe(2p) core line. Gupta and Sen (GS) ⁽¹⁸⁾ have calculated the multiplet structure exposed for core p levels of the free Fe^{+3} ion taking account of electrostatic and spin-orbit interactions and using the Hartree-Fock approximation of the free ion. The model is considered appropriate for highly ionic solids. The energy-intensity distribution calculated for the Fe(2p) spectrum of Fe^{+3} is plotted in Figure 3 for comparison with the experimental distribution

determined for the α and γ Fe_2O_3 spectra. The energy-intensity distributions of the experimental spectra clearly resemble that predicted for Fe(2p) multiplet splitting of the Fe^{+3} ion. The weak satellite 8 eV above the main Fe(2p 3/2) line is predicted at this energy by the level 2 model of GS, as a component of the Fe(2p 1/2) line multiplet splitting. The major peaks fitted within the Fe(2p 3/2) envelope correspond well to the predicted four line distribution for Fe(2p 3/2).

The measured splitting of the two most intense components of the $\alpha\text{Fe}_2\text{O}_3$ Fe(2p 3/2) line is 1.2 eV, as compared with 1.6 eV calculated for Fe^{+3} . An analysis of the same Fe(2p 3/2) envelope for $\gamma\text{Fe}_2\text{O}_3$ yields an intensity distribution almost identical to that in $\alpha\text{Fe}_2\text{O}_3$, but splitting is reduced by 0.2 eV resulting in the observed narrowing of the peak maximum. The mean binding energy of 711.0 ± 0.15 eV (weighted average of all components) is the same for α and γ Fe_2O_3 . The only change is in the multiplet splitting distribution within each peak.

The oxyhydroxide αFeOOH has a Fe(2p) spectrum similar, in many respects, to that for Fe_2O_3 (see Figure 4(a)). Evidence of several components under the Fe(2p 3/2) envelope is seen. The main core line is again asymmetric to the high binding energy side and a weak satellite is observed 8 eV above it. A least squares fit of the envelope (see Figure 4(b)) yields components similar to $\alpha\text{Fe}_2\text{O}_3$ in energy distribution, but with a somewhat altered intensity distribution. The mean binding energy of the line (711.85 ± 0.2 eV) has shifted 0.85 ± 0.1 eV above

that for Fe_2O_3 (see Table 1). $\text{Fe}(2p)$ chemical shifts of a similar magnitude and direction have been previously found between the equivalent oxides and hydroxides of copper, cobalt⁽¹⁹⁾, zinc and chromium⁽²⁰⁾. A shift of 0.9 eV is sufficiently large to permit FeOOH to be distinguished from Fe_2O_3 .

The $\text{Fe}(3p)$ spectra of α and $\gamma\text{Fe}_2\text{O}_3$ are identical, both in terms of intensity distribution and the measured binding energy of the main peak. The $\text{Fe}(3p)$ spectrum for αFeOOH has an intensity distribution similar to Fe_2O_3 , but is chemically shifted 0.6 ± 0.2 eV to higher binding energy (see Table 1). A low intensity satellite is observed 7.0 eV above the main $3p$ for all these compounds (see Figure 1). Neither this peak nor the shape of the main line can be explained by the $\text{Fe}(3p)$ multiplet splitting predicted for Fe^{+3} by GS⁽¹⁸⁾. However, electron correlation effects in the $\text{Fe}(3p)$ level are expected to be more important than in the deeper core lines and would be expected to affect strongly the observed $\text{Fe}(3p)$ intensity distribution⁽²¹⁾.

The $\text{Fe}(3s)$ peak for $\alpha\text{Fe}_2\text{O}_3$ (see Figure 1) is split into two major components as expected for a high spin d^5 ferric ion⁽²²⁾. The relative intensity of the components, 6:5, is in reasonable agreement with the 7:5 ratio expected from the $3s$ multiplet splitting of an ion with a 6S ground state. In addition to the two main components separated by 6.2 ± 0.2 eV, an additional weak line appears 13.2 eV above the main line which may be again due to correlation effects similar to

those seen in the MnF_2 Mn(3s) spectrum⁽²³⁾. The 3s spectrum for $\gamma\text{Fe}_2\text{O}_3$ shows identical splitting of the components.

The O(1s) spectra for α and $\gamma\text{Fe}_2\text{O}_3$ and αFeOOH are shown in Figure 5(a) - (c). The lattice oxygen binding energy in $\alpha\text{Fe}_2\text{O}_3$ is shifted 0.2 ± 0.05 eV lower than for $\gamma\text{Fe}_2\text{O}_3$ (see Table 1). For relatively clean α and $\gamma\text{Fe}_2\text{O}_3$ surfaces (Figures 5(a) and (b)), two additional low intensity bands are observed with quite similar binding energies. These are likely due to chemisorbed hydroxyl or carbonyl species. The very low intensity of these bands in the reference spectra of α and $\gamma\text{Fe}_2\text{O}_3$, indicates that surface hydroxides of iron do not complicate the spectra of these oxides.

The spectrum for αFeOOH (see Figure 5(c)) contains approximately equal contributions from hydroxyl and oxide oxygen, as expected from stoichiometry (0.9:1.0 ratio in Figure 5). Allen et al⁽⁴⁾ previously observed the broadened O(1s) band for FeOOH under lower resolution. The lattice oxygen ($\text{O}^{=}$) O(1s) line in FeOOH is shifted significantly higher (0.5 ± 0.1 eV) than that for the structurally similar $\alpha\text{Fe}_2\text{O}_3$. This suggests that the proton on the hydroxyl oxygen has some interaction with the $\text{O}^{=}$ oxygen. The binding energy for the hydroxyl oxygen is very similar to that in $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ ⁽¹⁹⁾.

(2) NiFe_2O_4 , CoFe_2O_4 and Fe_3O_4

The Fe(2P) and Fe(3p) spectra of mixed oxide NiFe_2O_4 are shown in Figure 6(a). In the 3p spectrum the Ni(3p)/Fe(3p) intensity ratio, corrected with the appropriate photoelectron cross-sections⁽¹²⁾, gives a Ni/Fe atom ratio of 2:1. The overall intensity distribution under

the Fe(2p) spectral envelope differs from that for γ or $\alpha\text{Fe}_2\text{O}_3$. In NiFe_2O_4 , the core line shape is almost symmetric and appears to contain none of the fine structure seen for the oxides discussed above. The satellite peak 8 eV above the Fe(2p) line, which is particularly characteristic of the Fe(2p) spectra of Fe_2O_3 and FeOOH , is not observed in the Fe(2p) spectrum of NiFe_2O_4 . Spectra of similar shape are obtained for CoFe_2O_4 . Using such characteristics of the Fe(2p) spectrum, it is possible to determine if iron oxide in a mixture with nickel or cobalt oxides is present mainly as a separate single oxide phase, i.e. Fe_2O_3 or if it has reacted with nickel or cobalt oxide to form a mixed inverse spinel oxide.

Table 1 lists binding energies of the major core line positions for CoFe_2O_4 and NiFe_2O_4 . No differences in binding energy were found between these ferrites. Core line chemical shifts between the ferrites and Fe_2O_3 are also quite small and are not very useful for analytical purposes.

The Fe(2p) and Fe(3p) spectra for pure and partially oxidized Fe_3O_4 are shown in Figures 6(b) and 6(c). The iron core line spectra for Fe_3O_4 can be compared with those for NiFe_2O_4 - an iron oxide of identical structure but containing only ferric ions. Both Fe_3O_4 and NiFe_2O_4 have inverse spinel structures with almost identical cell constants ($a_0(\text{Fe}_3\text{O}_4) = 0.8396$ nm. $a_0(\text{NiFe}_2\text{O}_4) = 0.8339$ nm.). It is assumed that ferric iron binding energies are not affected by the ex-

change of Ni^{+2} ions in the lattice for Fe^{+2} . This is supported by the fact that the ferric iron binding energies and peak shapes are identical for the inverse spinels CoFe_2O_4 and NiFe_2O_4 . From inspection, the Fe_3O_4 Fe(3p) spectra are clearly broadened on the low binding energy side compared with the NiFe_2O_4 spectrum. In the equivalent Fe(2p) spectra, the presence of an additional component is also apparent from the sharp shoulder around 708 eV. In both spectra the low binding energy components are ascribed to the presence of ferrous iron.

These Fe_3O_4 spectra were analyzed in detail using the least squares peak fitting program, allowing the ferric iron contribution under each Fe_3O_4 envelope to be represented by the equivalent iron core line spectrum of NiFe_2O_4 . In Figure 7(a), the Fe(3p) spectrum of NiFe_2O_4 was fitted using two peaks whose energy centroids, half-widths and relative intensities define its characteristic shape. These parameters were constrained within the limits of experimental reproducibility and the entire shape was fitted under the Fe_3O_4 Fe(3p) envelope, allowing only the overall intensity of the entire ferric contribution to vary. The remaining portion of the Fe_3O_4 spectrum was attributed to the ferrous ion contribution and the peak(s) representing this contribution did not have their parameters constrained.

In Figure 7(b), the Fe(3p) spectrum of pure Fe_3O_4 is analyzed using this procedure. The two peaks at higher binding energy represent the ferric iron contribution derived from the shape of the Fe(3p)

spectrum of NiFe_2O_4 . The lower binding energy peak (cross-hatched in Figure 7(B)) represents the ferrous iron contribution under the Fe_3O_4 envelope. The resultant "best fit" from the least squares analysis indicates that the ferrous contribution can be represented by a single, symmetric, relatively narrow peak (FWM = 2.4 eV). Its energy centroid is 2.1 eV below the center of gravity of the ferric component of the Fe_3O_4 spectrum. In the pure Fe_3O_4 Fe(3p) spectrum, the ferrous/ferric intensity ratio of the resolved components was found to be 0.52. This is in excellent agreement with the ferrous/ferric ion stoichiometry of 0.50 in Fe_3O_4 and is good evidence that proper discrimination of the ferrous and ferric components in the Fe(3p) spectrum has been achieved.

The above procedure has been applied to the analysis of Fe_3O_4 surfaces containing lower concentrations of ferrous ion (Sample II). In Figure 7(c) the Fe(3p) spectrum from Figure 6(c) has been analyzed. The resulting peak representing ferrous iron had the same shape, width and energy as in the analysis of pure Fe_3O_4 , but its intensity, relative to the ferric component was reduced to 0.15.

The Fe(2p) spectra of these Fe_3O_4 samples were analyzed using the same spectral line fitting procedure as outlined above. The Fe(2p $3/2$) spectrum of NiFe_2O_4 (see Figure 8(a)) is used as a model for the ferric iron contribution. The ferrous iron contribution which is deconvoluted from the Fe_3O_4 envelope using this procedure is a symmetric narrow peak (FWHM = 1.8 eV) centered at 708.3 eV (see Figure 8(b)). The

$\text{Fe}^{+2}/\text{Fe}^{+3}$ peak intensity ratio is 0.32, which is low compared to the "correct" value of 0.5 obtained from Fe(3p) line analysis. This discrepancy could arise from the presence of additional weak Fe^{+2} line components on the high binding energy side of the peak. Such components would be included as part of the ferric contribution using the present method of analysis.

The Fe(2p) spectrum for Fe_3O_4 with a lower Fe^{+2} concentration is shown in Figure 8(c). The $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio of 0.07 measured from this spectrum is 22% of the measured ratio for pure Fe_3O_4 in Figure 8(b). This corresponds well with a factor of 27% obtained from the Fe(3p) spectrum analysis. Thus, although the absolute ratio measured from the Fe(2p) spectrum analysis does not reflect the actual stoichiometry of the Fe_3O_4 surface, the change in this ratio appears to reflect changes in the ferrous/ferric ratio.

(3) FeO

The Fe(2p) spectrum of the divalent oxide is shown in Figure 9. As in the spectra of the ferric oxides, the Fe(2p 3/2) peak is quite broad and some evidence of structure is seen. A satellite band is located ~ 6 eV above the main peak.

The structure under the subtracted background Fe(2p 3/2) line was fitted, using compounds of the same shape and width as in the analyses

of the Fe_2O_3 spectra. Three major bands were required to fit the $\text{Fe}(2p\ 3/2)$ line. The energy splitting of these bands, and their approximate intensity distribution, were in reasonably good agreement with the multiplet splitting pattern calculated for the Fe^{+2} free ion by Gupta and Sen⁽²⁴⁾. This is seen from Figure 9, where the experimental line fit is compared with the calculated splitting.

Table 1 lists core line binding energies for FeO . The mean binding energy of the $\text{Fe}(2p\ 3/2)$ line (709.5 ± 0.2 eV) is shifted 1.5 ± 0.3 eV below that for Fe_2O_3 and chemical shifts of 1.0 eV and 1.1 eV are found for $\text{Fe}(3p)$ and $\text{Fe}(3s)$ lines respectively. Shifts of this magnitude are clearly useful for discriminating ferrous and ferric oxides.

The ferrous iron binding energies in Fe_3O_4 are substantially lower than those for ferrous iron in FeO . Moreover, the $\text{Fe}(2p)$ line shape for Fe^{+2} in Fe_3O_4 is considerably narrower and less complex than that in FeO . Probably, changes due to both multiplet splitting and the chemical shift are occurring here, affected by the presence of the ferric ion in one structure and not in the other.

B. VALENCE BAND SPECTRA

Figure 10 shows XPS valence band spectra for FeO , $\alpha\text{Fe}_2\text{O}_3$, $\gamma\text{Fe}_2\text{O}_3$ and Fe_3O_4 samples. Valence orbitals in iron oxides are formed from Fe 3d and O 2p atomic orbitals. Valence states with high p char-

acter have low cross-sections when excited by x-ray energies, so that the bands observed in the present spectra provide a measure of the partial densities of localized d states. The XPS spectrum of FeO (Figure 10(a)) has two maxima - a strong one at 4.0 eV and a shoulder at 1.5 eV. These spectral features agree with the partial densities of Fe(3d) states in FeO derived from a frequency dependent photoelectron study made recently by Eastman and Freeouf⁽²⁵⁾. The peaks at 1.5 eV and 4.0 represent excitations from e_g and t_{2g} levels respectively.

In the valence spectra of both α and γ -Fe₂O₃ (Figures 10(b) and 10(c)), three distinct peaks are observed. Following background subtraction, these spectra were subjected to a least squares fit using three bands of identical shape. The band positions and intensities resolved from the spectra (see Figure 11), are clearly different in the spectra for γ and α -Fe₂O₃. The two bands of lowest energy are assigned to excitations from $3e_g$ and $2t_{2g}$ orbitals respectively. A recent SCF X_α calculation for α -Fe₂O₃⁽²⁶⁾ has determined a splitting energy of 2.5 eV between the $3e_g$ and $2t_{2g}$ orbitals, in good agreement with our experimental value of 2.3 eV. The splitting found in γ -Fe₂O₃ is also 2.3 eV, but the absolute position of both bands has shifted 0.4 eV closer to the Fermi level and the relative emission intensities of the two bands has altered considerably. The third band in the α -Fe₂O₃ envelope located 2.4 eV above the $2t_{2g}$ band is identified with the $2e_g$ orbital, which also has strong 3d character. In the X_α calculations⁽²⁶⁾, this orbital was determined to lie approximately 2.5 eV below the $2t_{2g}$ level in the

energy level diagram. The center of gravity of the valence band system is 5.5 ± 0.1 eV for both γ and $\alpha\text{Fe}_2\text{O}_3$. This confirms that all bands result from orbitals with strong 3d character, since each band system is split about a common energy.

The valence band spectrum of pure Fe_3O_4 (Figure 10(d)) is too complex for detailed treatment, but it appears to contain features seen in both ferric and ferrous oxide spectra. Lower ferrous ion concentration in the Fe_3O_4 matrix results in a diminution of the peak around 4 eV.

C. AUGER SPECTRA

Wagner⁽²⁷⁾ has shown that the Auger Line chemical shifts observed for many compounds of the non-transition elements, are, in fact, larger than the equivalent photoelectron core line shifts. Changes in the $\text{Fe } M_{2,3}$ VV line shape with chemical structure have been observed by Seo et al⁽²⁸⁾, using electron excited Auger spectroscopy. Analysis using this particular line is not practical in XPS, but the more intense L_3 , $M_{4,5}M_{4,5}$ and $L_3 M_{2,3}M_{4,5}$ lines were investigated for several oxides to determine if they could provide further characterizable spectra. The $L_3M_{4,5}M_{4,5}$ lines for FeO , $\alpha\text{Fe}_2\text{O}_3$, $\gamma\text{Fe}_2\text{O}_3$ and Fe_3O_4 were quite broad (6-9 eV (FWHM)), because of the many overlapping Auger lines. Only slight alterations in the shape of the envelope were found and these were of little use for analytical purposes. No changes in the $L_3M_{2,3}M_{4,5}$ line shape were observed.

D. ION BOMBARDMENT EFFECTS

Analysis of iron oxide corrosion films by XPS frequently involves ion bombardment of the oxide, in order to obtain a concentration profile through the film. If characterization of the iron oxide within the film is to be made, the effects of ion bombardment on the chemical integrity of each possible oxide species must be known. Consequently, the oxides $\alpha\text{Fe}_2\text{O}_3$, NiFe_2O_4 , Fe_3O_4 and FeO were subjected to a 3 keV argon ion beam flux of 20 mA/m^2 for periods up to 10 minutes. This is equivalent to removal of $\sim 40 \text{ nm}$ of oxide film⁽¹²⁾.

Bombardment of an $\alpha\text{Fe}_2\text{O}_3$ surface resulted in almost complete reduction to FeO during the first few minutes of ion sputtering. This can be seen from the $\text{Fe}(2p)$ spectrum of sputtered Fe_2O_3 in Figure 12(a) which has the same structural features and mean binding energy as the spectrum of FeO in Figure 9.

Ion bombardment of the spinels Fe_3O_4 and CoFe_2O_4 also resulted in the appearance of a new low binding energy component in the $\text{Fe}(2p)$ and $\text{Fe}(3p)$ spectra that indicates their partial conversion to ferrous oxide. This is particularly clear in the $\text{Fe}(2p)$ spectrum of CoFe_2O_4 (Figure 12(b)), where only a single ferric component was visible before ion bombardment. The low binding energy component produced by sputtering was deconvoluted using the previously described procedure and was identified as FeO . For the more complex Fe_3O_4 spectra, the partial

reduction to FeO was inferred from the spectral broadening observed and the analagous behaviour of CoFe_2O_4 . No effect of ion bombardment on FeO was found.

Ion bombardment of ferric oxides under our conditions thus results in the conversion of at least a portion of the top several atomic layers to FeO. XPS Identification of a specific iron oxide phase thus becomes difficult following ion bombardment. However, in all cases studied, ion bombardment of iron oxides caused no reduction of oxide to metal. Thus, an oxide phase can be differentiated from iron metal by XPS following sputtering, even though its specific chemical structure cannot be readily identified.

DISCUSSION

Some of the iron oxide structures studied are identifiable on the basis of their chemical shift. A chemical shift results from a change in the average electrostatic potential field about an atom. This occurs, for example, in Fe_3O_4 where ferrous and ferric ions in the same lattice can be readily distinguished by the 2.0 eV difference in their core line binding energies. Similarly, in FeOOH, introduction of the more electronegative hydroxyl groups into the oxide lattice results in a decrease in the average charge on the ferric ion and this change is reflected in the increased binding energies for all core lines. The

presence of FeOOH, precipitated from alkaline solution, has been detected on actively corroding iron surfaces, using the distinctly higher Fe(2p) and Fe(3p) core binding energies for this species ⁽²⁹⁾. The chemical shift between Fe₂O₃ and FeO is useful for characterizing the initial oxide species formed during oxidation of a clean iron metal surface. Kishi and Ikeda ⁽³⁰⁾ report a mean Fe(2p) binding energy difference of 0.8 eV between that for the initial oxide and the Fe₂O₃ which predominates after increased oxygen exposure. The initial oxide phase which nucleates during exposure of an iron surface to oxygen has been identified as FeO in earlier LEED studies ⁽³¹⁾.

Among the simple and mixed ferric oxides, very little change in mean core line binding energy is evident, and characterization by means of binding energy is not possible. However, differences in the Fe(2p) core line spectra due to multiplet interaction are clearly present and these can be used to provide "fingerprint" identification of the particular oxide species present. For example, the product of the oxidation of an Fe₃O₄ surface in air could be identified as α or γ -Fe₂O₃ on the basis of the Fe(2p) peak shape provided this product layer were sufficiently thick (3 nm) to obscure any contribution from the original Fe₃O₄.

In their treatment of multiplet interaction in free transition metal ions, Gupta and Sen ⁽²⁴⁾ point out that the crystal field could be important in determining the final terms of the ion, particularly if the degeneracy of the ground state is removed by this field, resulting in a redistribution of the intensities of the predicted lines. However, even

without crystal field and other effects being taken into account, remarkably good agreement has been achieved between the predicted energy-intensity distributions and those observed experimentally for a number of transition metal compounds with high spin. In addition to the reasonably good accord shown here between the Fe^{+2} and Fe^{+3} free ion models and their respective oxides, Kowalczyk et al. (23) have found even better correspondence between Gupta and Sen's predicted $\text{Mn}(2p)$ structure for high spin Mn^{+2} and their experimentally observed structure for MnF_2 . The exceptionally good agreement probably results from the highly ionic nature of the compound used. Signorelli (32) has also compared multiplet structure in the $\text{Fe}(2p)$ spectra of high spin ferric organometallic complexes with the Fe^{+3} results of Gupta and Sen.

A study of the XP spectra of both structures of Fe_2O_3 is useful in isolating some of the factors affecting chemical shifts and multiplet splitting in different core levels. In both γ and $\alpha\text{Fe}_2\text{O}_3$, the metal core line binding energies are identical, within experimental error, suggesting that the average potential about the metal ion is the same. This is also suggested by the identical $\text{Fe}(3s)$ multiplet structure observed for both α and $\gamma\text{Fe}_2\text{O}_3$. Because this multiplet results from 7S and 5S final spin states, it is affected only by the average charge about the metal ion. The two iron oxide structures do differ in the symmetry of the crystal field about the metal ion, and it is this difference that likely affects the observed change in multiplet splitting of the $\text{Fe}(2p)$ levels. The energy splitting of the two main multiplets

is 0.20 eV larger for $\alpha\text{Fe}_2\text{O}_3$ than for $\gamma\text{Fe}_2\text{O}_3$. In the hexagonal close packed $\alpha\text{Fe}_2\text{O}_3$ structure, the octahedrally situated oxygens create a symmetric field about each ferric iron, while in the distorted spinel structure of $\gamma\text{Fe}_2\text{O}_3$ an axial field component is present. It is possible for such an axial field to result in reordering of final states and change of the splitting. This could arise from the interaction of an axial field with a low-lying P or D initial state to result in a final state which was more stable than the ^7P or ^5P states calculated for Fe^{+3} (18).

The multiplet structure in the Fe(2p) spectrum of FeOOH is similar to that observed in Fe_2O_3 , except that some alteration in the relative intensity of the components appears likely. As in $\alpha\text{Fe}_2\text{O}_3$, the ferric ions are octahedrally surrounded by oxygen, but three of these are hydroxyl ions which create a slightly asymmetric field on the metal ion. No component structure is observed in the Fe(2p) spectra of the iron spinels, NiFe_2O_4 and CoFe_2O_4 . The absence of structure comparable to that calculated for the Fe^{+3} free ion may be at least partly associated with the high axial field component present in these oxides.

Since satellite structure observed in the oxides can at least be qualitatively accounted for by multiplet interaction, shape-up interaction does not appear to make a major contribution to the spectra. However, Carlson (33) has shown that the shape-up process is responsible for strong satellites in the Fe(2p) spectra of a number of ferric and

ferrous salts. In the case of the oxides, the probability of the $(O(2p) \rightarrow M(3d))$ charge transfer transition, thought responsible for shake-up in these compounds ⁽³⁴⁾, is apparently very low.

ACKNOWLEDGEMENTS

The authors acknowledge helpful discussions with S.K. Sen, R.P. Gupta and C.R. Brundle. They also would like to thank P.R. Tremaine, J. LeBlanc and T.E. Rummery for supplying several of the iron oxides, M. Duclos for x-ray characterization, and L. Coatsworth for assistance with the peak fitting program.

18. R.P. Gupta and S.K. Sen, Phys. Rev., B10, 71 (1974).
19. N.S. McIntyre and M.G. Cook, Anal. Chem. 47, 2208 (1975).
20. N.S. McIntyre and P.H. Tewari, J. Colloid Interfac. Sci. (in press).
21. S.P. Kowalczyk, L. Ley, F.R. McFeely and D.A. Shirley, Phys. Rev. B11, 1721 (1975).
22. C.S. Fadley in "Electron Spectroscopy" D.A. Shirley, ed. American Elsevier Company/New York) 1972, p. 781.
23. S.P. Kowalczyk, L. Ley, R.A. Pollak, F.R. McFeely and D.A. Shirley, Phys. Rev. B7, 4009 (1973).
24. R.P. Gupta and S.K. Sen, Phys. Rev. B12, 15 (1975).
25. D.E. Eastman and J.L. Freeouf, Phys. Rev. Lett, 34, 395 (1975).
26. J.A. Tossell, D.J. Vaughan and K.H. Johnson, Nature (Physical Science), 244, 42 (1973).
27. C.D. Wagner, Disc. Faraday Soc. 60, 000(1976).
28. M. Seo, J.B. Lumsden and R.W. Staehle, Surface Science 50, 541 (1975).
29. N.S. McIntyre, unpublished results.
30. K. Kishi and S. Ikeda, Bull. Chem. Soc. Japan, 46, 341 (1973).
31. C. Leygraf and S. Ekelund, Surface Science, 40, 609 (1973).
32. A. Signorelli, Ph. D. Thesis, University of Notre Dame (1975) University Microfilms 75-1860.
33. T.A. Carlson, Disc. Faraday Soc., 60, 000 (1976).
34. K.S. Kim, Chem. Phys. Lett., 26, 234 (1974).

REFERENCES

1. See, for example, U.R. Evans, "The Corrosion and Oxidation of Metals", Edward Arnold Ltd. (London), 1968.
2. T.E. Rummery and B. Montford, Atomic Energy of Canada Limited, Report AECL-4444 (1975).
3. C.D. Stockbridge, P.B. Sewell and M. Cohen, J. Electrochem. Soc., 108, 928 (1961).
4. G.C. Allen, M.T. Curtis, A.J. Hooper and P.M. Tucker, J.C.S. 14, Dalton, 1525 (1974).
5. T.P. Hoar, M. Talerman and P.M.A. Sherwood, Nature (Physical Science), 240, 116 (1972).
6. J.P. Coad and J.G. Cunningham, J. Electron Spectrosc., 3, 435 (1974).
7. G. Okamoto, K. Tachibana, T. Shibata and K. Hoshino, J. Japan Inst. Metals 38, 117 (1974).
8. I. Olefjord, Metal Science, 9, 263 (1975).
9. K. Asami, K. Hashimoto and S. Shimodaira, Corrosion Science, 16, 35 (1976).
10. G. Hagg, Z. Physik, Chem., B29, 95 (1935).
11. G. Johansson, J. Hedman, A. Berndtsson, M. Klasson and R. Nilsson, J. Electron Spectrosc., 2, 295 (1973).
12. N.S. McIntyre and D.G. Zetaruk, J. Vac. Sci. Technol., 14, 000 (1977).
13. J. Smiltens, J. Chem. Phys. 20, 990, (1952).
14. P.R. Tremaine and N.S. McIntyre, unpublished results.
15. A. Noerlund Christensen, Acta Chemica Scandinavica, 22, 1487 1 (1975).
16. A. Barrie and F.J. Street, J. Electron Spectrosc., 7, 1 (1975).
17. G.M. Bancroft, I. Adams, L.L. Coatsworth, C.D. Bennewitz, J.D. Brown and W.D. Westwood, Anal. Chem., 47 586 (1975).

TABLE 1

Binding Energies of Major Core Lines in The
Iron Oxides^a

<u>COMPOUND</u>	<u>Fe(2p 3/2)^b</u>	<u>Fe(3p 3/2, 1/2)^c</u>	<u>Fe(3s)^c</u>	<u>O(1s)^c</u>
Fe metal	706.7 ± 0.10	53.0 ± 0.15	90.9 ± 0.3	
FeO	709.5 ± 0.2	54.9 ± 0.3	92.5 ± 0.2	530.0 ± 0.2
Fe ₃ O ₄ { Fe ⁺²	708.3 ± 0.15	53.9 ± 0.2		530.2 ± 0.2
{ Fe ⁺³	d	d	d	
NiFe ₂ O ₄	710.6 ± 0.2	55.9 ± 0.2	93.5 ± 0.2	530.1 ± 0.2
CoFe ₂ O ₄	710.6 ± 0.2	55.9 ± 0.2	93.5 ± 0.2	
αFe ₂ O ₃	711.0 ± 0.15	55.7 ± 0.15	93.6 ± 0.2	529.8 ± 0.10
γFe ₂ O ₃	711.0 ± 0.15	55.7 ± 0.15	93.6 ± 0.2	530.0 ± 0.10
αFeOOH	711.9 ± 0.2	56.6 ± 0.2	94.2 ± 0.2	{ 530.3 ± 0.2 531.4 ± 0.2

a Errors quoted are one standard deviation

b Refers to mean binding energy taken as the weighted average of all discernible components of the line.

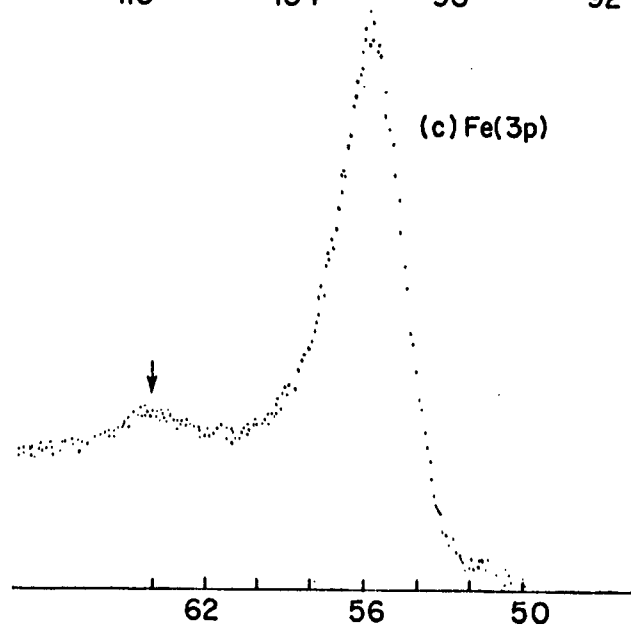
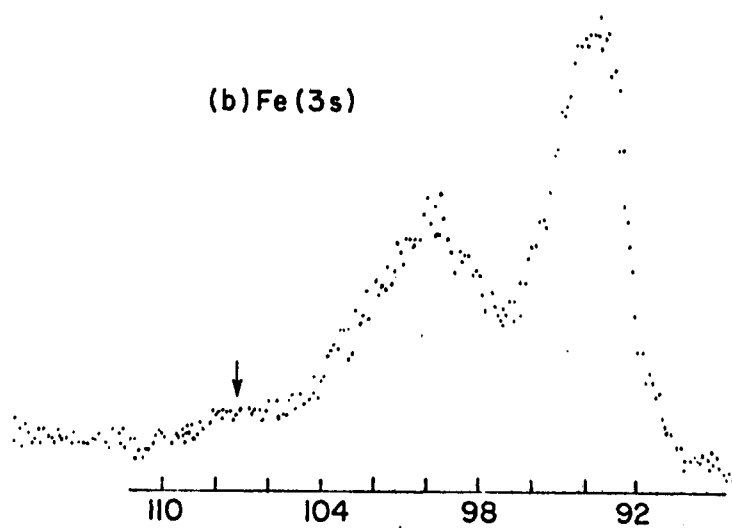
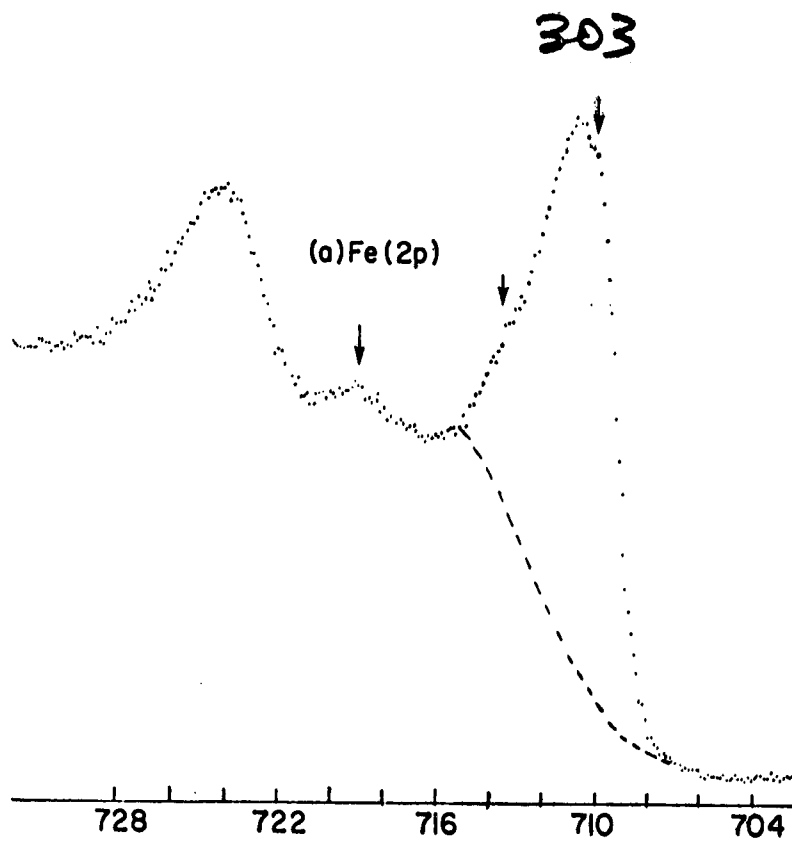
c Refers to peak maximum binding energy.

d Inferred from binding energies of NiFe₂O₄ and CoFe₂O₄ (see text).

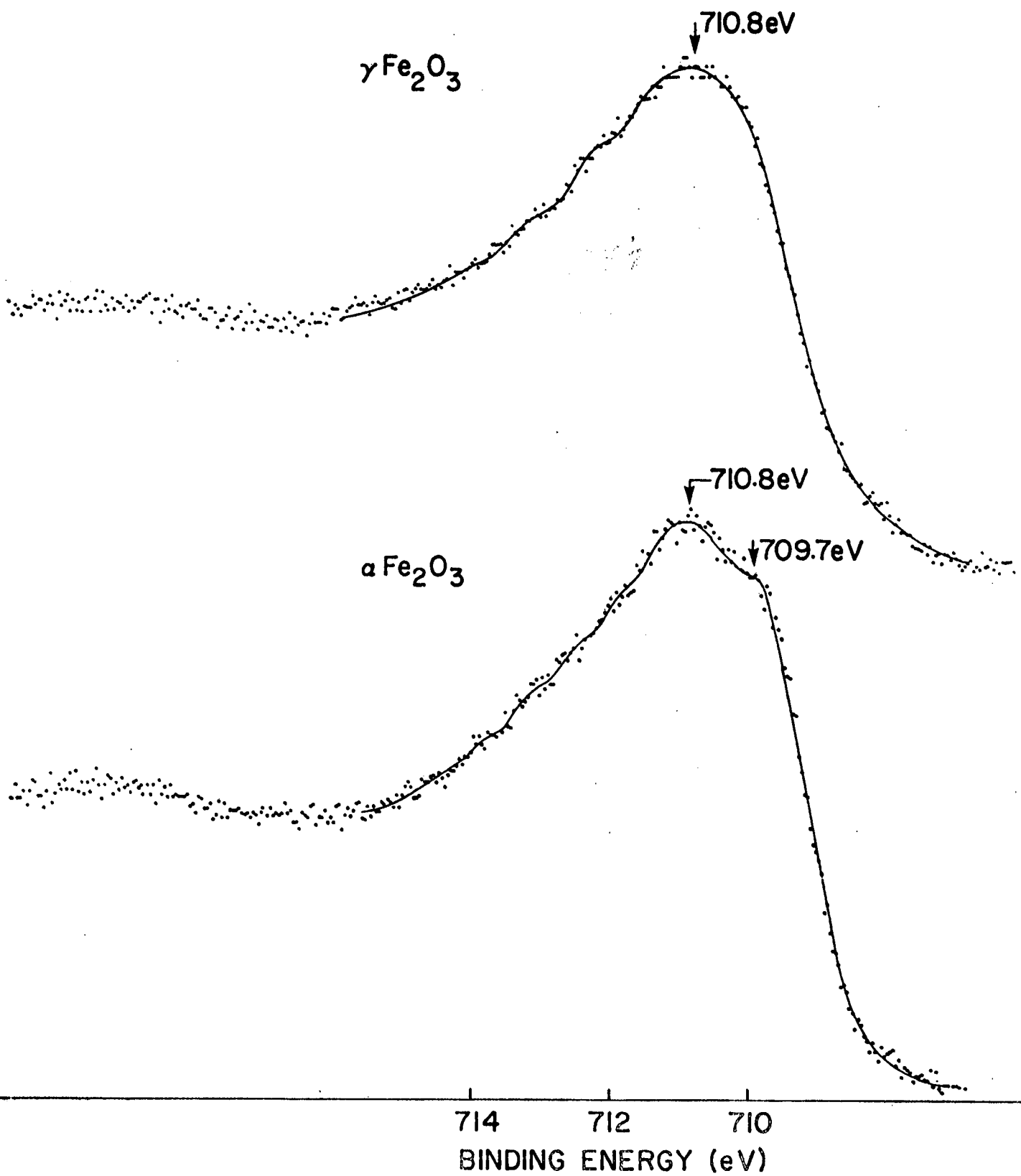
LIST OF FIGURES

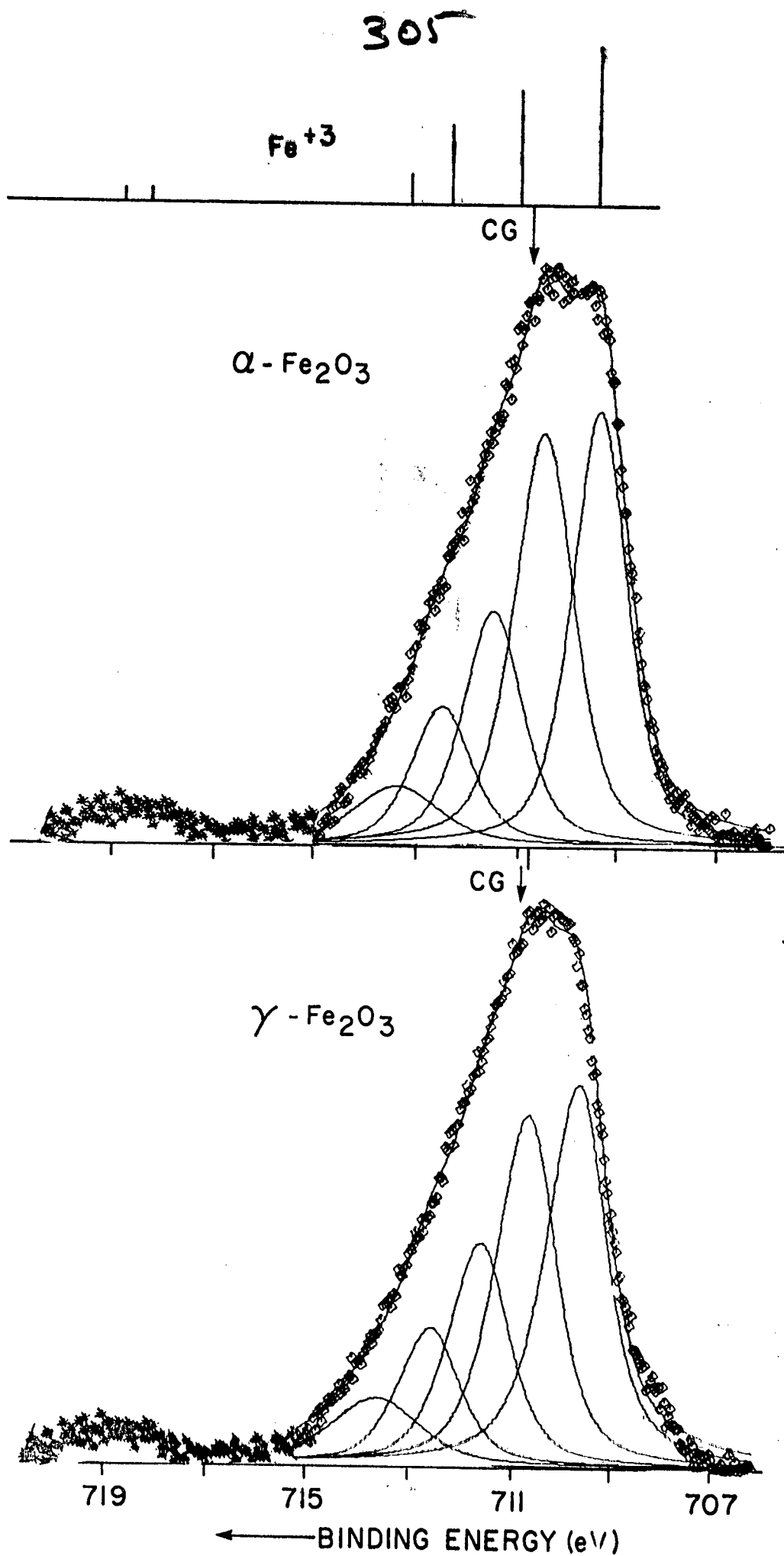
- FIGURE 1 - Major core line photoelectron spectra of α Fe_2O_3 . (a) Fe(2p) spectrum (b) Fe(3s) spectrum (c) Fe(3s) spectrum. The dashed line in the Fe(2p) spectrum represents the form of background function subtracted during peak fitting procedures. Arrows indicate spectral features discussed in text.
- FIGURE 2 - Detailed Fe(2p 3/2) spectra of (a) $\gamma\text{Fe}_2\text{O}_3$ (b) $\alpha\text{Fe}_2\text{O}_3$.
- FIGURE 3 - Spectral line fit of (a) $\alpha\text{Fe}_2\text{O}_3$ (b) $\gamma\text{Fe}_2\text{O}_3$. Calculated splitting and relative intensities for a free Fe^{+3} ion are shown by the solid bars. CG denote peak center of gravity. The solid line drawn through the points is the sum of the individual bands in the envelope.
- FIGURE 4 - (a) Fe(2p) spectrum of αFeOOH (b) Spectral line fit of Fe(2p 3/2) envelope using peaks of identical width to those in Figure 3(b). CG denotes peak center of gravity.
- FIGURE 5 - O(1s) spectra for (a) $\alpha\text{Fe}_2\text{O}_3$ (b) $\gamma\text{Fe}_2\text{O}_3$ (c) FeOOH . The ratio of hydroxide to oxide peak areas is 0.9. The presence of some adsorbed species appears likely at binding energies above 532 eV.
- FIGURE 6 - Fe(2p) and Fe(3p) spectra of (a) NiFe_2O_4 (b) pure Fe_3O_4 (c) partly oxidized Fe_3O_4 .
- FIGURE 7 - Spectral line fits of the Fe(3p) line for (a) NiFe_2O_4 (b) pure Fe_3O_4 (c) partly oxidized Fe_3O_4 . The peak parameters obtained for the NiFe_2O_4 spectrum in (a) were constrained to these values in spectra (b) and (c). Cross-hatched areas are ascribed to the ferrous iron contribution.
- FIGURE 8 - Spectral line fits of the Fe(2p 3/2) line for (a) NiFe_2O_4 (b) pure Fe_3O_4 (c) partly oxidized Fe_3O_4 .
- FIGURE 9 - (a) Fe(2p 3/2) spectrum for FeO (b) Spectral line fit of a portion of the FeO Fe-2p 3/2 spectrum.
- FIGURE 10 - Valence band photoelectron spectra for (a) FeO (b) $\alpha\text{Fe}_2\text{O}_3$ (c) $\gamma\text{Fe}_2\text{O}_3$ (d) Fe_3O_4 . Exciting radiation used was $\text{MgK}\alpha$ (1253.6 eV).

- FIGURE 11 - Spectral line fits of the valence band spectra for (a) $\gamma\text{Fe}_2\text{O}_3$ (b) $\alpha\text{Fe}_2\text{O}_3$. CG denotes envelope center of gravity.
- FIGURE 12 - Fe(2p 3/2) spectra of (a) Fe_2O_3 (b) CoFe_2O_4 (c) Fe_3O_4 following 2 minutes of bombardment with 3 KeV argon ions with a flux of 20 ma/m².

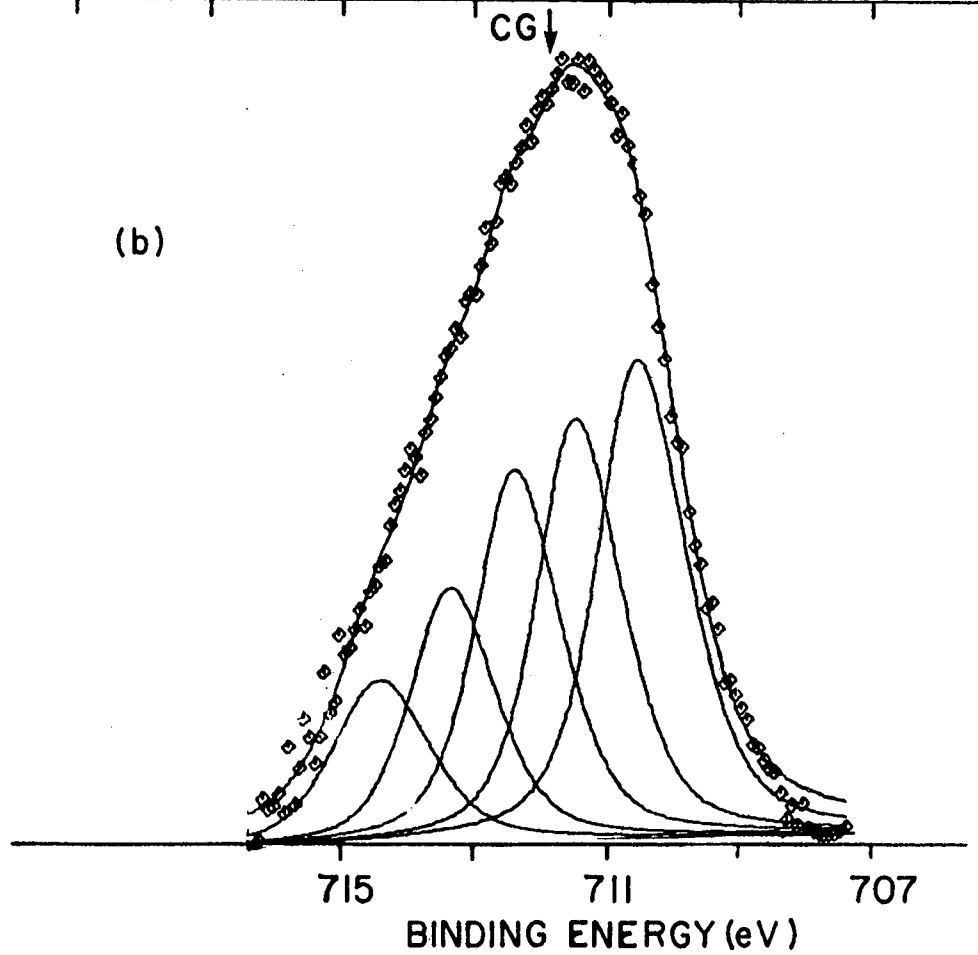
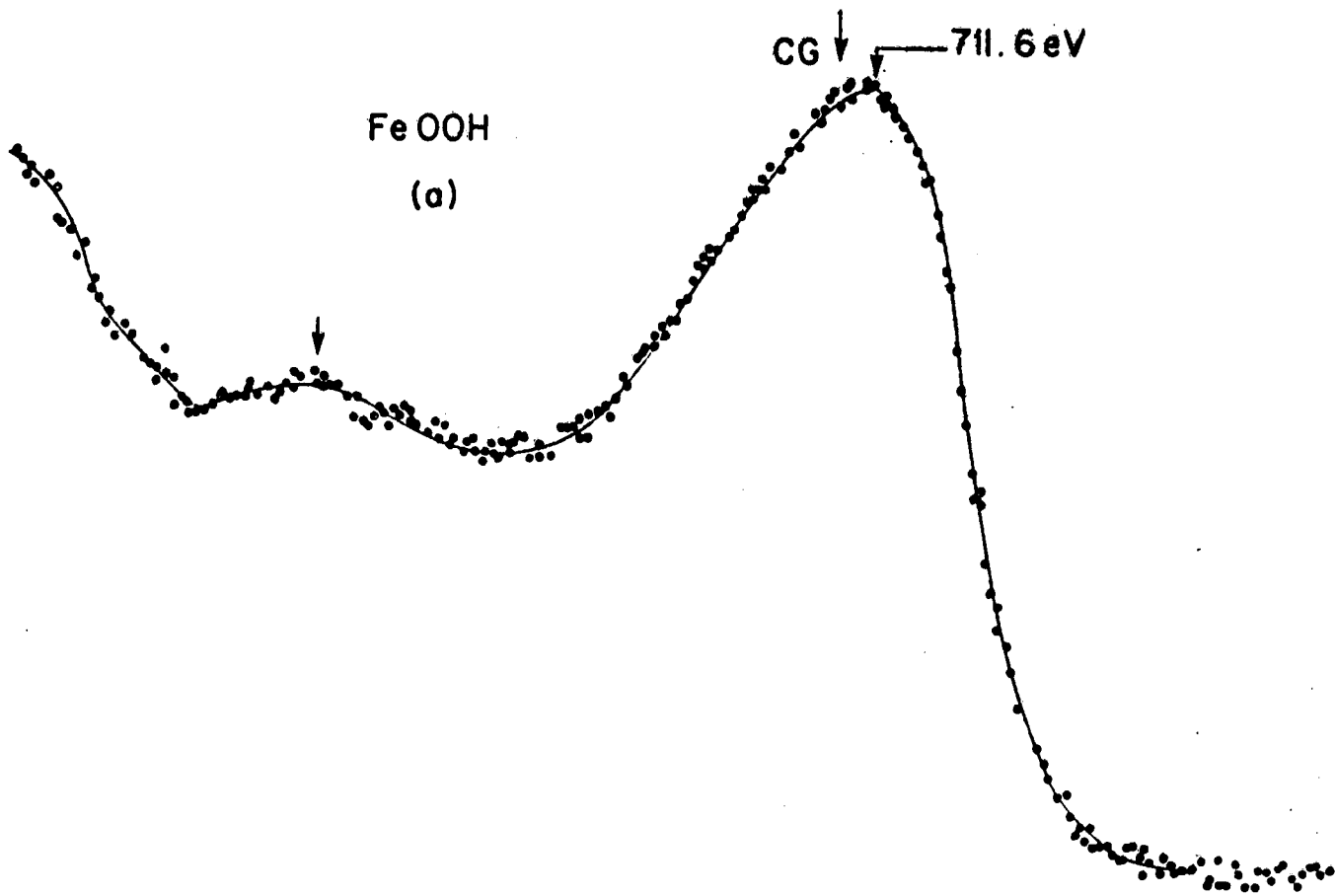


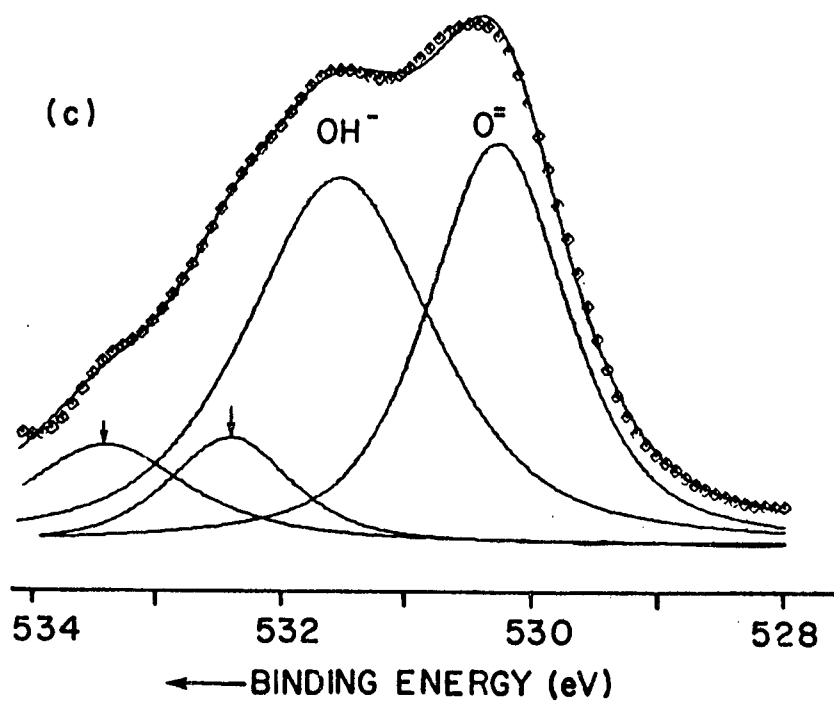
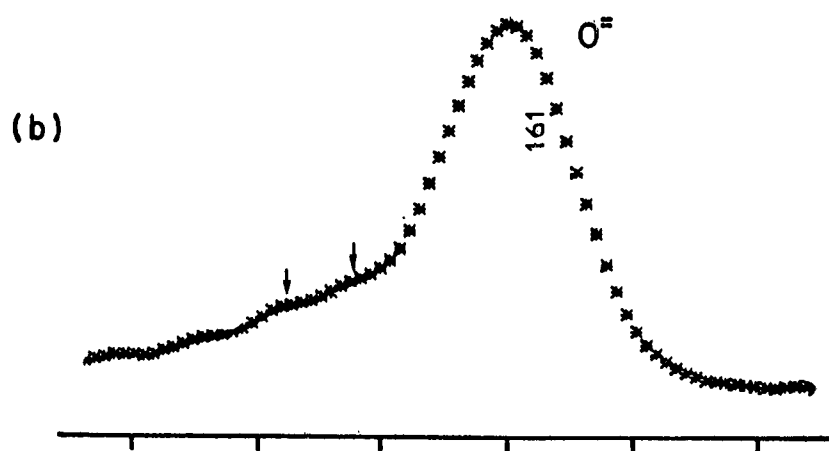
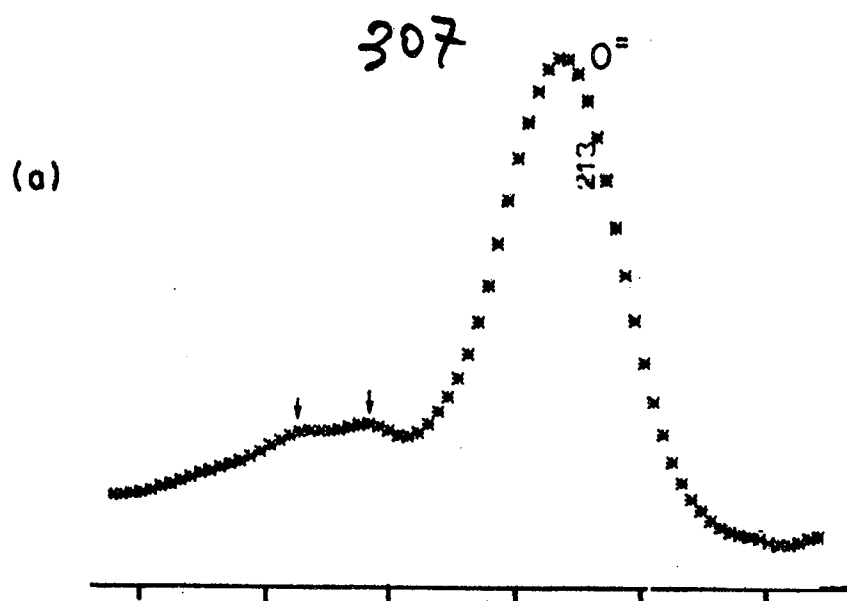
304

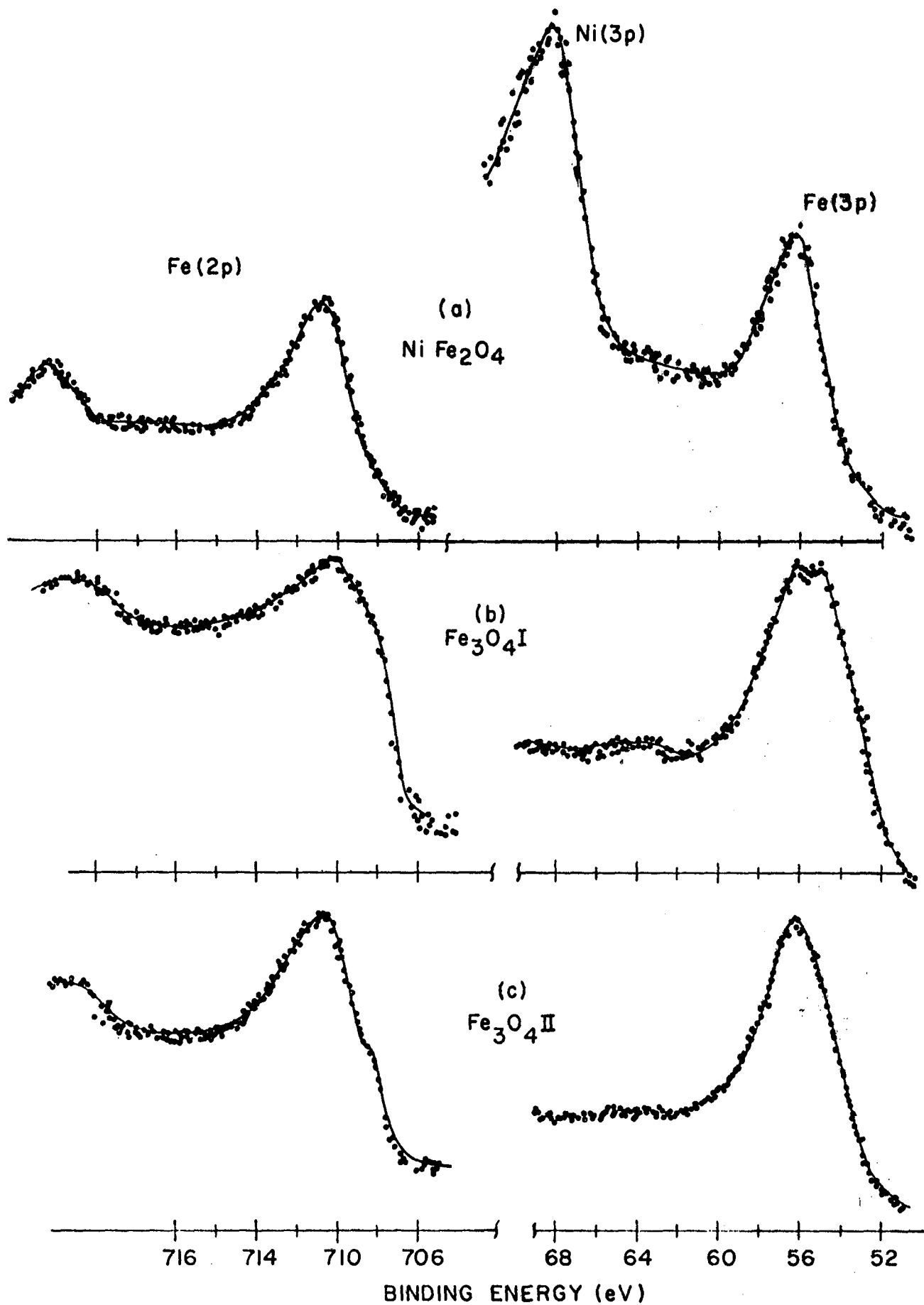




306



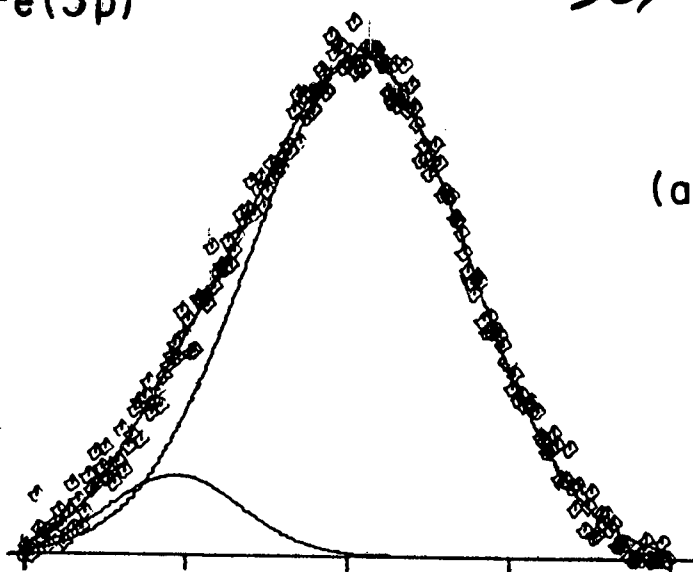




Fe(3p)

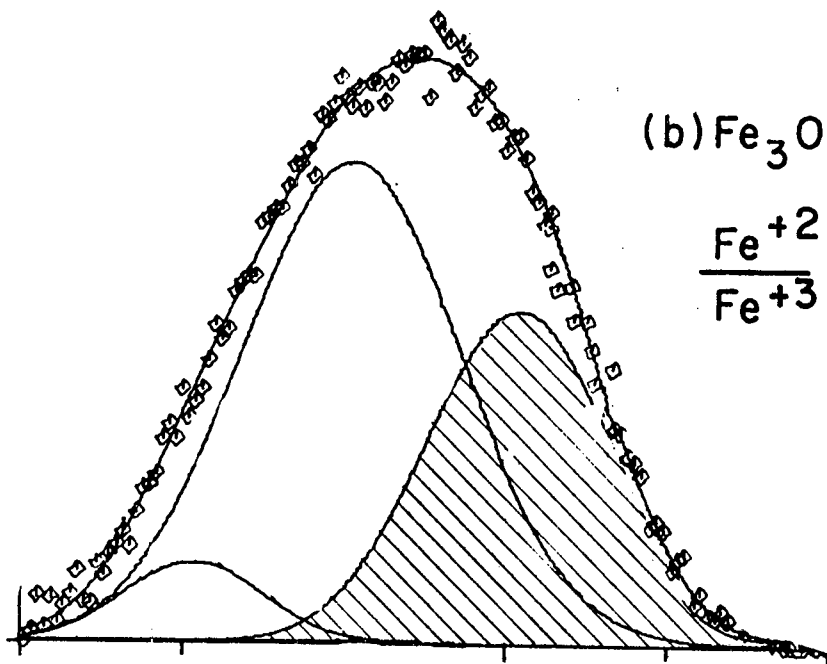
309

(a) NiFe_2O_4



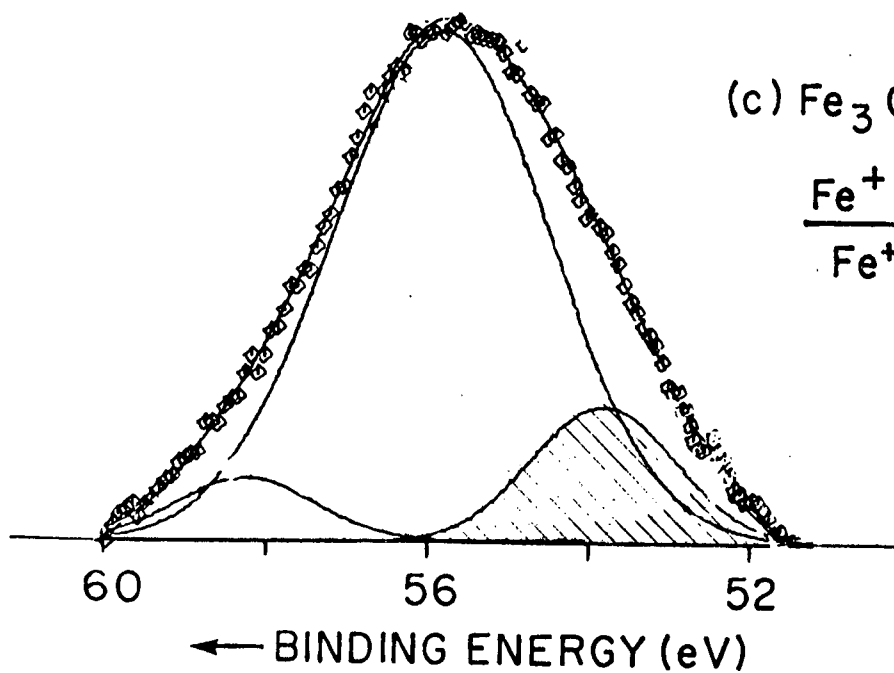
(b) Fe_3O_4 I

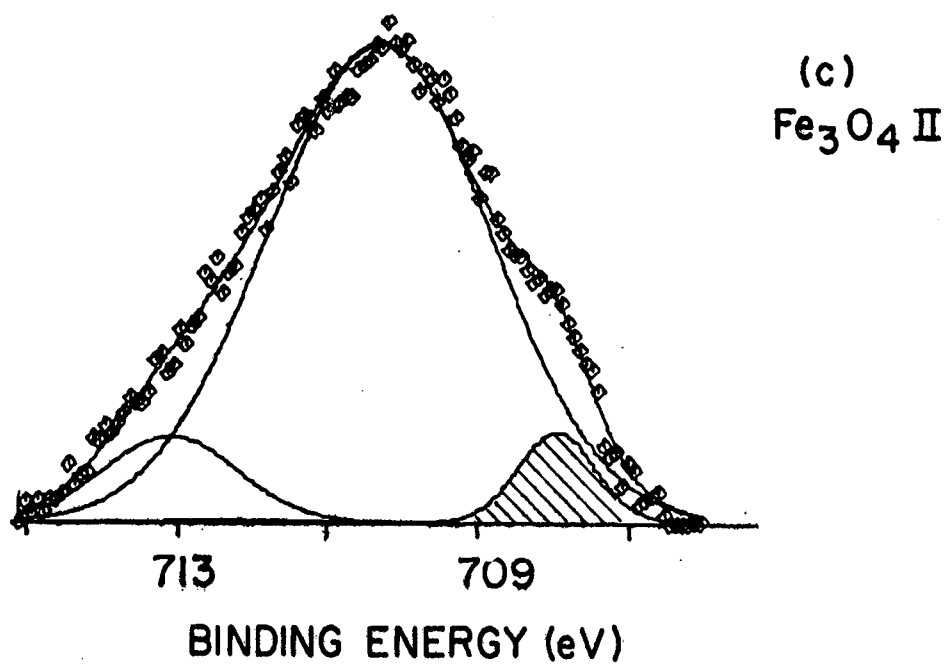
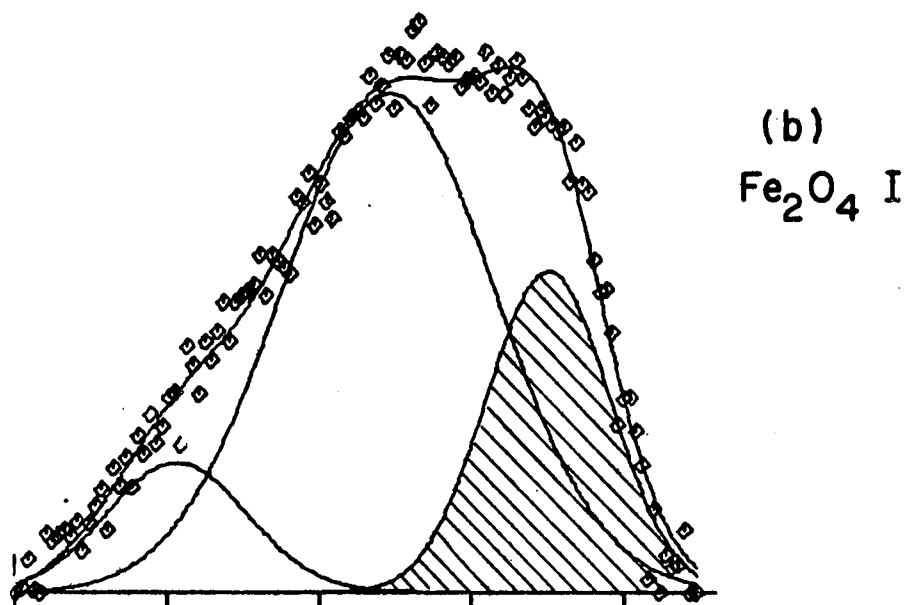
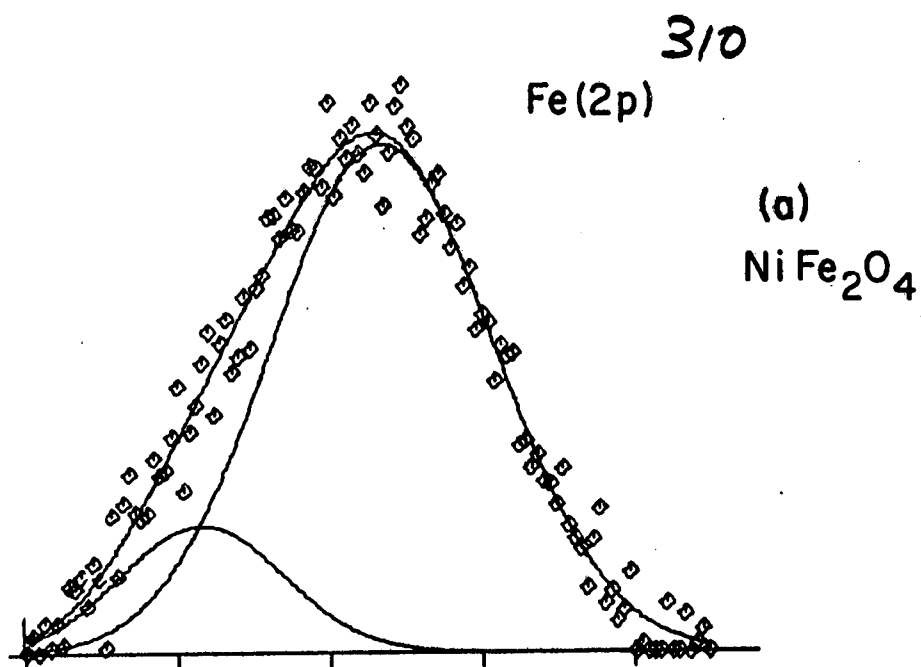
$$\frac{\text{Fe}^{+2}}{\text{Fe}^{+3}} = 0.52$$



(c) Fe_3O_4 II

$$\frac{\text{Fe}^{+2}}{\text{Fe}^{+3}} = 0.15$$





3H

FeO

← BINDING ENERGY (eV)

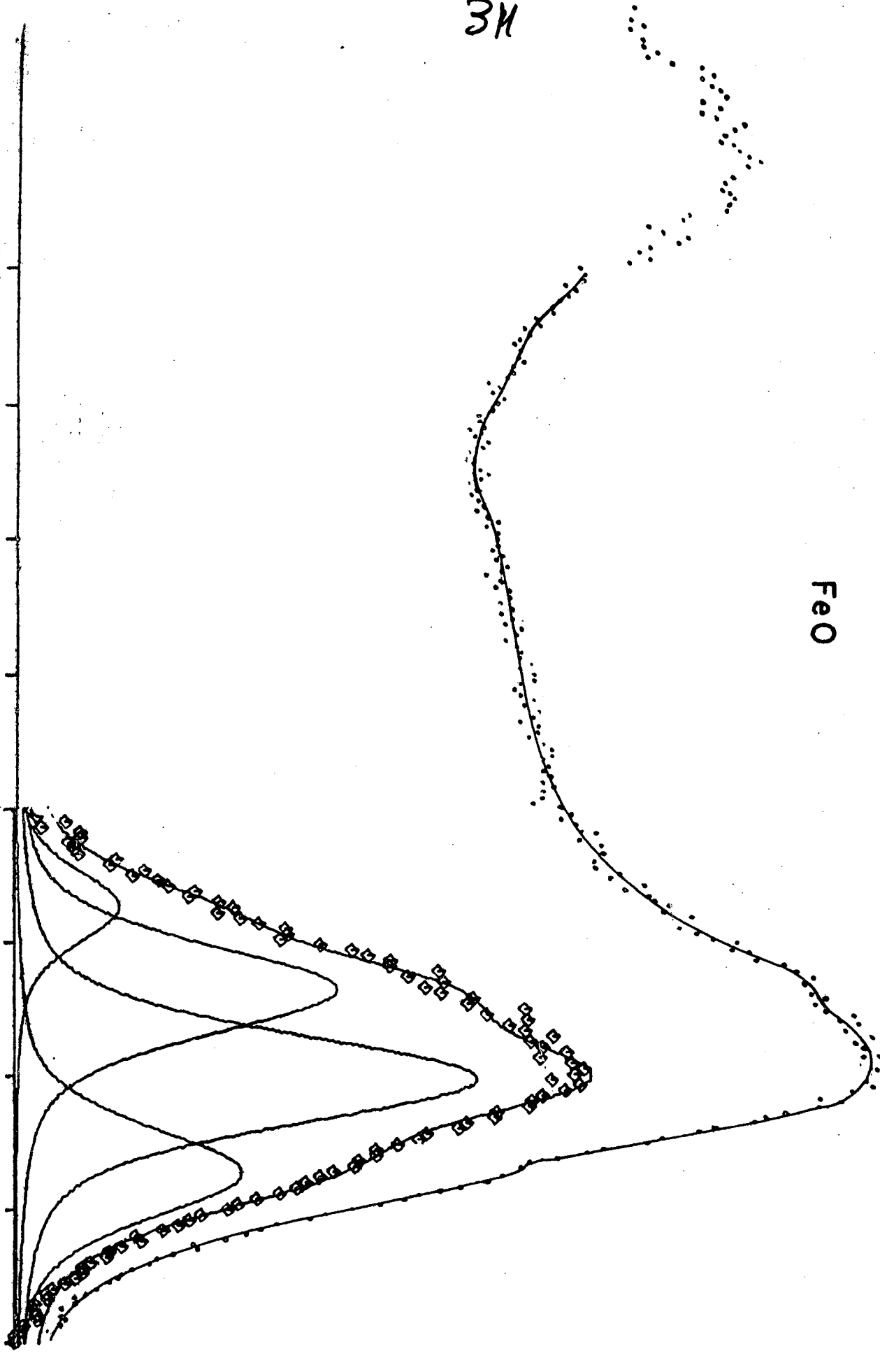
719

715

713

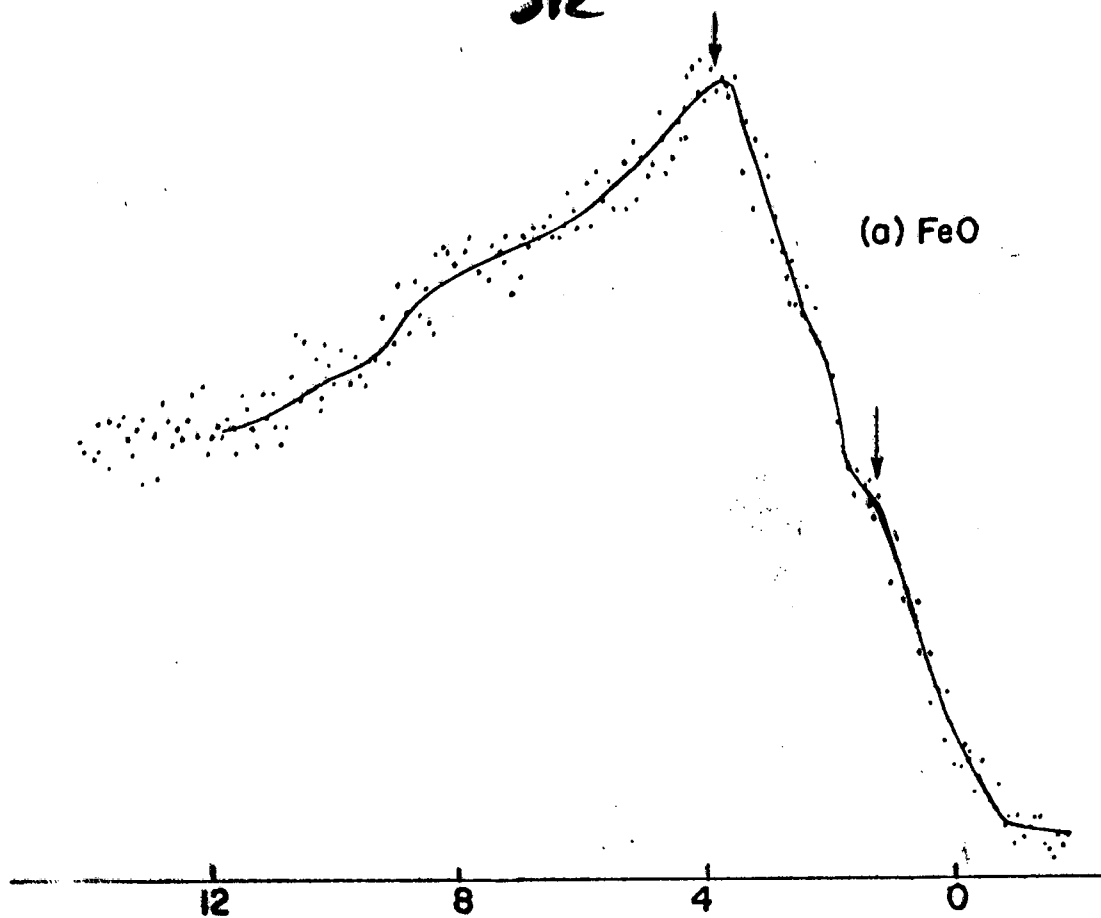
709

705

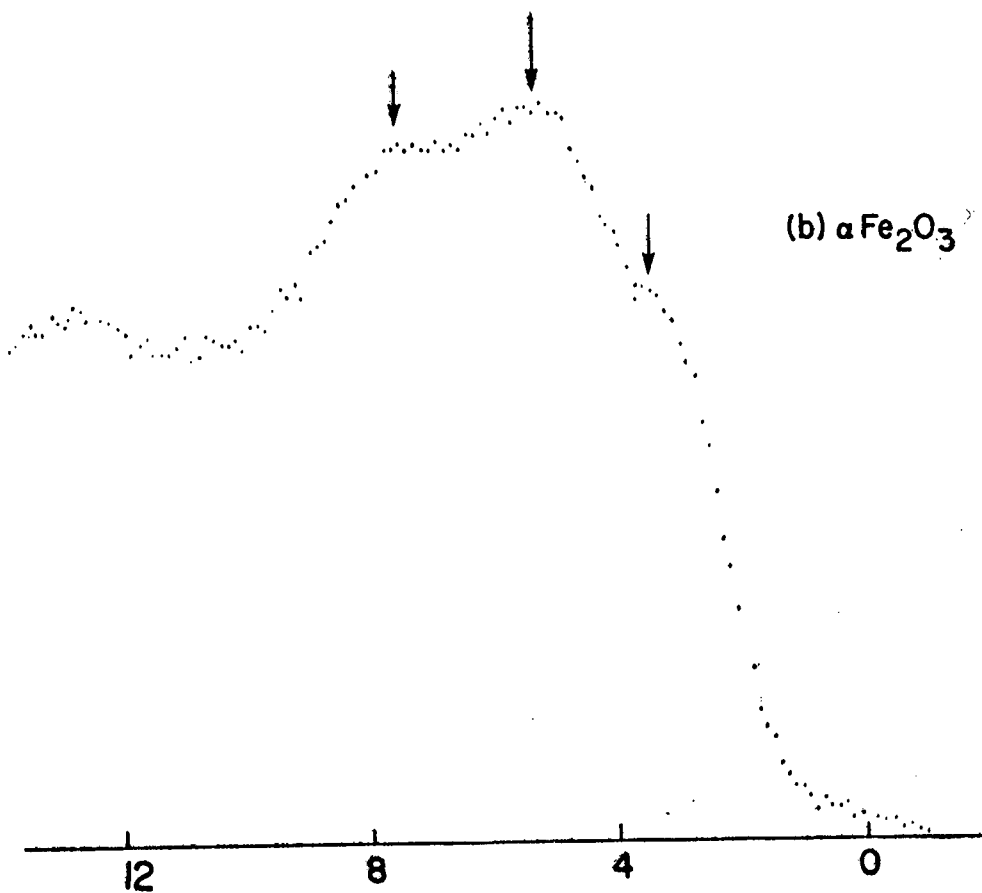


512

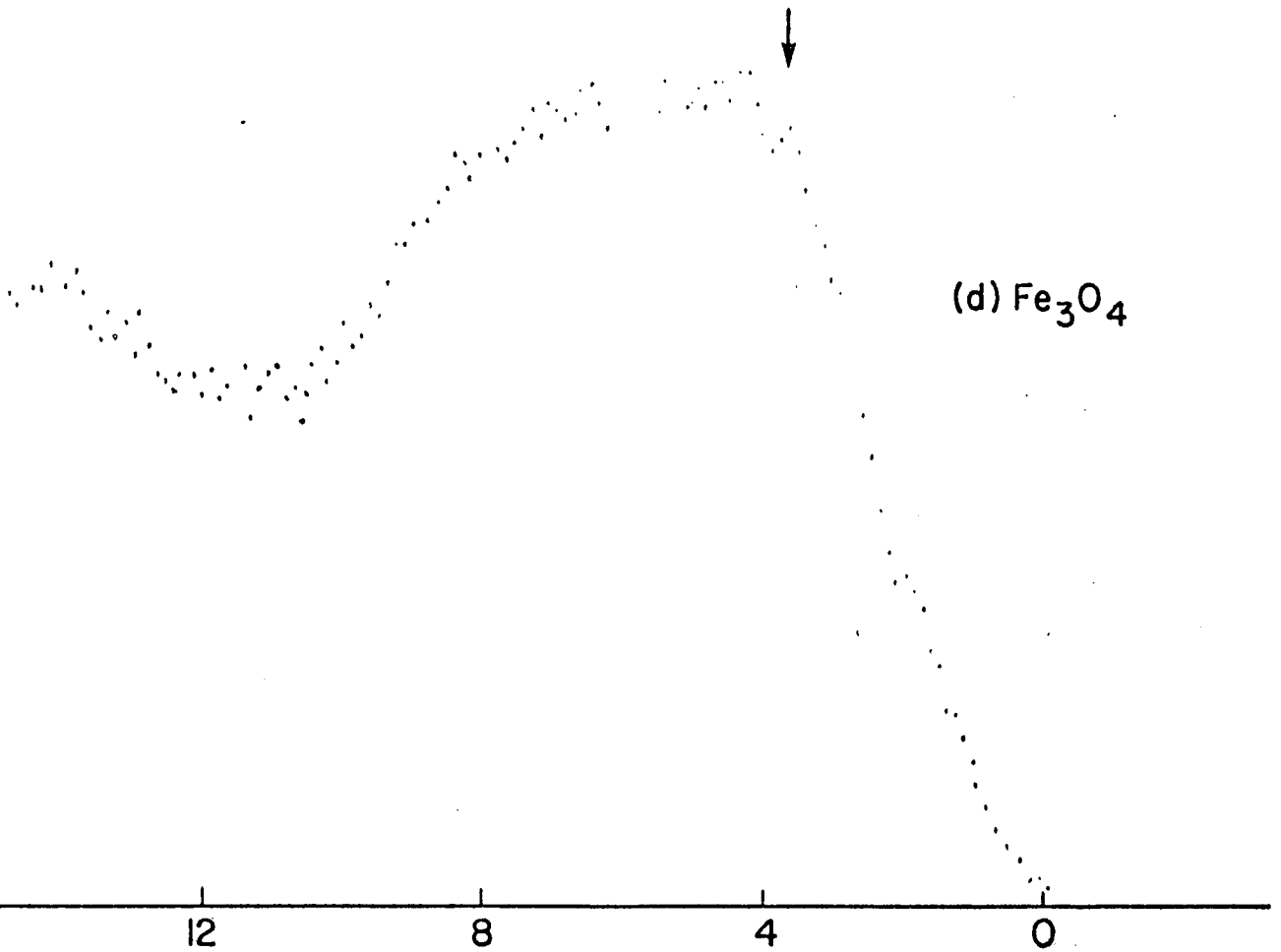
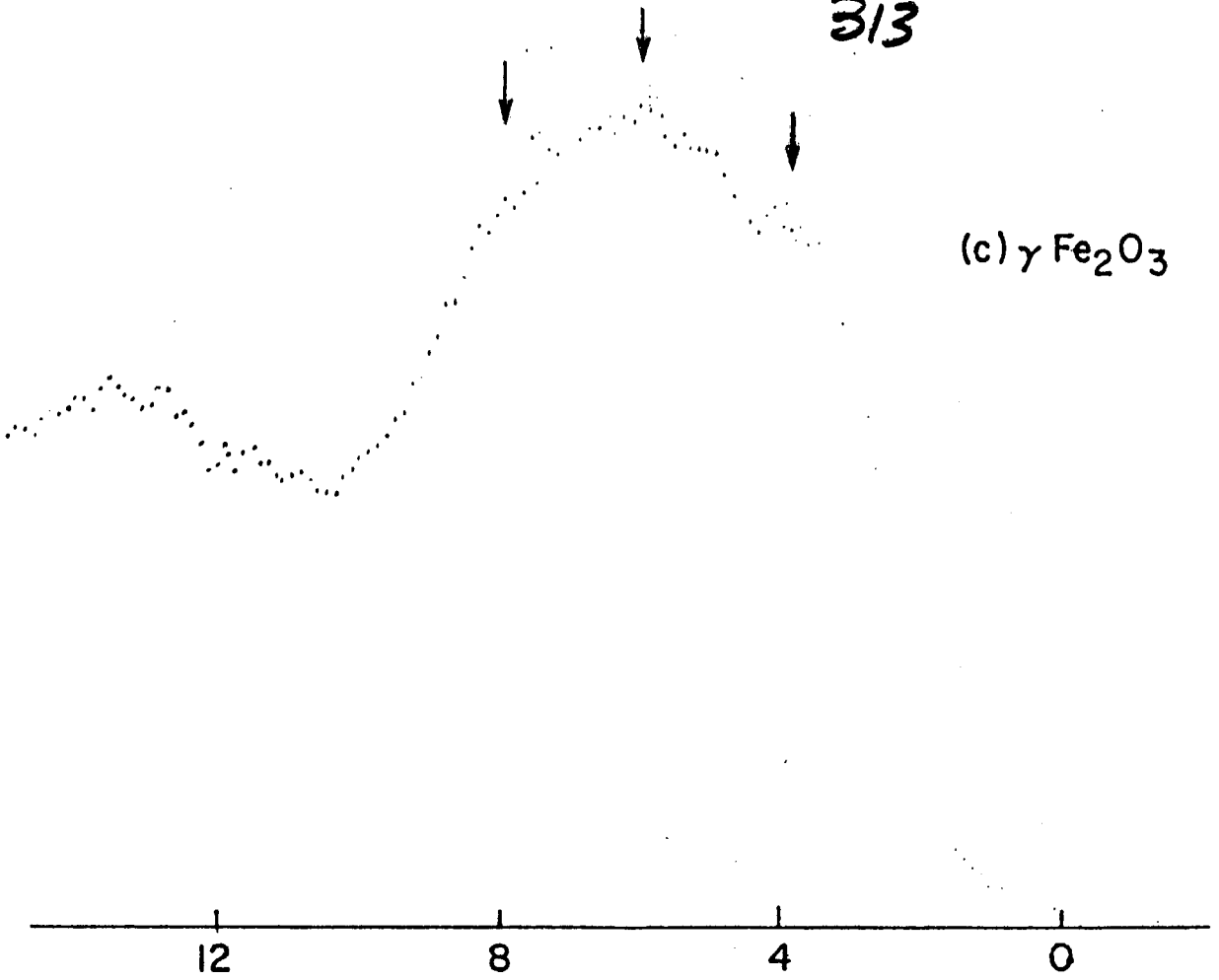
(a) FeO



(b) $\alpha\text{-Fe}_2\text{O}_3$

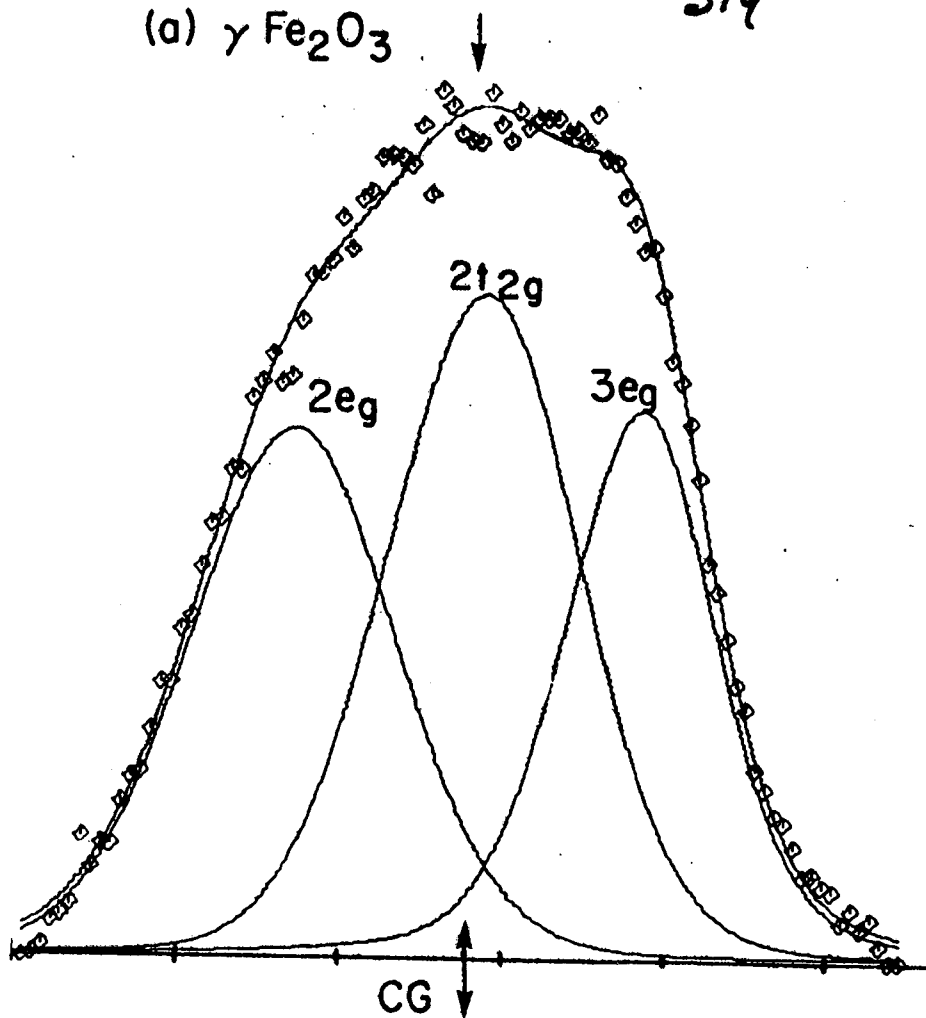


313

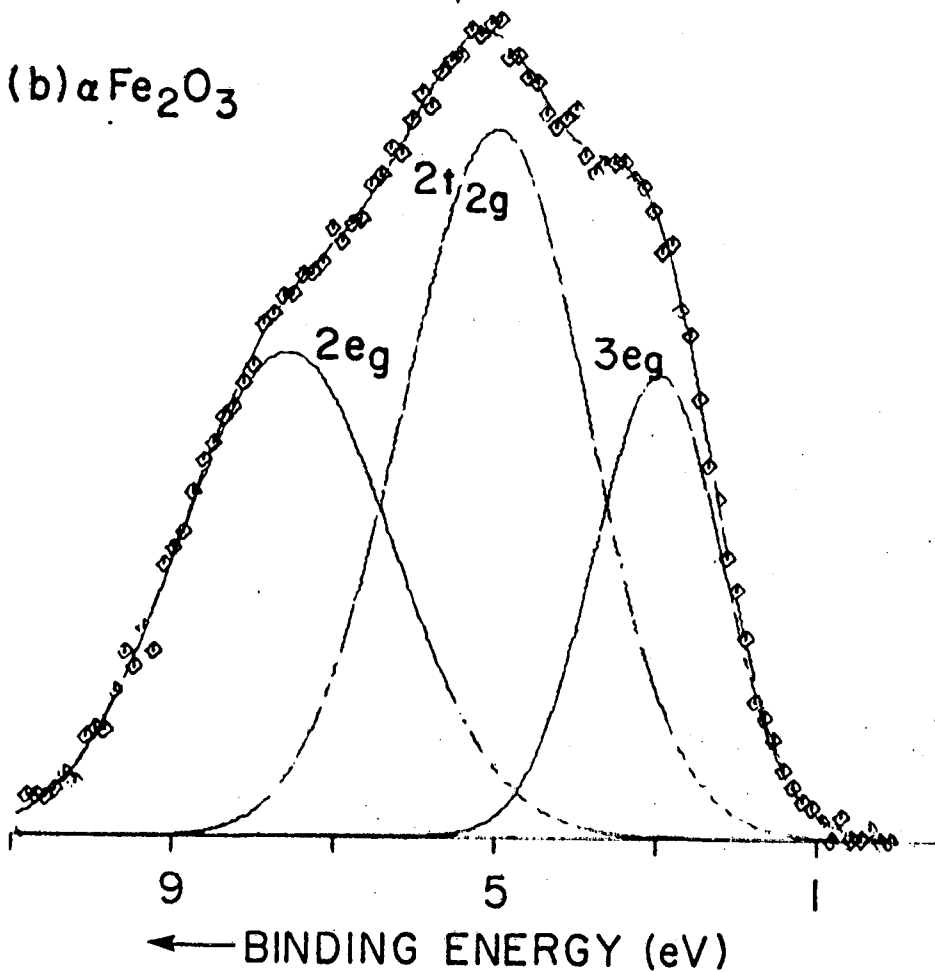


314

(a) $\gamma \text{Fe}_2\text{O}_3$



(b) $\alpha \text{Fe}_2\text{O}_3$



Fe(2p)

3/5

709.7 eV →

(a)

Fe_2O_3
SPUTTERED

710.9 eV →

(b)

CoFe_2O_4
SPUTTERED

710.1 eV →

(c)

Fe_3O_4
SPUTTERED

718

714

710

706

BINDING ENERGY (eV)

ESCA-STUDIES OF THE COMPOSITION PROFILE OF LOW TEMPERATURE OXIDE FORMED ON CHROMIUM STEELS—I. OXYDATION IN DRY OXYGEN*

I. OLEFJORD

Dept. of Engineering Metals, Chalmers University of Technology, S-402 20 Göteborg, Sweden

Abstract—ESCA (Electron Spectroscopy for Chemical Analysis) has been used to analyse the composition of oxide films formed on chromium steels with 6–20%Cr at room temperature in pure oxygen at 0.2 atm. during different times from 2 min to 46 h. Ion etching was used to clean the surface before oxidation and to investigate the composition profile by successive stripping of the oxide layer.

It is demonstrated that the total chromium content in the oxide is proportional to the concentration in the metal, but that it varies with depth inside the film. At the oxide-gas boundary the chromium concentration is less than in the metal, while chromium is enriched at the metal phase boundary. It is suggested that the oxide consists of $(\text{Fe,Cr})_2\text{O}_3$ in the outermost zone and FeCr_2O_4 at the inside, with the reservation that the method is not sensitive to deviations from stoichiometry.

The thickness of the layer has been determined as 25 Å from the intensity ratio of the deconvoluted ESCA peaks of the metallic and oxidized states. The thickness and the composition profile of the film do not vary noticeably with the oxidation time.

INTRODUCTION

EARLIER ESCA studies¹⁻⁴ of oxide films formed on austenitic stainless steel (18–10–1.8Mn) have shown that the composition of the films depends on reaction temperature and time. At high temperatures, the oxide was found to be enriched with the easily oxidizable elements Cr and Mn. After oxidation at room temperature^{1,2} and at an intermediate temperature (250°C),³ iron was found to be the dominating component in the top layer of the oxide. Investigation of the top layer after oxidation at 500°C for different times⁴ showed an increase of chromium content with oxidation time. It has also been demonstrated³ that heating a specimen with a clean metallic surface in high vacuum in the 10^{-8} Torr region results in a layer (or islands) of chromium oxide on the surface. These studies are now continued by ESCA analyses of films formed on synthetic, highly pure ferritic steels in dry and wet corrosion media at room temperature. The chromium content of the steels is in the range from 4 to 30%. The present paper (part I) deals with oxidation in pure oxygen for different times.

ESCA (Electron Spectroscopy for Chemical Analysis) is a relatively new surface sensitive technique which has been developed by Professor K. Siegbahn in Uppsala⁵ during the last decade. The principle of the method rests on the energy analysis of photoelectrons emitted from a sample on irradiation with monochromatic X-rays. The difference between the incident photon energy and the measured kinetic energy of the photoelectrons is approximately equal to the binding energy of the electrons within the atoms of the sample, and serves to identify the atomic species.

The binding energies of the core electrons change when an outer electron is removed or added by oxidation or reduction. The difference between the oxidized and the

*Manuscript received 2 April 1975; in revised form 2 July 1975.

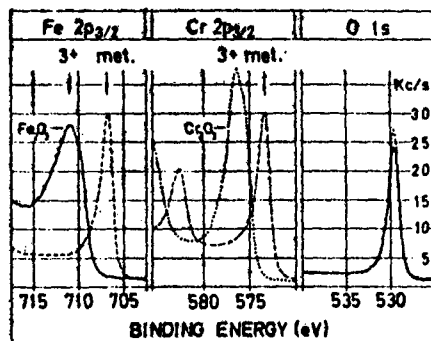


FIG. 1. ESCA spectra of synthetic Fe_2O_3 and Cr_2O_3 . Solid and dotted peaks—oxidic state; dashed peaks—metallic state.

metallic state is called a *chemical shift*. An example is shown in Fig. 1. The solid and the dotted peaks show the ESCA spectra of Fe_2O_3 and Cr_2O_3 respectively. The dashed peaks show the metallic states of Fe and Cr. The chemical shifts are 4.0 and 3.2 eV respectively.

The photoelectrons forming these peaks come from a zone near the surface whose depth is of the order of 20–50 Å which is in the same order of magnitude as the thickness of oxide films formed at room temperature and that of passive layers. The chemical shifts allow one to distinguish the signals of the oxide from those of the underlying metal. This is the most important property of ESCA in corrosion research.

The instrument used is a Hewlett Packard ESCA (HP 5950 A), to which a special specimen preparation and handling system with a reaction chamber has been added. The system has been described elsewhere.^{3,4} The main features are complete UHV-design, with separate ion pumping and the possibility to expose the specimen to any desired atmosphere in the chamber after separation from the ESCA by a cut-off valve. The specimen is moved to and from the analysis position without breaking the vacuum through this valve. In the preparation chamber, the specimen can be heated and subjected to high- and low-energy ion bombardment as well as a variety of other treatments. Ion bombardment has been used to clean the specimens before oxidation. It has also been used for determining the composition profile of the oxide layer.

Semi-quantitative evaluation of ESCA spectra

The chromium content in the oxide layers can be estimated by an approximative deconvolution of the $\text{Fe } 2p_{3/2}$ and the $\text{Cr } 2p_{3/2}$ peaks in their metallic and oxidized states. These are the most intense peaks of Fe and Cr. A calibration of the relative yields of these elements in the oxide state was obtained from analyses of synthetic Fe_2O_3 and Cr_2O_3 (Fig. 1), using the intensity of the oxygen's peak as a joint reference. This is a good approximation because the two oxides have the same oxidation state, formula and crystal structure. The analyses were performed on oxide films formed on pure Fe and Cr by oxidation in air for 15 min at 500 and 800°C respectively. The oxide film thickness was greater than the escape depth of the photoelectrons, but in the case of chromium oxide it was thin enough to prevent charging, which would have broadened the oxygen and the chromium peaks.⁴

The total intensity of Fe, I_{Fe} , is expected to be greater than that of Cr, I_{Cr} , because the yields of any electronic level increase with the atomic number.⁸⁻⁹ This is satisfied if integrated intensities are estimated by multiplying peak height with half width. The half widths are 5.6 for Fe^{3+} and 2.9 eV for Cr^{3+} , and the peak heights are in the ratio $S(Fe)^{3+} : S(Cr)^{3+} = 1 : 1.2$. The intensity ratio obtained, $I_{Fe} : I_{Cr} = 1.6$, is in good agreement with Jørgensen's yield figures.⁹

The broadening of the Fe^{3+} peak is inherent in the electronic structure of the ion and is not expected to change with its environment. Therefore it appeared permissible to use peak height, (S), for comparison of Fe^{3+} with Cr^{3+} making allowance for the different half-widths by using a weight factor of 1.2 for Fe^{3+} . Thus the *integral* Cr concentration in the oxide phase is obtained as

$$C_{Cr}^{Ox} = \frac{S_{Cr}^{Ox}}{S_{Cr}^{Ox} + 1.2 S_{Fe}^{Ox}} \quad (1)$$

For the metallic state, the Cr and Fe peaks have almost the same half width. Therefore, one only has to correct for the yield ratio by multiplying the iron peak height with $1/1.6 = 0.625$:

$$C_{Cr}^M = \frac{S_{Cr}^M}{S_{Cr}^M + 0.625 S_{Fe}^M} \quad (2)$$

The term integral concentration is used because the Cr content may—and, as will be seen, does in fact—vary with depth below the oxide/gas interface. The intensity, $I(z)$, from a film of thickness a may be written as

$$I(z) = K \int_0^a C(x) P(z) \exp \left(- \frac{x}{\sin 38.5^\circ \cdot \lambda(z)} \right) dx, \quad (3)$$

where z is an index for the electron energy level and elements, and x is the depth coordinate, with origin at the outer oxide surface. $C(x)$ describes the concentration profile in the layer. The absorption of the X-rays is assumed to be constant throughout the thin layer. The expression $\exp(-x/(\sin 38.5^\circ \cdot \lambda(z)))$ is the probability that a photoelectron from a distance x underneath the surface will leave the sample without energy loss. λ is the escape depth of the photoelectrons. The x -coordinate is divided by $\sin 38.5^\circ$, because 38.5° is the angle between the surface of the specimen and the entrance of the spectrometer including the electron transmission function of the analyser. The constant K represents all other factors affecting the intensity. $P(z)$ is the photoionization function and is the only parameter which changes when Fe is exchanged for Cr in analysing thick layers of Fe_2O_3 and Cr_2O_3 . No investigation of escape depth in the iron-chromium-oxygen system has been performed and a value of λ must be guessed, using as a guideline studies in the same energy region of Au and Al. The escape depths of these elements are 19 Å in the metallic state,^{10,11} and 13 Å¹⁰ for Al in Al_2O_3 . A brief discussion of mean free paths is given by Powell.¹² The value for the $2p_{3/2}$ peaks of iron and chromium in both metallic and oxidic state will be assumed to be 15 Å.

If the thickness of an oxide film is of the same order of magnitude as the electron escape depth, a metallic peak will be found beside the oxide peak. The film thickness can be estimated from the intensity ratio of these peaks, applying the reasoning behind the expression for integral concentrations above. The calculation is most conveniently done in chromium equivalents, since the ratio between the yields of Fe and Cr is known. The intensities from the layer and from the metal beneath then are proportional to the expressions $[1 - \exp(-a/(\sin 38.5^\circ \cdot \lambda(z)))]$ and $2 \exp(-a/(\sin 38.5^\circ \cdot \lambda(z)))$ respectively with the same proportionality constant. The factor 2 in the second expression comes from the fact that the density of metal atoms per unit volume in metal is roughly twice the density in oxide. The ratio between the intensity of oxide and metal signals is $1/2 (\exp(a/(\sin 38.5^\circ \cdot \lambda(z))) - 1)$. The thickness a is calculated by equating this expression with the ratio of the weighted, measured intensities, assuming an average value of $\lambda = 15 \text{ \AA}$ in both the metal and the oxide. Thus, the film thickness becomes

$$a = \lambda(z) \ln [2 \cdot \frac{1.2 \cdot S_{\text{Fe}}^{\text{ox}} + S_{\text{Cr}}^{\text{ox}}}{0.625 \cdot S_{\text{Fe}}^{\text{M}} + S_{\text{Cr}}^{\text{M}}} + 1] \cdot \sin 38.5^\circ. \quad (4)$$

A similar expression has been used by Carlson.¹³ It will be noted that both in the estimation of film thickness and in the calculation of the integral Cr contents, λ has the character of a scale factor so that even if the guess of λ should be wrong, the results to be presented below will be correct in terms of a depth scale expressed in fractions of λ .

EXPERIMENTAL

The samples are laboratory-produced binary iron-chromium alloys. The chemistry of the specimens is shown in Table I.

TABLE I. THE CHEMISTRY OF THE SPECIMENS IN WT %

Cr	C	Ti	Si	Mn	Ni	Mo	Cu	P	S	N	Fe
5.8	0.002	0.12	0.02	0.10	0.02	0.02	0.007	0.007	0.003	0.004	Balance
11.0	0.002	0.13	0.02	0.10	0.02	0.06	0.007	0.007	0.003	0.005	"
19.9	0.002	0.13	0.02	0.10	0.02	0.06	0.006	0.010	0.003	0.002	"

After casting, the specimens were diffusion annealed at 1250°C for 1 h and then hot forged at 1050°C. Finally, they were annealed at 920°C for 20 min and quenched. The microstructure is ferritic with uniform grain size.

The samples were machined out of sheets in the dimensions $1.30 \times 8 \times 12 \text{ mm}^3$ and prepolished on emery paper in steps down to no. 400. Final polishing was performed on paper no. 600 in methanol of p.a. grade. Then they were transferred to the preparation chamber under a stream of pure nitrogen. These precautions were taken to minimize oxide film formation on the surface. After introduction in the specimen handling chamber, the sample surfaces were cleaned by ion bombardment. The energy of the argon ions was 400 eV and the ion density was about 10^{-6} A/cm^2 . Oxygen was then admitted into the chamber at 0.2 atm. and 25°C and allowed to react for 2 min, 2 h and 46 h.

In recording the ESCA spectra, a long scan between 0 and 1000 eV binding energy was run for each specimen to check for impurities. Narrow scans of $2p_{3/2}$ and $3p$ levels of Fe and Cr and $1s$ level of oxygen were then recorded. The $3p$ levels were selected because the kinetic energy of these photoelectrons is roughly twice that of electrons from the $2p$ levels of Fe and Cr. Comparison of the metal and oxide peaks in the $2p$ and $3p$ levels yields qualitative information about the uniformity of the thickness of the layer.

After analysis of the top surface of the oxide layer, the specimens were again bombarded with 400 eV Ar ions to remove successive zones of the oxide film in order to establish the concentration

profile below the surface. The thickness of the remaining layer could be estimated in each case by the procedure described above.

RESULTS

Figure 2 is a collection of the ESCA spectra recorded before and after oxidation for 2 h. The dashed peaks show the "clean" surface after the ion cleaning which preceded oxidation. The as-oxidized state is shown as solid curves, while the dotted peaks are the spectra recorded after roughly half of the layer had been removed by ion bombardment.

The spectra of the ion-cleaned surface show Fe and Cr in their metallic states, but minority peaks of oxide remain. Small peaks of oxygen and carbon are also present. The latter appears as a double peak. The high binding energy component of this is found in all ESCA spectra owing to contamination by hydrocarbons. The low energy component appears only after ion etching, and its position agrees with the position of carbon in metal carbides.¹⁴ It appears that after ion cleaning, the impurities O and C are present as islands or as a thin layer (at most a monolayer) of compounds with Cr and perhaps also Fe.

After oxidation at all times the spectra show that the top layer consists mostly of iron oxide. The positions of the iron and chromium peaks are 711 and 576.5 eV respectively, corresponding to the three-valent states in the synthetic oxides (Fig. 1). Also the oxygen peak position agrees with that found in the synthetic oxides. The

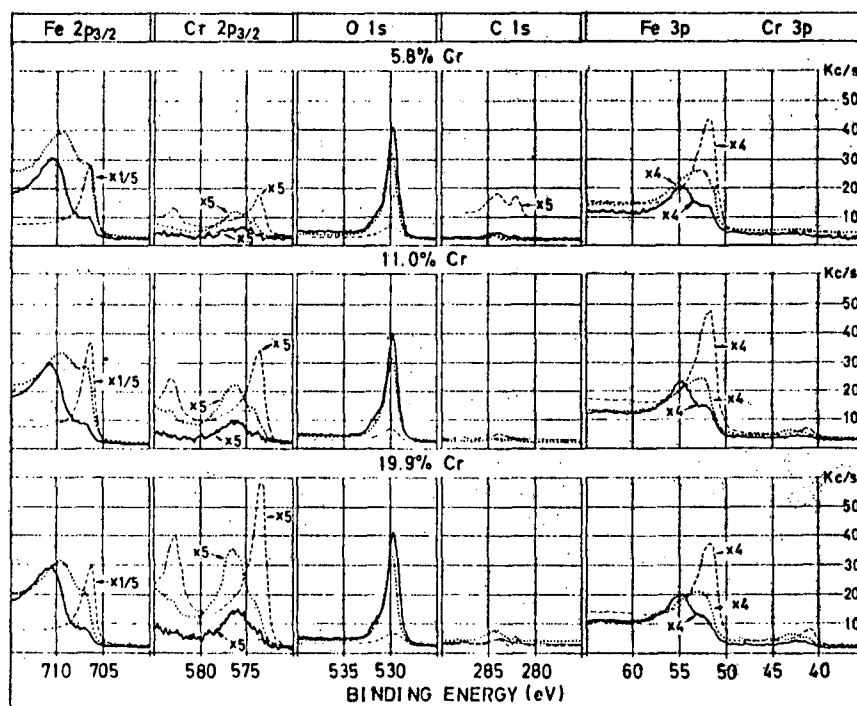


FIG. 2. ESCA spectra of Fe-Cr alloys after oxidation for 2 h (solid lines). Dashed peaks—cleaned surfaces before oxidation; dotted peaks—oxidized specimens after 15 min of ion etching.

shoulder on the left-hand side of the oxygen peak is attributed to surface contamination by adsorbed oxygen and/or other oxygen-containing gases. This contamination is small, but part of it persists or recurs even after ion bombardment.

Ion bombardment reveals an increase of Cr content below the oxide/gas phase boundary. To evaluate the integral chromium content, the partial overlap of oxidic and metallic states in the recorded peaks must be deconvoluted. The peaks of the metallic state are subtracted—after suitable scaling-down, and with their experimentally recorded half-width and high-energy tails (Fig. 1)—from the recorded peaks. The heights of the deconvoluted peaks are inserted in eqn. 1 to calculate the integral Cr content in the remaining zones of the layer. Figure 3 shows the integral Cr content (expressed as fraction of all cations) vs thickness of the remaining layer (as determined from equation 4) for films formed during different exposure periods.

It appears that all films are poor in chromium at the outer surface; in all three cases, the Cr content is about half that of the metal. In the centre of the layer the integral chromium content agrees roughly with the concentration in the metal, while at the metal phase boundary it is slightly higher. The true Cr gradients must be a good deal steeper than those of the integral Cr contents shown in Fig. 3.

The thickness of the layer is found to depend very little on either the chromium content of the alloy or the oxidation time. Only at the highest chromium content and the shortest oxidation time is a slightly thinner layer formed. Otherwise the differences are within the limits of error.

At the present state of the art, quantitative composition analyses are seldom attempted with ESCA. The absolute reliability of the calculated values should not be overvalued. Rough verification is obtained by comparison of the nominal Cr-contents of the alloys with the Cr-signals recorded for the ion-cleaned specimens. These are shown as horizontal lines to the left of each ordinate in Fig. 3(a-c). Only in one case (11%Cr steel, specimen oxidized for 2 min) is the agreement perfect; in the remaining cases, the ESCA signal indicates Cr levels which are somewhat low. Nevertheless, the results may be characterized as semiquantitatively correct. It must be remembered that the metallic spectra were recorded from surfaces which may have been covered with a very thin oxide and/or carbide film.

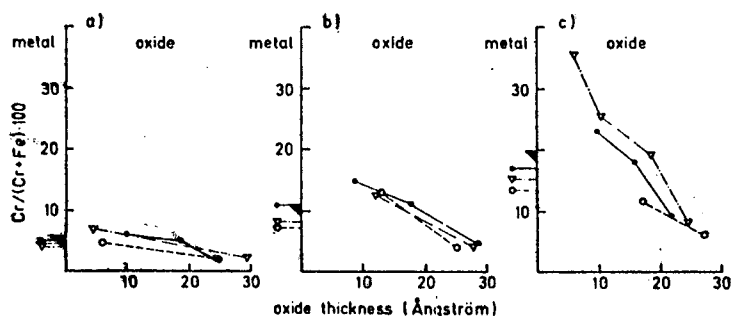


FIG. 3. Integral chromium content in metal and oxide: (a) 5.8%, (b) 11.0%, (c) 19.9% chromium.
oxidation times: 2 min (—), 2 h (---), 46 h (- · -).

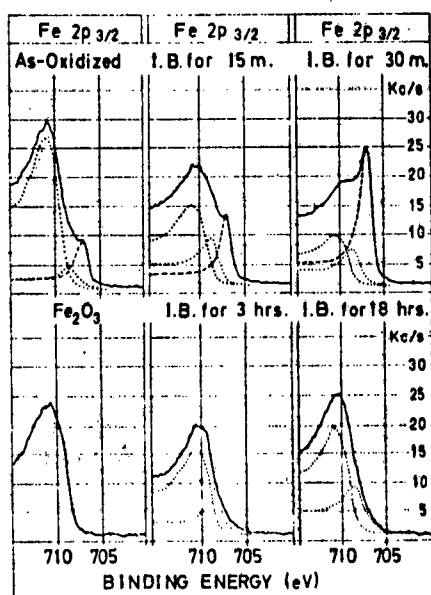


FIG. 4. Row 1: Deconvolution of the $2p_{3/2}$ level of alloy Fe-5.8 Cr oxidized for 2 min and after ion bombardment for 15 and 30 min. Characteristic peak positions: metallic at 707 eV, divalent at 709 eV, and three-valent at 711 eV.

Row 2: Synthetic Fe_2O_3 before and after ion bombardment for 3 and 18 h.

For both rows: The broadening after ion etching has been deconvoluted into divalent and three-valent peaks (dotted lines).

If the ratio of nominal to ESCA-determined Cr content in each specimen is applied as a correction factor to the integral Cr contents in the oxide film, the Cr profiles become almost identical and independent of oxidation time. This implies that the film is built up very quickly, so that the shortest exposure time, 2 min, is already well within the stationary range.

Figure 4, row 1, shows the specimen containing 5.8% chromium after oxidation for 2 h. The peaks are recorded in the as-oxidized state (solid lines) and after 15 and 30 min of ion bombardment. They have been approximately deconvoluted in terms of metallic and oxidized contributions. The peak of metallic iron in Fig. 1 has been scaled down and subtracted from the recorded peak. The remaining peak is due to the oxide. In comparison with the Fe^{3+} peak of Fig. 1, it appears somewhat broadened to the right, indicating a possible Fe^{2+} contribution. Deconvolution of the divalent and the three-valent peak was performed by subtracting the Fe^{3+} peak of Fig. 1, with variously reduced scale factors, from the total peak until the remainder had the proper shape for an ESCA peak. This remaining peak is found to lie at 709 eV, which agrees very well with the standard position of Fe^{2+} .⁴ The result is that Fe is present in the as-oxidized state mainly as Fe^{3+} , with a small admixture of Fe^{2+} .

After the top layer of the oxide has been removed, the ratio of Fe^{2+} to Fe^{3+} increases. If one assumed that the sputtering yields of all elements were equal, and that no change occurred in the chemical state of the remaining oxide, the results

would indicate that the oxide layer consists of Fe^{3+} in the surface region, with a gradual transition towards Fe^{2+} at the metal/oxide phase boundary. However, such an assumption is not immediately justified because there is evidence that ion bombardment of some compounds may change their valence states. S. Hüfner¹⁵ has demonstrated that ion bombardment of Fe_2O_3 may reduce the three-valent state of iron to the metallic state. Kim¹⁶ has shown that the tendency to reduction depends on the free energy of the compounds. These studies indicate also that the reduction depends on the kinetic energy of the ions used, the sputtering rate and the pressure of the residual oxygen.⁴

Figure 4, row 2, shows ESCA spectra of synthetic Fe_2O_3 before and after ion bombardment for 3 and 18 h. The shape and position of the peaks are quite similar to those of the oxidized state of iron in Fig. 1(a). After ion bombardment the peak broadens on the low binding energy side. Deconvolution in the same way as above reveals the shoulder as a contribution from the divalent state. However, even after 18 h no metallic component occurs, in contrast to Hüfner's results. The ratio between Fe^{2+} and Fe^{3+} is approx. 0.4 after both 3 and 18 h of ion bombardment, suggesting that a steady state has been established. The absence of metallic iron after bombardment may be due to re-oxidation of the metal atoms to the divalent state, in view of the low sputtering rate and the non-negligible partial pressure of oxygen in the chamber.⁴

While ion etching, as has been shown above, may produce a certain amount of Fe^{2+} , it is clear that not all of the divalent ions revealed in the deeper zones of the oxide films can have been produced in this way. The ratio of Fe^{2+} to Fe^{3+} is 0.6 in the film after only 30 min of ion bombardment, while much longer bombardment of the synthetic specimen brings this ratio to only 0.4. Furthermore, the removal of oxygen which must be the first event in the chain leading to the formation of Fe^{2+} by sputtering, is likely to be more difficult in a $(\text{Fe,Cr})_2\text{O}_3$ mixed oxide than in pure Fe_2O_3 , considering the difference in the oxygen affinity of the elements.

DISCUSSION

This study confirms earlier results¹⁻⁴ that oxidation of stainless steels at room temperature and normal pressure does not lead to films consisting predominantly of chromic oxide. However, profiling by ion bombardment reveals a chromium gradient in the film, and chromium appears to be considerably enriched near the metal/oxide interface. The enrichment must, in fact, be even more intense than indicated by Fig. 3, because if the profiles were converted from integral to actual (local) concentrations, the gradient would become still steeper.

Thermodynamically, Cr_2O_3 is more stable than Fe_2O_3 ; the free energies of formation of the oxides are -250.5 and -176.8 kcal/mole respectively. Therefore the selective oxidation of chromium would be favoured by a higher driving force. Because of the low atomic mobility at room temperature, it seems plausible that the very first layer formed on contact between metal and oxygen will contain iron and chromium in roughly the same proportions as the alloy. Later on, however, chromium atoms will move preferentially into the film, substituting for iron which in turn will migrate outwards and form further oxide. Depletion of Cr in the metal next to the oxide interface will accentuate the decrease of Cr concentration in the outer zones of the oxide

film, which are formed at a later stage. In this way, a film structure with outwardly decreasing chromium content will be established, in accordance with the classical theory of selective alloy oxidation.

The build-up period of this structure seems to be very short, in any case shorter than the 2 min which was the shortest exposure time in this study. Also the film thickness, as calculated from the ESCA peak ratio of oxide and metal, has almost finished increasing after only 2 min of exposure.

While both iron and chromium are present in their three-valent states in the outer zones of the oxide, it has been shown in this study that divalent iron appears in the innermost, chromium-rich zone. Chromium is three-valent in all zones.

These findings can be considered to support the view¹⁷ that the room-temperature oxidation of Cr-containing steels at normal pressures produces a spinel-like composition near the metal/oxide boundary, and a mixed Fe-Cr-sesquioxide at the oxide/gas boundary. (It is not possible to say whether the spinel-like composition is present as a film or in the form of islands.)

In room temperature oxidation, oxygen pressure must be of decisive importance for the composition of the first-formed film. Obviously at very low oxygen pressure there will be time enough for the majority of adsorbed oxygen atoms to react preferentially with chromium atoms.

The present conclusions fit well into the pattern established by our earlier studies, which indicate that under conditions allowing more extensive diffusion, i.e. higher temperature and/or longer time, the Cr content of the film increases also in the outer zones.

Acknowledgements—The author is grateful to SANDVIK AB for the preparation of the samples and to Prof. H. Fischmeister for suggesting this field of study and for continued advice and discussions; further to Mr. U. Jelvestam and Mrs. Y. Olefjord for their competent experimental assistance. Financial support from the Swedish Board for Technical Development (STU) is gratefully acknowledged.

REFERENCES

1. I. OLEFJORD, Application of ESCA in corrosion research. In *Proc. 6th Scand. Corrosion Congress*, pp. 11-3-11-9. Swedish Corrosion Institute, Stockholm (1971).
2. H. FISCHMEISTER and I. OLEFJORD, *Monatshefte für Chemie* **102**, 1486 (1971).
3. I. OLEFJORD, *Scandinavian J. Metallurgy* **3**, 129 (1974).
4. I. OLEFJORD, *Metal Science* **9**, 263 (1975).
5. K. SIEGBAHN, C. NORDLING, A. FAHMAN, R. NORDBERG, K. HAMRIN, J. HEDMAN, G. JOHANSSON, T. BERGMARK, S-E. KARLSSON, I. LINDGREN and B. LINDGREN, *ESCA Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy*, Almqvist & Riksch AB, Stockholm, Sweden, 1967.
6. A. BEARDEN, *J. appl. Phys.* **37**, 1681 (1966).
7. G. RAKARY and A. RON, *Phys. Rev.* **159**, 50 (1967).
8. C. WAGNER, *Anal. Chem.* **44**, 1050 (1972).
9. C. JØRGENSEN and H. BERTHOUD, *Faraday Discussions of the Chemical Society*, No. 54, the Photoelectron Spectroscopy of Molecules (1972).
10. M. KLASSON, J. HEDMAN, A. BERNDTSSON, R. NILSSON and C. NORDLING, *Physica Scripta* **5**, 93 (1972).
11. H. KANTER, *Phys. Rev.* **81**, 2357 (1970).
12. C. J. POWELL, *Surf. Sci.* **44**, 29 (1974).
13. T. CARLSON and G. MCGUIRE, *J. Electron Spectrosc.* **1**, 161 (1972).
14. L. RAMQVIST, *J. Phys. Chem. Solids* **30**, 1835 (1969).
15. S. HÜFNER, R. COHEN and G. WERTHEIM, *Physica Scripta* **5**, 91 (1972).

325

696

I. OIEFJORD

16. K. KIM, W. BAITINGER, J. AMY and N. WINOGRAD, *Proc. Int. Conf. Electron Spectroscopy* Namur (1974), Elsevier, Amsterdam (1974).
17. K. HAUFFE, *Oxidation of Metals*, Plenum, New York (1965).

ESCA STUDIES OF THE COMPOSITION PROFILE OF LOW TEMPERATURE OXIDE FORMED ON CHROMIUM STEELS—II. CORROSION IN OXYGENATED WATER*

I. OLEFJORD and H. FISCHMEISTER

Dept. of Engineering Metals, Chalmers University of Technology, S-402 20 Göteborg, Sweden

Abstract—ESCA (Electron Spectroscopy for Chemical Analysis) has been used to analyse the chemical composition of passive films formed on chromium steels with 4–30%Cr at 25 and 70°C in oxygenated water for different times. The composition-depth profile of the films has been investigated by successive stripping of the film by ion etching.

The composition of the film varies with exposure time; short time yields an Fe-Cr ratio corresponding to that of the alloy; prolonged exposure produces increasing enrichment of chromium through the whole layer, with the highest concentration at the outer surface. The passive film generally seems to consist of two layers: outermost one of $(\text{Cr}(\text{OH})_3)_n$ and underneath one of iron-chromium oxide ($\text{Fe}_{1-x}\text{Cr}_x\text{O}_2$). The low alloy steels (3.9 and 7.8%Cr) were passive for a limited time during which the Cr enrichment was high (8 times); after breakdown of the chromium-rich passive layer, it was replaced by FeOOH .

When a dry-formed oxide film, which consists mainly of iron oxide, is exposed to water, its composition slowly changes until that of a water-formed film is reached.

INTRODUCTION

SINCE the days of Schönbein,¹ who in 1836 pointed out that iron could be made passive by anodic polarization, studies of the corrosion behaviour of pure metals and alloys have been performed mostly by electrochemical methods. Very little is known about the chemical composition of the passive films, in spite of the great importance of alloys like stainless steel, whose usefulness depends on the ability to passivate. The main reason lies in the fact that the films are extremely thin. Ellipsometric investigations^{2–6} have shown that the thickness of the passive film on stainless steels and Fe-Cr alloys is in the region of 10–60 Ångströms, depending on the potential and the composition of the alloy and the medium. Electron diffraction studies^{9–11} revealed no distinct crystalline diffraction pattern; the amorphous character of the films makes their analysis by diffraction methods very difficult.

Surface sensitive electron spectroscopic methods such as ESCA (Electron Spectroscopy for Chemical Analysis)¹² and Auger spectroscopy, which have become available during the last years, enable one to analyse the chemistry of such thin layers. The special advantage of ESCA is that it easily distinguishes between the different valence states of a species. The sensitivity and resolution are good enough to detect a fraction of a monolayer of oxygen adsorbed on an oxide substrate. These properties are particularly useful in passivation research because they allow an experimental check of the two hypothetical models of the passive state, i.e. the oxide film theory and the adsorption theory. The former, going back to Faraday, assumes a solid diffusion barrier, the existence of which was first experimentally verified by Tronstad³ using optical methods. The arguments for the adsorption theory are analogous to those of

*Manuscript received 2 April 1975; in revised form 2 July 1975.

Langmuir,¹³ who showed that oxygen at low pressure and high temperature does not react with a metal, but is only chemisorbed at the surface, where it will change the electron emission and affect the further reaction with oxygen. This model is believed to fit data for transition metals such as chromium.⁴ Fontana¹⁴ observed that stainless steels in sulphuric acid and seawater will lose passivity after vacuum treatment, but regain it after exposure in air. This he interpreted as support of the adsorption theory. A link between these two theories is presented by Mueller¹⁵ who suggests a first stage in which the unprotected surface is covered by a monolayer of oxygen which decreases the anodic dissolution, and a second stage with film formation by a chemical compound.

This paper reports an experimental investigation by ESCA of the compositions of passive films formed on Fe-Cr steels in oxygenated water for different times. It will be seen that this new technique yields essential and detailed insight into the process of passive film formation.

EXPERIMENTAL

The ESCA-instrument used is a HP 5950 A, equipped with a home made specimen preparation and handling system, which has been described elsewhere.^{16,17} The specimens are synthetic binary Fe-Cr alloys, from the same series as used in the preceding communication on dry-formed films.¹⁶ Chemical analyses of the samples are shown in Table I.

TABLE I. THE CHEMISTRY OF THE SPECIMENS IN WT%

Cr	C	Ti	Si	Mn	Ni	Mo	Cu	P	S	N	Fe
3.9	0.002	0.13	< 0.02	< 0.10	< 0.02	< 0.06	0.006	0.007	0.004	0.002	Balance
5.8	0.002	0.12	< 0.02	< 0.10	< 0.02	< 0.06	0.007	0.007	< 0.003	0.004	"
7.8	0.002	0.15	< 0.02	< 0.10	< 0.02	< 0.06	0.006	0.007	< 0.004	0.002	"
11.0	0.002	0.13	< 0.02	< 0.10	< 0.02	< 0.06	0.007	0.007	< 0.003	0.005	"
15.7	0.003	0.12	< 0.02	< 0.10	< 0.02	< 0.06	0.006	0.008	< 0.003	0.002	"
19.9	0.002	0.13	< 0.02	< 0.10	< 0.02	< 0.06	0.006	0.007	< 0.003	0.002	"
29.9	0.002	0.12	< 0.02	< 0.10	< 0.02	< 0.06	0.006	0.007	< 0.003	0.002	"

Titanium was added to the alloys in order to bind sulphur and to prevent precipitation of Fe-Cr sulphide, which can change the electrochemical properties of the alloys. The specimens were passivated at 25 or 70 °C for 2 min, 1 h, 50 h and 300 h in oxygen-saturated double-distilled water.

Precautions were taken to prevent formation of oxide films in air before passivation, and structural changes after passivation. After prepolishing on emery paper down to #400, the final polishing was performed either in the passivating medium itself (for the room temperature experiments) or in methanol of p.a. grade (for experiments at 70 °C).

The specimen was then picked up under liquid in a small cup, the protecting liquid was exchanged and the specimen rinsed by running the passivating medium through a funnel to the bottom of the cup. Afterwards the specimen was transferred—again under liquid—to a beaker, where oxygen was led through a glass tube into the water in such a way that the specimen was surrounded by a curtain of oxygen bubbles. After this treatment the specimen was transferred to the specimen handling chamber of the ESCA under a stream of pure nitrogen through a special sluice.

Analysis of the specimens started by recording a long scan between 0 and 1000 eV binding energy to check for impurities. Thereafter, narrow scans of the $2p_{3/2}$ and $3p$ levels of Cr and Fe and the $1s$ levels of oxygen and carbon were recorded. The composition gradient in the film was determined by alternating ion bombardments and ESCA analyses.

RESULTS

Figure 1 shows examples of the ESCA spectra obtained after passivation for 1 h at 25 and 70 °C. The specimens represent the extremes of chromium content in the

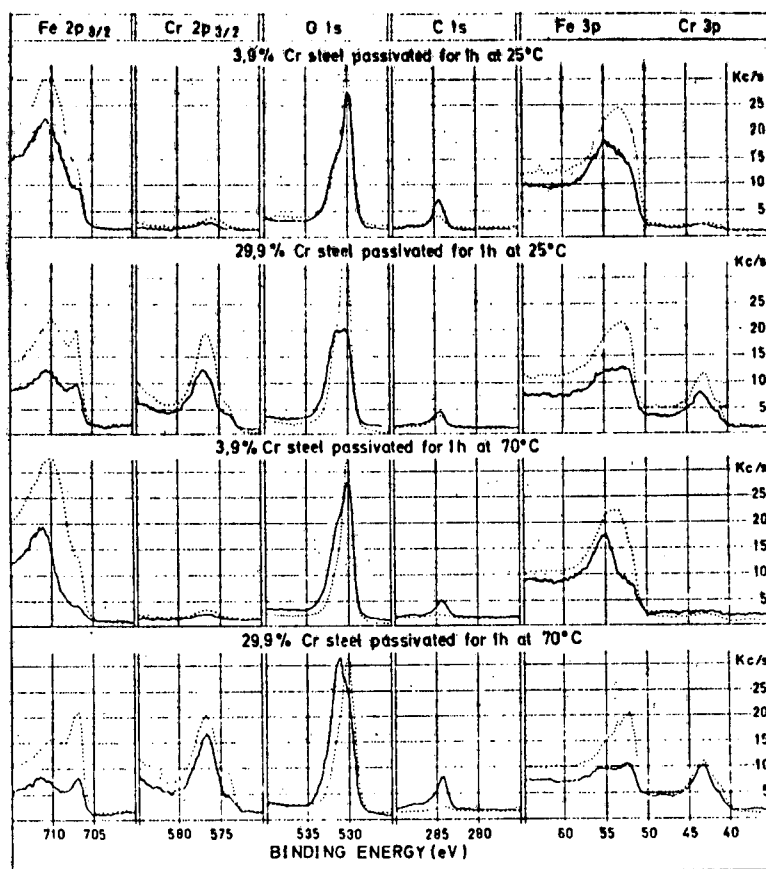


FIG. 1. ESCA spectra of Fe-Cr steels after passivation for 1 h at 25 and 70°C (solid lines). Dotted peaks show spectra after 15 min of ion bombardment. (The peaks of Fe 3p and Cr 3p are scaled up 5 ×).

series, i.e. 3.9 and 29.9%. The solid lines represent the as-passivated state, while the dotted peaks were recorded after the top layers of the films had been removed by ion bombardment. Further stages of ion etching have been recorded but are not shown to keep the figure clear.

In the as-passivated state, both metallic and oxidic states of the metals are found. The binding energies of the metallic components of Cr and Fe are 574 and 707 eV respectively, while their oxidized states lie about 3 and 4 eV higher. The presence of metallic signals indicates that the thickness of the layers is in the region of a few tens of Ångströms, where photoelectrons escaping from the metal substrate can still pass through the oxide film. The ratio between the metallic and the oxidic components of the 3p level is greater than for the corresponding 2p level, which indicates that the layer is uniformly thin.

The integral chromium content (in terms of the cation fraction, $\text{Cr}/(\text{Cr} + \text{Fe})$) in the films was determined for all specimens in Table 1 after passivation for 1 h at 25 and 70°C, by the method described in the preceding communication.¹⁸ The figures

presented in the following are the integral values; they differ from the real, local concentrations wherever chemical gradients exist.

Figure 2 shows the chromium content in the films vs that of the alloys. The dots

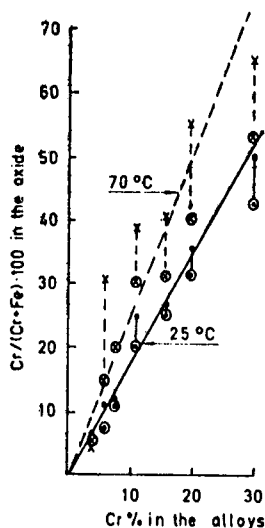


FIG. 2. The integral chromium content (cation %) in the films after passivation for 1 h at 25°C (dots) and 70°C (crosses). Crosses and dots represent the as-passivated state; ringed symbols are for ion etched surfaces.

and the crosses represent the as-passivated state after passivation at 25 and 70°C respectively. The sloping lines are the least square fits of the series. These demonstrate two things: first, at least at room temperature the chromium content in the surface region of the film is proportional to the bulk chromium content of the alloy for all alloy compositions studied here; second, the enrichment of chromium in the film is greater at the higher temperature (the enrichment factors are 1.7 and 2.5 at low and high temperature respectively). Analysis after removal of the top layer by ion bombardment (ringed symbols) indicates an inward chromium gradient in the passive film.

Depth profiles of the integral chromium content in the films are shown in Fig. 3. The alloy compositions are marked by the black triangular flags on the ordinates. The thickness of the layers has been calculated by the approximative method explained in the preceding communication.¹⁸

Figure 3 shows that passivation time has an important influence on the composition of the layer. At the shortest time (2 min) the chromium fraction in the film is approximately constant throughout the film, and equal to that in the alloy. Passivation for 1 h and longer times produces enrichment of chromium in the film and a marked gradient, with the highest chromium content in the outermost zone.

It appears from Fig. 2 that the enrichment factor of chromium with respect to the bulk content of the alloy is approximately the same for all alloys after 1 h exposure, but on prolonged exposure the relation between the compositions of the film and the alloy is no longer linear. After 50 h the enrichment factor of the low alloy steel (3.9%Cr) is four times higher than that of the high alloy steel (29.9%Cr). The

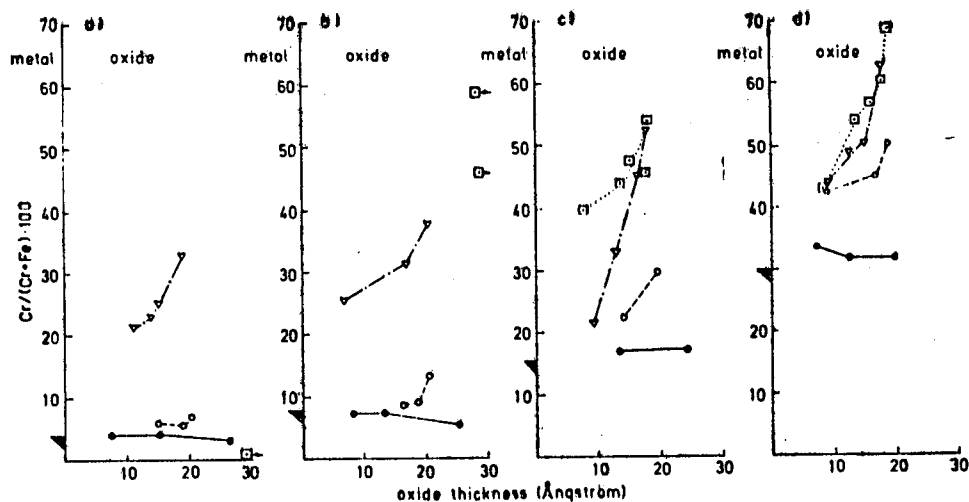


FIG. 3. Integral chromium content (cation per cent) at various depths in the oxide film before and after ion bombardment.

Alloys: (a) Fe-3.9%Cr, (b) Fe-7.8%Cr, (c) Fe-15.7%Cr, (d) Fe-29.9%Cr.

Exposure times: ● — ● 2 min ▽ — ▽ 50 h
○ — ○ 1 h □ . . . □ 300 h

chromium content of the film on the high alloy steels does not increase markedly when the treatment is carried on to 300 h. On the other hand, it was not possible to keep the low alloy steel (3.9%Cr) in its passive state for more than 50 h. Thereafter passivity broke down and a thick layer of corrosion product, formed on the surface, which yielded only iron and oxygen peaks. The 7.8%Cr steel passivated for 300 h shows a high concentration of Cr in the outermost region of the film. The metallic states of Fe and Cr are just detectable, indicating that the thickness of the oxide is about 40 Å; this is the only case where longer exposure in the passive state produced a thicker film.

In all spectra of as-passivated specimens, the oxygen signals have two components *ca.* 1.5 eV apart; their positions can be seen in the lowest and high chromium specimens shown in Fig. 1. The low binding energy (righthand) component corresponds to the position of oxygen in Fe-Cr oxides.¹⁸ The ratio between the intensities of the high and low binding energy components varies not only with chromium content but also with ion bombardment.

The recorded oxygen peaks were deconvoluted into their two components. The ratio of the high binding energy peak intensity (0 (h.b.)) to the total signal intensity is plotted in Fig. 4 vs the integral chromium fraction in the films. It is found to be closely related to the chromium content in the film, which invites a more detailed study.

The positive shift of the oxygen peak, together with the proportionality with Cr content, suggest the presence of a chromium-rich hydroxide, at least in a surface layer. Support for the chromium hydroxide hypothesis is obtained from two separate experiments. First, synthetic $\text{Cr}(\text{OH})_3$ was precipitated on a gold plate and analysed by ESCA. Second, pure chromium was passivated for a few minutes at 25°C in the same way as the other specimens. Solid $\text{Cr}(\text{OH})_3$ is a very poor conductor; therefore

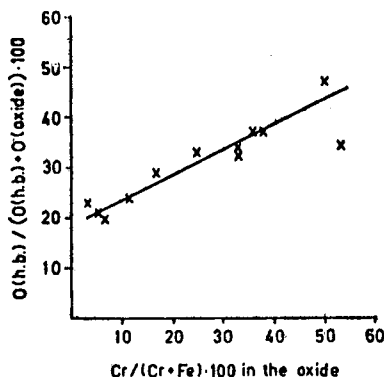


FIG. 4. The ratio of the high binding energy component of oxygen, O(h.b.), and the intensity of the total oxygen peak vs the chromium content in the top layer of the film.

the layer must be kept very thin to avoid spurious shifts due to specimen charging. This was achieved by precipitating $\text{Cr}(\text{OH})_3$ from a solution of 0.01M CrCl_3 into which one drop of NH_4OH was introduced. The $\text{Cr}(\text{OH})_3$ sedimented in a very thin layer (not visible to the naked eye) on to the gold substrate. The ammonium chloride formed in the reaction was removed by dilution in such a large volume of water that neither nitrogen nor chloride could be detected in the spectra (Fig. 5a).

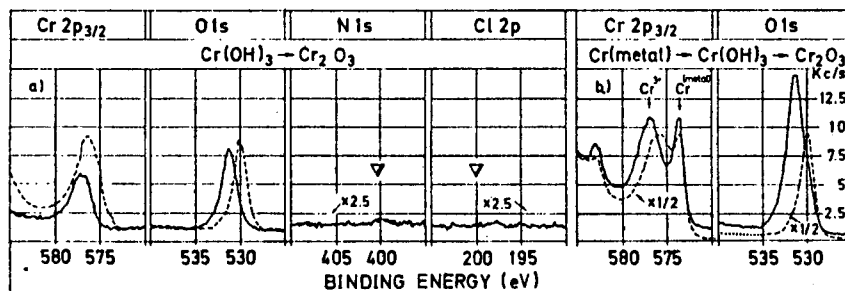


FIG. 5. ESCA spectra of: (a) $\text{Cr}(\text{OH})_3$ (solid peaks) and Cr_2O_3 (dashed peaks) formed by heating $\text{Cr}(\text{OH})_3$ to 300°C (arrows ∇ indicate expected peak positions for NH_4Cl); (b) Chromium metal as-passivated (solid peaks) and after heating to 300°C .

The solid peaks in Fig. 5(a and b) show the synthetic $\text{Cr}(\text{OH})_3$ and the passive film formed on pure chromium. The position of the metallic Cr peak in Fig. 5b is the normal one for this element, showing that spurious shifts due to surface charging are absent. Since the peak positions of the synthetic hydroxide agree with those of the passivated chromium, we may conclude that also Fig. 5a is free from spurious shifts. The agreement between Figs. 5(a and b) leads to the interesting hypothesis that chromium passivates by forming a layer of $\text{Cr}(\text{OH})_3$.

This was tested in two ways. First, both samples were heated in vacuum to 300°C , which should lead to the transformation $\text{Cr}(\text{OH})_3 \rightarrow \text{CrOOH} \rightarrow \text{Cr}_2\text{O}_3$. The dashed peaks in Fig. 5(a and b) show the spectra recorded after heating. In both cases, the

oxide peaks have moved to the position of the low-energy peak in Fig. 1, i.e. the normal position of the O^{2-} peak in oxides. It was possible, in fact, to follow the steps of the reaction sequence at intermediate temperatures by the gradual decline of the high-energy peak and the growth of the low-energy peak, including the stage where equal intensities of both peak components indicated the presence of $CrOOH$. A second test was based on the intensity ratios of the oxygen and the chromium peaks before and after heating. The ratio of the photoelectron yields for oxygen and chromium can be determined from the spectrum of Cr_2O_3 (Ref. 18); it is found to be *ca.* 0.4. This would give an oxygen/chromium intensity ratio of 0.6 for Cr_2O_3 and of 1.2 for $Cr(OH)_3$; the observed values were 1.12 and 1.24 for the synthetic hydroxide and the passive film on chromium before heating, and 0.60 and 0.51 respectively after heating.

Thus the conclusion seems justified that chromium passivates by forming a layer of $Cr(OH)_3$, and that the oxygen peak at 531.5 eV is to be assigned to oxygen in hydroxyl ions. Objections could be raised against this argument, because the hydroxide component of oxygen overlaps with adsorbed oxygen components as H_2O , CO and CO_3^{2-} . A contamination layer of these compounds is certainly present. It shows a carbon peak, which disappears after a very short time of ion bombardment. However, no correlation exists between the intensity of the hydroxyl (plus adsorbed oxygen and hydroxide) peak and that of the carbon peak. The contribution of a monolayer of adsorbed oxygen to the total observed oxygen peak intensity would be about 15%. more than 3 atomic layers would be required to produce the correlation obtained in the cases with high chromium content in the surface region of the films. It is not probable that the bonding between the molecules of oxygen in a layer of this dimension is strong enough to keep it on the surface in vacuum.

With this background, the "high binding energy component" of the oxygen peaks in spectra of the outermost zone of the layer formed on chromium steels (Fig. 1) may be identified as a hydroxide peak. This leads to the conclusion that the passivating film consists of an outer layer of $Cr(OH)_3$, possibly with small content of three-valent iron. The surface layer is obviously very thin, since the shape of the oxygen peak changes very quickly from hydroxyl to oxide on ion bombardment. After deconvolution of the hydroxide and oxide components, one can estimate the thickness ratio of the hydroxide and oxide layers. With a total film thickness of *ca.* 20 Å (see below), the hydroxide layer is found to be between 3 and 5 atomic layers thick. Below this there is a layer of oxide containing only O^{2-} ions. The iron peaks in Fig. 1—both Fe 3p and Fe 2p_{3/2}—each show a minor contribution of the divalent state, recognizable as a broadening of the peaks towards the right. This suggests that the bottom layer may consist of a spinel type oxide $Fe_{1-x}Cr_xO_4$, as in the case of dry-formed films.¹⁸

The total thickness of the passive films can be determined by the method described in Ref. 18. It is found to depend both on alloy composition and on exposure time. Figure 3 shows that the films actually became thinner with prolonged exposure, and thus with increasing chromium content in the film. The thinnest films (*ca.* 20 Å) are found after long exposure on specimens with high Cr content. For pure chromium, the film is extremely thin (*ca.* 10 Å).

Figure 6 shows the spectra recorded after exposure for long time of the low alloy steel. It shows iron in its three-valent state. No chromium can be detected. The double peak with equal intensities of O^{2-} and OH^- indicates that the corrosion product is

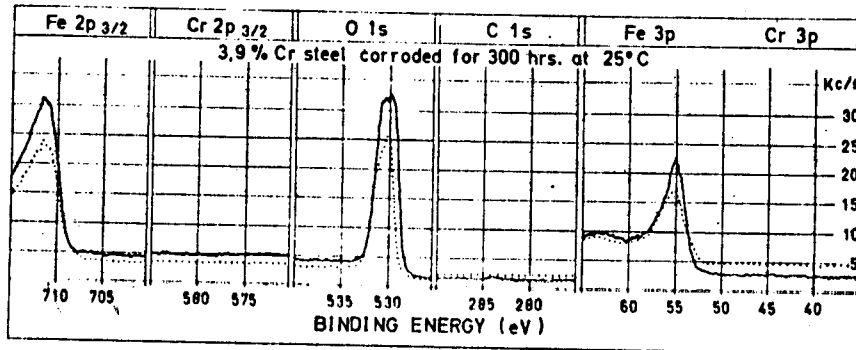


FIG. 6. ESCA spectra of the 3.9% chromium specimen after exposure for 300 h at 25°C (solid lines) and after removal of ca. 100 Å of the top layer by ion etching (dotted lines). Fe 3p scaled up 5 ×.

FeOOH. The film is much thicker than those formed in the passive state. The shape of the peaks did not change after long ion bombardment (100–200 Å removed), and a discoloration was visible on the specimen.

A comparison of the profiles in Fig. 3 with those of films formed in dry oxygen¹⁸ shows that the enrichment of chromium occurs at the opposite phase boundaries. In dry oxidation, chromium is depleted in the outer parts of the film; in aqueous medium, chromium is increasingly enriched with time in the outer part. This difference made it important to learn whether an air-formed oxide film would adjust its composition gradient when exposed to water. Specimens with 5.8, 11.0 and 19.9% Cr were cleaned by ion bombardment, oxidized in pure oxygen at 0.2 atm for 46 h, and the top layer analysed. Then the specimens were treated in oxygenated water at 25°C for 3.5 h.

The triangles in Fig. 7 shows the integral chromium contents at the top layer after

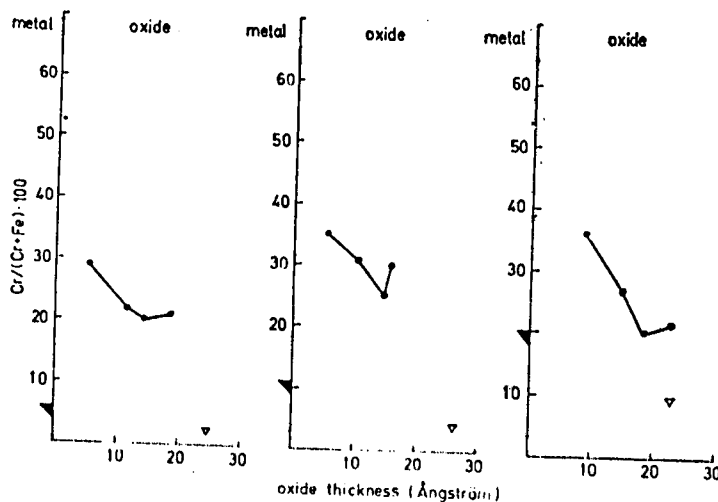


FIG. 7. Integral chromium content (cation %) in the surface region of dry-formed oxide (▽) and composition profiles after exposure to water for 3.5 h. (a) Fe 5.8 Cr, (b) Fe 11 Cr, (c) Fe 19.9 Cr.

oxidation in pure oxygen. The profiles obtained after exposure to water are marked by the solid lines. The figure demonstrates that air-formed oxide films, which consist mainly of iron oxide at the surface, slowly change their composition when treated in water. The result is a superposition of the two gradients during the transitory stages of this adjustment.

CONCLUSIONS

There is a striking contrast in the composition profiles of passive films formed on Cr-steels in oxygenated water and of films formed on the same steel in dry oxygen. As shown in the preceding communication¹⁸ dry oxidation at room temperature produces an average composition in the film corresponding to that of the alloy. It also leads to a depletion of chromium in the outermost region of the film and a slight enrichment at the metal/oxide interface in agreement with classical oxidation theory.¹⁹ When the metal is exposed to oxygenated water, the film composition at first also agrees with that of the alloy, owing to the low diffusivity at room temperature. Prolonged exposure, however, causes the chromium content to increase in accordance with the higher affinity of chromium to oxygen. In contrast to dry oxidation, chromium is now mainly enriched in the outermost region of the film, where the chromium content in fact approaches 100% after long exposure.

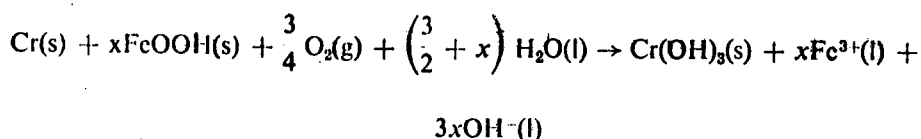
The passive film in its stationary state consists of two layers: a bottom layer of iron-chromium oxide, possibly of spinel type $\text{Fe}_{1+x}\text{Cr}_{2-x}\text{O}_4$, and a very thin top layer of hydroxide $\text{Cr}(\text{OH})_3$. Support for this is found in the following: (i) the agreement between the oxygen peak positions of the hydroxide and the oxide components of the film spectra with the corresponding peaks from synthetic compounds; (ii) the correlation between the chromium content in the outermost layer and the intensity of the hydroxide peak; and (iii) the separate study of pure chromium which showed that the passive layer on that metal consists of an extremely thin film of $\text{Cr}(\text{OH})_3$. This last observation demonstrates that chromium hydroxide is a very effective barrier to the reaction of chromium metal with oxygenated water.

It is known that the chromium content of iron-chromium alloys must exceed a threshold value to allow the development of persistent passivity. The results of this ESCA investigation suggest a possible mechanism. The composition of the first-formed film, with respect to the metal ions, will correspond to that of the alloy, because the low atomic mobility in the metal precludes preferential reaction at short times. Later on, the composition changes in accordance with the greater thermodynamic stability of Cr-rich oxides. These changes, and the observation that the films actually become thinner with time, can be explained by an exchange process, where iron dissolves preferentially into the liquid, while chromium remains behind in the film. Such preferential dissolution has been demonstrated by Kolotykin,²⁰ who monitored the iron and chromium concentrations in electrolytes in contact with ferritic chromium steels in the passive region by activation analysis. Continued dissolution of iron at a faster rate than chromium will build up the observed chromium enrichment towards the outer surface of the film. Preferential migration of Cr may contribute to the enrichment since the decrease in film thickness is not fully in accordance with the degree of conversion.

The presence of hydroxide at the oxide/water interface seems plausible for a

system close to equilibrium, where exchange of the ionic species must proceed at similar rates in both directions. Top layers of hydroxide have also been found in an ESCA study of films formed on pure iron passivated in aqueous environment by means of inhibitors.²¹ Initially, the top film of ferritic chromium steels may be assumed to be mainly FeOOH. As the chromium content of the underlying oxide rises, this will be replaced by Cr(OH)₃ with varying, but finally very small, contents of iron. At this stage, the transport of iron through the double layer will have reached a low, stationary rate, corresponding to the rate of dissolution and renewal of the passive film. It may be noted in passing that the solubility product of FeOOH is higher than that of Cr(OH)₃.

The process of preferential dissolution of Cr, and the change in composition of the hydroxide film, may be described as follows:



where x is a time dependent parameter ($1 < x < 2$).

In the case of the low-alloy steels studied here, chromium is rapidly enriched in the film during the first stages of exposure, but depletion in the alloy underneath the film and the low atomic mobility at room temperature make it impossible to uphold the necessary chromium content in the film for prolonged periods. Consequently, the film will break down and be replaced by the non-protecting corrosion product of the Cr-depleted metal, FeOOH.

At the present time, it seems difficult to decide whether the chromium hydroxide layer plays an active role in establishing passivity in chromium steels by presenting an added resistance to the passage of iron ions from the oxide to the water, or whether it is only a corollary of the chromium enrichment in the film.

Many investigators have proposed that chromium is one of the metals which is passivated by adsorption. This is not necessarily in conflict with the present results because most of the studies on chromium have been performed in acids; e.g. Armstrong *et al.*²² inferred that chromium is passivated in 0.5M H₂SO₄ by forming a monolayer of oxygen on the surface. On the other hand, an ESCA analysis of Okamoto^{23,24} has demonstrated the formation of compact layers on austenite stainless steel in acids; the enrichment of chromium was found to depend on the passivation potential.

For pure iron, the formation of a second phase within the passive film has been suggested earlier in the literature. Nagayama and Cohen²⁵ proposed an inner layer of Fe₃O₄ and an outer of γ-Fe₂O₃ with high defect content, while Sato *et al.*²⁶ inferred Fe₂O₃·0.4 H₂O with an inner anhydrous ferric oxide layer and an outer layer of hydrous oxide. The presence of water molecules in the passive films cannot be excluded by the present study.

Acknowledgements: The authors are grateful to SANDVIK AB for the preparation of the samples and to Mr. U. Jelvstam and Mrs. Y. Olefjord for their competent experimental assistance. Financial support from the Swedish Board for Technical Development (STU) is gratefully acknowledged.

REFERENCES

1. C. SCHÖNBEIN, *Pogg. Ann.* **37**, 590 (1836).
2. L. TRONSTAD, *Trans. Farad. Soc.* **29**, 502 (1933).
3. A. B. WINTERBOTTOM, *J. Scient. Instrum.* **14**, 203 (1937).
4. T. H. HEUMANN and F. W. DICKÖLTER, *Z. Electrochem.* **62**, 745 (1958).
5. V. V. ANDREEVA, *Corrosion* **20**, 351 (1964).
6. K. N. GOSWAMI and R. W. STAHLER, *Electrochim. Acta* **16**, 1895 (1974).
7. G. M. BULMAN and A. C. C. TSEUNG, *Corros. Sci.* **12**, 415 (1972).
8. G. M. BULMAN and A. C. C. TSEUNG, *Corros. Sci.* **13**, 531 (1973).
9. E. M. MAHLA and M. A. NILSEN, *Trans. electrochem. Soc.* **89**, 167 (1946).
10. T. N. RHODIN, *Corrosion* **12**, 1231 (1956).
11. T. N. RHODIN, *Corrosion* **12**, 4651 (1956).
12. K. SIEGBAHN, C. NORDLING, A. FAHLMAN, R. NORDBERG, K. HAMNIN, J. HEDMAN, G. JOHANSSON, T. BERGMARK, S.-E. KARLSSON, I. LINDGREN and B. LINDGREN, ESCA-atomic, molecular and solid state structure studied by means of electron spectroscopy, Almqvist & Wiksell AB, Stockholm, (1967.)
13. I. LANGMUIR, *J. Amer. Chem. Soc.* **38**, 2221 (1916).
14. M. G. FONTANA, *Corrosion* **3**, 567 (1947).
15. W. A. MUELLER, *J. electrochem. Soc.* **107**, 157 (1960).
16. I. OLEFJORD, *Scandinavian J. Metallurgy* **3**, 129 (1974).
17. I. OLEFJORD, *Metal Science* **9**, 263 (1975).
18. I. OLEFJORD, this issue.
19. C. WAGNER, *J. electrochem. Soc.* **99**, 369 (1952).
20. Y. M. KOLOTYRKIN, *Electrochim. Acta* **18**, 593 (1973).
21. I. OLEFJORD, N-G. VANNERBERG, ESCA studies of passive films formed on steels by oxidizing inhibitors. In Proc. 7th Scand. Corrosion Congress in Trondheim, p. 434-443, Royal Norwegian Council for Scientific and Industrial Research (1975).
22. R. D. ARMSTRONG, M. HENDERSON and H. R. THIRSK, *J. electroanal. Chem.* **35**, 119 (1972).
23. G. OKAMOTO, *Corros. Sci.* **13**, 471 (1973).
24. G. OKAMOTO, K. TACHIBANA, T. SHIBATA and K. HOSHINO, *J. Japan Inst. Metals* **38**, 117 (1974).
25. M. NAGAYAMA and M. COHEN, *J. electrochem. Soc.* **109**, 781 (1962).
26. N. SATO, K. KUDO and T. NODA, *Electrochim. Acta* **16**, 1909 (1971).

X-Ray Photoelectron Spectroscopic Study of the Aqueous Oxidation of Monel-400

N. S. McIntyre, T. E. Rummery, M. G. Cook, and D. Owen

Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada

ABSTRACT

The surface of Monel-400 alloy was exposed to high pH, aqueous corrosion at 285°C, under both oxidizing and reducing conditions. After exposures lasting from 0.3 to 335 hr the surfaces were examined by x-ray photoelectron spectroscopy, scanning electron microscopy, and other techniques. Under reducing conditions, no corrosion film forms on the metal surface, but under oxidizing conditions, the first corrosion layer which forms at the solution interface is entirely $\text{Ni}(\text{OH})_2$. This hydroxide, which persists for long times at $\text{pH} \sim 10$ but which rapidly converts to NiO at $\text{pH} \sim 14$, is shown to result from a precipitation process. The composition of the corrosion film is determined by the relative solubilities of nickel and copper at the interface. A composition profile of the corrosion layer beneath the outermost film shows a gradual increase in cuprous ion concentration with increasing depth, probably due to solid-state migration. This suggests that the aqueous corrosion of Monel-400 involves both solid-state oxide growth and an ionic dissolution and precipitation mechanism.

Monel-400¹ (66% Ni, 32% Cu) is one of the alloys used as heat-exchanger tubing in CANDU-PHW² power reactors. As part of a study of the transport of radionuclides in reactor coolant systems, we have investigated the aqueous corrosion behavior of Monel-400 under conditions of high temperature and pressure which simulate those found in the coolant of a power reactor.

Most aqueous corrosion studies of nickel-copper alloys have concentrated on film growth rates (1-10) or on the composition and structure of oxide films which were formed over lengthy periods of corrosion (11-13). One study used electron diffraction to identify the corrosion products $\text{Ni}(\text{OH})_2$, NiOOH , and NiO which had formed on some copper-nickel alloys after several hours of aqueous corrosion (14). With the development of other analytical techniques sensitive to surface films no thicker than a few atomic layers, both composition and structure can be determined qualitatively and quantitatively following very brief exposures to corrosion conditions.

In this work, corroded surfaces were studied by x-ray photoelectron spectroscopy (XPS or ESCA) as well as scanning electron microscopy, and, where possible, by x-ray diffraction. In XPS, photoelectrons produced by an impinging x-ray beam emerge from the top 1-2 nm of a surface and their kinetic energies are analyzed (15). The exact kinetic energy of the photoelectron reflects not only the atomic number of the originating element, but also the chemical environment of this element. If this technique is combined with ion sputtering to remove successive layers of surface film, it is possible to obtain a profile of the elemental distribution through the corrosion layer.

XPS provides an average analysis of the elements on several square millimeters of surface. Complementary information about the distribution of crystallites within this area can be obtained using scanning electron microscopy. Also, where a film of sufficient thickness (~ 0.1 - $1 \mu\text{m}$) has formed, x-ray diffraction can be used to confirm the XPS analysis.

In two previous XPS studies, corroded copper-nickel surfaces have been examined. Illet and co-workers (16) examined films on a 70:30 cupronickel alloy which had been anodized in sodium chloride solutions. Above

the passivation potential, the surface was found to consist primarily of a nickel-oxygen species whose identity could not be absolutely established. The XPS core line spectra of the nickel-rich surface did not, however, correspond to stoichiometric NiO . Castle (17), however, examined 70:30 copper-nickel alloy surfaces heated in oxygen and in this case was able to identify the nickel phase as NiO . The surface of the oxidized alloy was enriched in nickel compared with the bulk metallic phase. Both cuprous and cupric oxide phases were identified under different oxidizing conditions.

In this work, the corrosion films formed on Monel-400 were studied following brief exposures of the alloy to alkaline ($\text{pH} = \sim 10$ - 14), high temperature (285°C) solutions saturated with respect to either hydrogen or oxygen. In each case the XPS spectra of the corrosion products could be clearly identified with the spectra of known nickel or copper species. From the analysis of the surface corrosion products and the elemental depth profile, a mechanism for the aqueous corrosion of Monel-400 is proposed.

Experimental

Mechanically abraded Monel-400 coupons of 3 cm^2 surface area were exposed to 0.1 liter of 1.0 mol/kg and 1×10^{-4} mol/kg $\text{Li}(\text{OH})$ solutions at 285°C in a Teflon-lined titanium autoclave. The autoclave was initially purged and filled to a pressure of 0.1 MPa at 25°C with reagent grade hydrogen or oxygen. The inner surfaces of the autoclave, in contact with solution, were lined with Teflon since it was found that even after thorough cleaning microquantities of metallic contaminants remained on the titania surfaces and were readily transported to the Monel-400 surfaces during exposure. The Teflon liner was pretreated under reaction conditions for over 50 hr to eliminate any significant contribution of fluoride and chloride ion to the solution and the absence of these impurities on the Monel-400 surface after treatment was confirmed by photoelectron spectroscopy. Photoelectron spectroscopy also confirmed the absence of elemental impurities, other than adsorbed oxygen and minor quantities of hydrocarbon, on the Monel surfaces prior to exposure.

Effective exposure periods varied from 0.3 to 335 hr. The effective period was taken to be the time at which the surface was corroded at temperatures between 225° and 285°C, and allowed for the time of additional corrosion during heating-up and cooling-down. Following

Key words: Monel, nickel hydroxide, aqueous oxidation, photoelectron spectroscopy, corrosion.

¹Trade name of the International Nickel Company of Canada Limited.

²CANDU-PHW = Canada deuterium uranium-pressurized heavy water.

exposure, coupons were cooled *in situ*, washed with distilled water, and transferred to the spectrometer. When the effects of dissolved hydrogen were studied, particular care was required to prevent possible oxidation of the surfaces after exposure, and the transfer to the spectrometer was done under an argon atmosphere. The total quantities of copper and nickel products in solution from each corrosion reaction of Monel were determined using flame or flameless atomic absorption spectroscopy.

A McPherson ESCA-36 XPS spectrometer with a cryogenically pumped sample chamber was used. The excitation radiation used was either the Mg K_{α} or Al K_{α} line. The instrument work function (3.8–4.2 eV) was set so that the Au(4f 7/2) peak was at 84.00 eV for a gold metal surface. Rather large charging shifts (1–3 eV) were encountered for all Monel surfaces exposed to aqueous oxidation. The surface charging was corrected by measuring the shift of the background carbon C(1s) line, which normally occurs at 285.0 ± 0.2 eV. In some cases a gold film was evaporated onto the surface and its equivalent charging shift was measured (18). In general, agreement between the two measurements, however, was within ± 0.2 eV. Such corrections, however, substantially affect the precision of the peak assignment and the errors quoted result from ten determinations of the peak position.

Appropriate relativistic energy corrections were made to all binding energies reported. A 10 keV argon ion gun was used for depth profile studies. Ion flux on these surfaces was limited to $5 \mu\text{A cm}^{-2}$ to minimize effects of chemical decomposition and preferential sputtering. Surface morphology was determined with a Cambridge "Stereoscan" Mark 2A scanning electron microscope. X-ray diffractometry was carried out using a Philips vertical goniometer with monochromated Cu K_{α} radiation.

XPS Spectra

The x-ray photoelectron spectra of a number of oxides and hydroxides of copper and nickel have been studied in this (19) and other (20–22) laboratories. The binding energies associated with the more prominent metal and oxygen core lines as well as the energy of the major metal LMM Auger transition are given in Table I. In Fig. 1 and 2 the M(2p) and M(3s) spectra for some oxides and hydroxides of copper and nickel are shown. Cuprous oxide is distinguishable from copper metal only by the shift of the Cu Auger LMM line. Cupric oxide and hydroxide are characterized by their differing metal and oxygen core binding energies as well as by the metal "shake-up" satellite spectra located on the high binding energy side of most cupric compounds (23). In the case of the nickel-oxygen system, NiO and Ni(OH)₂ can be clearly distinguished using similar criteria as in the copper spectra. Spectra of another nickel-oxygen species have been reported by Kim and Winograd (22) following the low pressure oxidation of polycrystalline nickel surfaces. They suggest that this species is a defect structure containing Ni³⁺. Similar spectra have been observed in this laboratory (24) during room temperature oxidation of nickel surfaces. Although this oxide has metal and oxygen core line energies rather close to those for nickel hydroxide, the separation is still adequate to provide characterization of either species,

Table I. Some metal and oxygen core binding energies of copper and nickel oxygen compounds

Compound	M(2p 3/2) eV	M(3p 3/2) eV	O(1s) eV	M(LMM Auger) eV
Cu metal	932.4 ± 0.1	75.1 ± 0.1	—	919.0 ± 0.2
Cu ₂ O	932.4 ± 0.1	75.1 ± 0.1	530.5 ± 0.2	917.4 ± 0.3
CuO	933.7 ± 0.2	76.6 ± 0.25	529.6 ± 0.15	917.7 ± 0.3
Cu(OH) ₂	934.2 ± 0.25	77.0 ± 0.25	531.2 ± 0.2	—
Ni metal	852.5 ± 0.1	66.3 ± 0.15	—	842.3 ± 0.3
NiO	854.0 ± 0.2	67.4 ± 0.2	529.6 ± 0.15	839.5 ± 0.4
Ni(OH) ₂	855.9 ± 0.3	68.1 ± 0.2	531.4 ± 0.3	838.4 ± 0.3

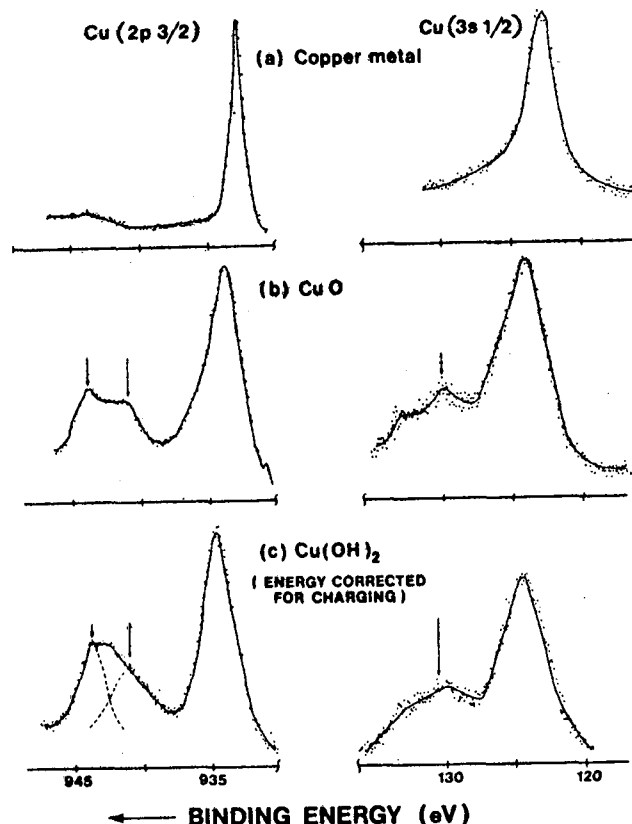


Fig. 1. XPS Cu(2p 3/2) and Cu(3s) core line spectra for Cu metal, CuO, and Cu(OH)₂. The arrows indicate satellite peaks due to multi-electron excitation (shake-up) or multiplet interaction processes.

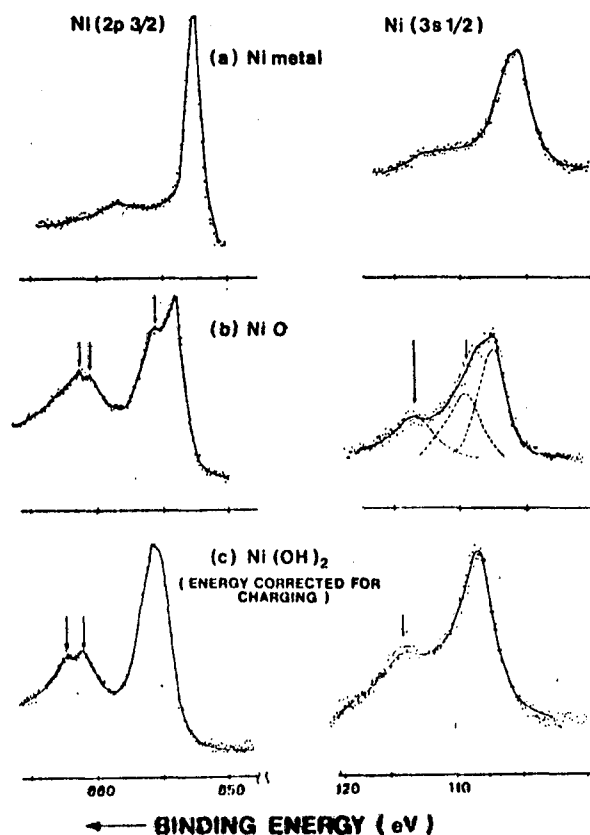


Fig. 2. XPS Ni(2p 3/2) and Ni(3s) core line spectra for Ni metal, NiO, and Ni(OH)₂. The arrows indicate satellite peaks due to multi-electron excitation (shake-up) or multiplet interaction processes.

particularly when combined with the quite different satellite and Auger spectra produced by each. The "surface nickel oxide" species of Kim and Vinograd (22) was not observed during the present work.

Results

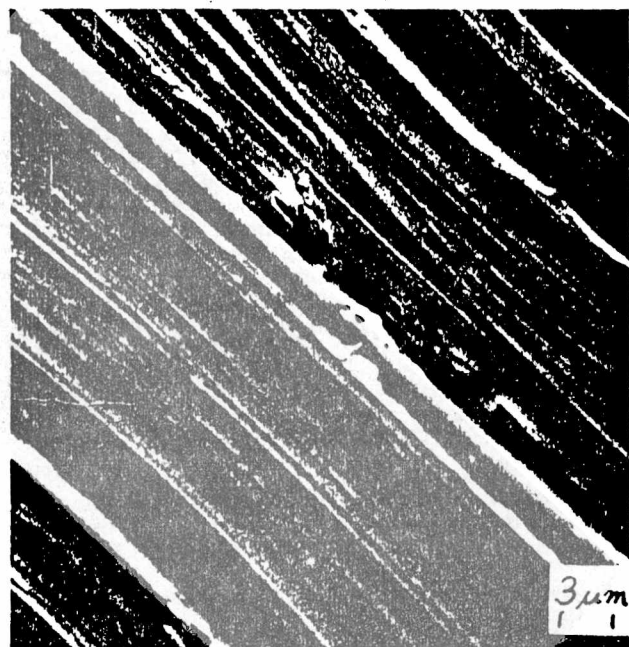
Exposure in 10^{-4} mol/kg Li(OH)—0.1 MPa H_2 overpressure.—After exposure of a Monel coupon in 285°C solutions (pH ~ 10) under hydrogen for periods up to 335 hr, no evidence of any significant oxidation product on the surface was seen using XPS. Spectra of the Cu(2p 3/2) and Ni(2p 3/2) lines for a Monel surface were the same as those for pure metal surfaces [Fig. 3(a)]. As little as 0.3 of a monolayer of NiO or Ni(OH)₂ could be detected using these lines. The O(1s) spectrum of the Monel surface [Fig. 3(a)] shows a small peak at 531.7 eV due to minor concentrations of a surface oxygen species. Such complexes are normally observed on metal surfaces not treated under vacuum prior to examination. The copper-nickel ratio of the surface was determined from both M(2p) and M(3p) integrated line intensities using prepared copper-nickel alloys of known composition as intensity standards (25). Using the M(2p) line ratios a nickel:copper atom ratio of $75:25 \pm 10\%$ (2σ) was determined while an atom ratio of $65:35 \pm 7\%$ (2σ) was found using the M(3p) line ratios. The M(3p) photoelectrons with kinetic energies of 1200 eV have a mean escape depth (1–2 nm) around three times larger than the M(2p) photoelectrons which have kinetic energies of 300–400 eV (26). Although the more deeply sampled surface layer has, within experimental error, copper-nickel ratio equivalent to that in bulk of Monel-400, the extreme outer surface appears to be depleted in copper. This could be due to a preferential dissolution of copper or surface segregation as discussed below.

The absence of any oxide is consistent with thermodynamic calculations. Comparison of calculated equilibrium partial pressures for hydrogen reduction of NiO, Cu₂O, and CuO (27) with the hydrogen overpressure of 0.1 MPa used in these experiments indicates that the metallic phase is thermodynamically stable for both nickel and copper.

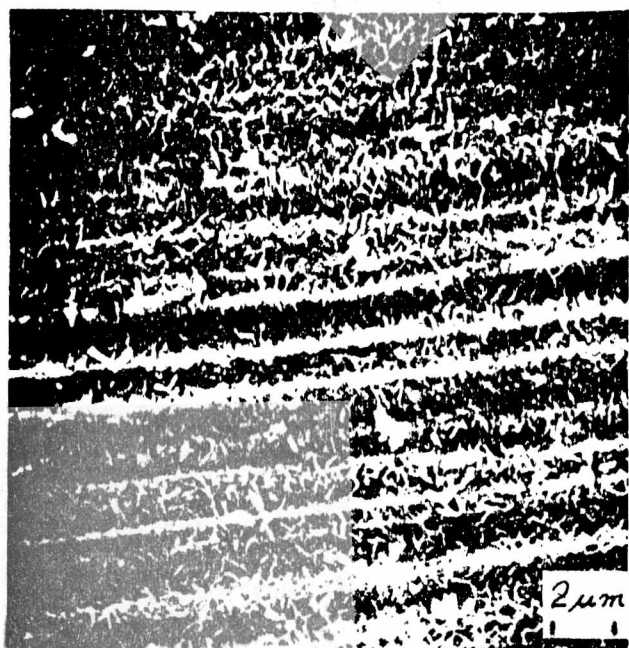
Exposure in 10^{-4} mol/kg Li(OH)—0.1 MPa O_2 overpressure.—The exposure of Monel-400 under conditions

as described above except for an oxygen overpressure resulted in rapid growth of a corrosion film. After an effective exposure of 0.3 hr, a scanning electron micrograph of the surface [Fig. 4(b)] indicated a layer of acicular crystals 0.1 μ m in diameter. A micrograph of the reduced surface [Fig. 4(a)] is included for comparison. The needlelike morphology of the crystals suggests that they were formed by precipitation from solution rather than by a solid-state growth process.

Only a nickel phase was detected on the outer surface using XPS. If copper was present at all, it constituted less than 5 atomic per cent (a/o) of the corrosion layer (expressed as CuO). Spectra of the Ni(2p 3/2), Cu(2p 3/2), and O(1s) line regions are shown in Fig. 3(b). The binding energies of the principal lines



(a)



(b)

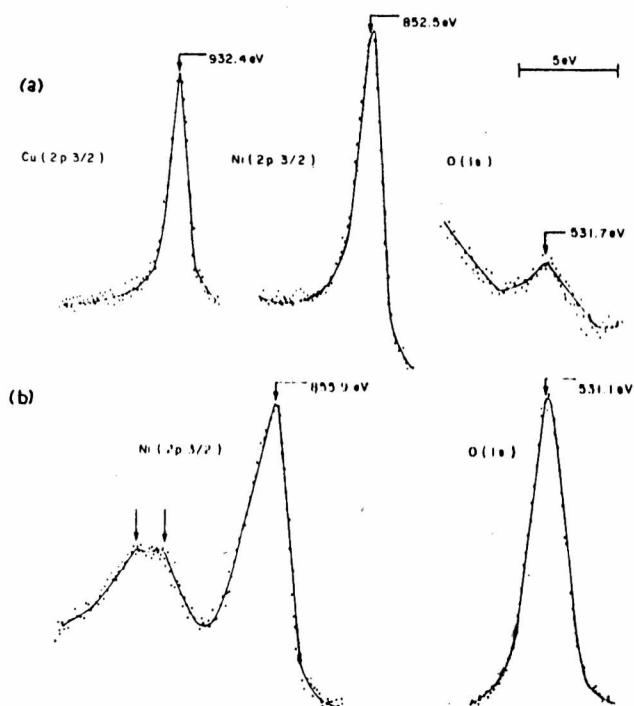


Fig. 3. XPS Cu(2p 3/2), Ni(2p 3/2), and O(1s) core line spectra for Monel-400 surface exposed to 1×10^{-4} M Li(OH) at 285°C for 0.3 hr; (a) hydrogen overpressure, (b) oxygen overpressure.

Fig. 4. Scanning electron micrograph of a Monel-400 surface exposed to 1×10^{-4} M Li(OH) at 285°C for 0.3 hr, (a) hydrogen overpressure, (b) oxygen overpressure.

correspond within 0.2 eV to those given for bulk $\text{Ni}(\text{OH})_2$ in Table I. Moreover, the characteristics of the $\text{Ni}(2p\ 3/2)$ shake-up spectrum (twin peaks at 5.1 and 6.8 eV above the principal line) and $\text{Ni}(3s)$ spectrum (strong satellite at 5.1 eV) are the same as those observed for $\text{Ni}(\text{OH})_2$. Confirmation of this assignment of $\text{Ni}(\text{OH})_2$ as the outer layer was not possible by x-ray diffraction because of the very thin surface film developed, but diffraction analysis of Monel surfaces exposed for periods of 48 hr indicated the presence of $\text{Ni}(\text{OH})_2$ as the sole detectable corrosion product phase.

Several possible mechanisms for $\text{Ni}(\text{OH})_2$ formation were considered: (i) hydration at high temperature or during cool-down of a predominantly NiO surface phase could yield an external film of $\text{Ni}(\text{OH})_2$; (ii) $\text{Ni}(\text{OH})_2$ is known to be unstable in a nonaqueous environment at 285°C (28). Thus the $\text{Ni}(\text{OH})_2$ observed could have formed during cooling of the autoclave; (iii) $\text{Ni}(\text{OH})_2$ could form at high temperature by direct precipitation of an excess of nickel at the solid-liquid interface.

The first premise was tested by exposing a suspension of stoichiometric NiO under similar autoclave conditions for 48 hr, with oxygen or hydrogen overpressures. Under neither condition was there any indication of a significant quantity of surface $\text{Ni}(\text{OH})_2$, although when NiO was exposed to oxygen-saturated solutions, evidence of some change in the oxide structure was seen. Production of $\text{Ni}(\text{OH})_2$ on Monel surfaces by hydration of NiO is thus not considered likely.

Significant precipitation of $\text{Ni}(\text{OH})_2$ during cooling of the autoclave is also considered unlikely. Solubilities of $\text{Ni}(\text{OH})_2$ in 10^{-4} mol/kg $\text{Li}(\text{OH})$ solutions have recently been determined experimentally in the temperature range 25°-300°C (29). From these, it is estimated that the change in solubility of $\text{Ni}(\text{OH})_2$ in cooling down from 300°C is less than 10^{-6} mol/kg. Precipitation of this magnitude would result in a coverage of the sample surface no greater than 0.1 monolayers which is three to four orders of magnitude below the thickness of the $\text{Ni}(\text{OH})_2$ films observed in this work.

If $\text{Ni}(\text{OH})_2$ is the major corrosion product at 285°C, its stability under such hydrothermal conditions is surprising considering the known instability in nonaqueous conditions at these temperatures (28). Recently, however, Swaddle (30) has measured the stability of bulk $\text{Ni}(\text{OH})_2$ under hydrothermal conditions similar to those above. It was found that, although the $\text{Ni}(\text{OH})_2$ phase did indeed decompose to NiO at 280°-300°C, the rate was quite slow, typical half-lives being of the order of several hours. Thus, with continual precipitation on the Monel-400 surface it is possible to rationalize the existence of a significant layer of $\text{Ni}(\text{OH})_2$ at these temperatures.

The aqueous oxidation of Monel was also carried out for periods considerably longer than 0.3 hr. In all cases, XPS studies of the outermost surface showed the major product to be $\text{Ni}(\text{OH})_2$, although small quantities of copper in cupric form were sometimes observed. X-ray diffraction of samples exposed for these periods indicated the presence of $\text{Ni}(\text{OH})_2$, but no other copper or nickel corrosion products were detected. Scanning electron microscopy coupled with energy dispersive x-ray spectrometry showed that a second crystallite phase develops on the surface at these longer exposure times. This phase, indicated with an arrow in Fig. 5, contains both copper and nickel and is quite localized, covering no more than 10% of the surface area.

The effect of increased concentration of copper ion in solution on the surface composition was studied by adding a 300 cm² copper foil to the autoclave. The surface composition was largely unaffected by the addition except that the surface concentration of cuprous oxide increased to 10-15 a/o compared to <5 a/o observed with no copper source present. SEM photomicrographs (Fig. 6) showed that the morphology of the

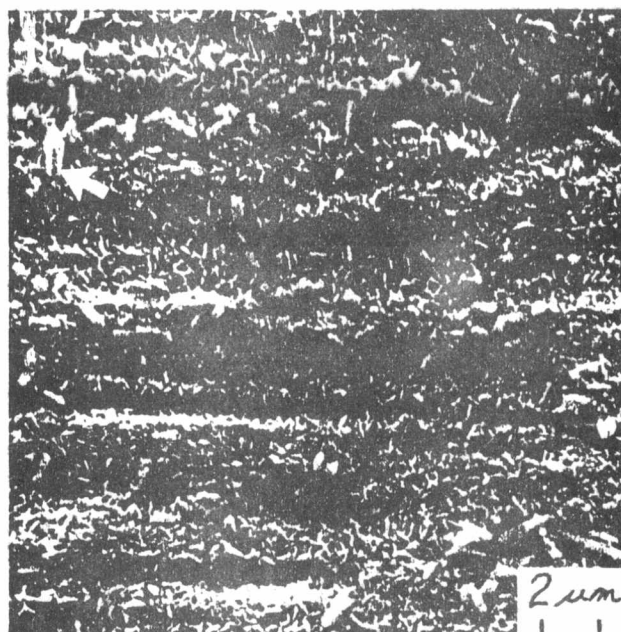


Fig. 5. Scanning electron micrograph of a Monel-400 surface exposed as in Fig. 4(b) for a period of 48 hr. A cupronickel phase is indicated by the arrow.

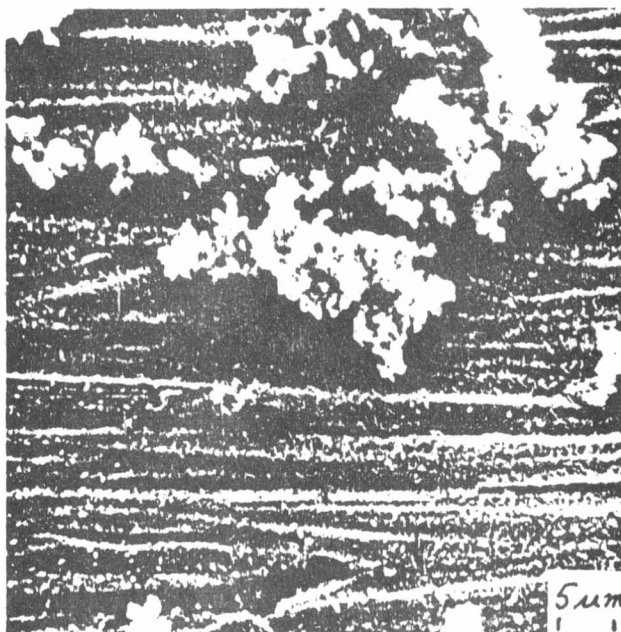


Fig. 6. Scanning electron micrograph of a Monel-400 surface exposed as in Fig. 5 with an additional copper source present in the autoclave.

deposited copper phase is much different from the film observed on a Monel surface with no copper source present (Fig. 5). The addition of an external source of copper causes, at saturation, the formation of relatively pure, localized, large crystallites of a copper phase on the film, leaving the major surface area as $\text{Ni}(\text{OH})_2$.

Elemental intensity profiles of the Monel-400 corrosion films were obtained using argon ion bombardment and a typical one is shown in Fig. 7. Of particular note is the copper phase, undetectable or barely detectable at the original outer surface, but which increases in concentration until it reaches a value about 25% of the nickel concentration [pure Cu_2O and $\text{Ni}(\text{OH})_2$ used as intensity standards]. The depth attained in this and in similar profiles was estimated to be 20-100 nm.

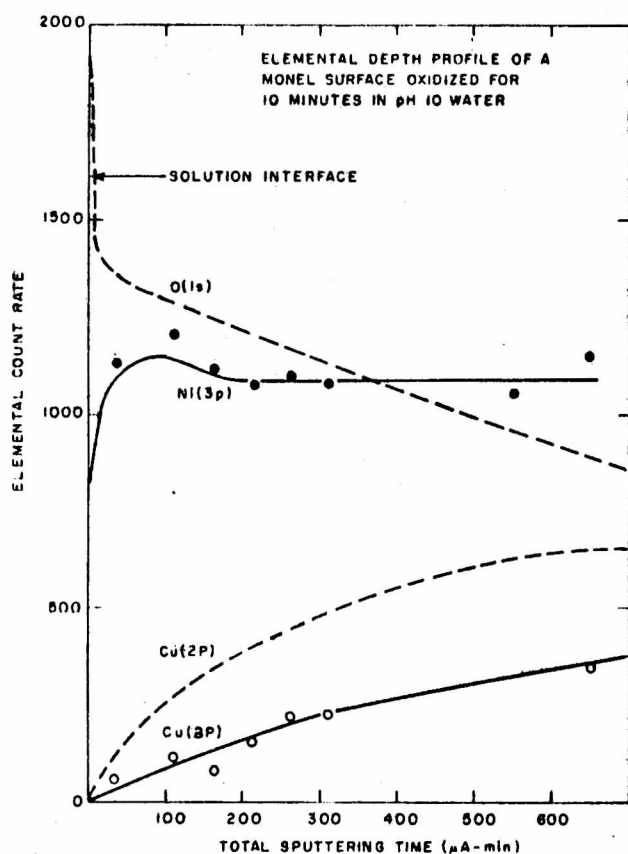


Fig. 7. Elemental intensity profile as a function of integrated sputtering current for a Monel-400 surface exposed to $1 \times 10^{-4} \text{ M Li(OH)}$ at 285°C for 0.3 hr under oxygen.

The $\text{Cu}(2p\ 3/2)$, $(3p\ 3/2)$ and Auger LMM energies indicated the presence of only cuprous oxide. Although 10 keV ion bombardment of cupric oxide has been found to result in some reduction to cuprous oxide, some contribution due to CuO usually remains, particularly in the $\text{Cu}(3p)$ spectrum. The $\text{Cu}(3p)$ line, because of its higher kinetic energy, samples the surface to a greater depth than the $\text{Cu}(2p)$ line and thus minimizes the effect of sputtering damage which occurs largely, but not completely, in the outer 1 nm of surface remaining.

As each film was initially sputtered (0-10 $\mu\text{A-min}$), rapid changes in metal and oxygen binding energies indicated a partial dehydration of Ni(OH)_2 to NiO . This can also be seen from the sharp change in slope of the $\text{O}(1s)$ intensity in Fig. 7. The presence of at least some of the NiO is almost certainly due to sputtering-induced decomposition, for it is likely that such a major amount of NiO distributed throughout the film would have been detected by x-ray diffraction. During the remainder of the sputtering profile the ratio $\text{NiO}/\text{Ni(OH)}_2$ gradually increased, and it is not clear whether this represents the appearance of an NiO phase which was actually present in the original film during formation, or whether it is due to additional ion bombardment damage.

The effect of exposing an oxidized Monel-400 surface for a second period in the autoclave with a hydrogen overpressure was studied. The coupon initially was exposed for 0.3 hr in 0.1 MPa oxygen followed by replacement with a hydrogen atmosphere and continued exposure for 335 hr. SEM photomicrographs showed that features of the surface film were basically unchanged from those seen in Fig. 4(b). XPS analysis of the outer surface indicated that both NiO and Ni(OH)_2 were present in comparable quantities, but that no metallic nickel was present on the surface. Thus, aside from some decomposition of Ni(OH)_2 to NiO , the surface film was not greatly affected by long exposure to

hydrogen, indicating that the reduction of Ni(OH)_2 (and NiO) to elemental nickel is very slow under these aqueous conditions.

Attempts to estimate solution concentrations of copper and nickel during the high temperature exposures gave unreproducible results ranging from 10-100 $\mu\text{g/liter}$ for both elements.

Exposure in 1.0 mol/kg Li(OH) —0.1 MPa O_2 overpressure.—To further understand the role played by solution phenomena in the corrosion of Monel-400, experiments were also carried out at 285°C in 1.0 mol/kg Li(OH) ($\text{pH} \sim 14$). At this pH, solubilities of both copper and nickel were found to be much higher than at pH 10, and autoclave solution concentrations could be estimated and correlated with film surface composition. After a 48 hr autoclave exposure, a film several micrometers in thickness had developed with a morphology much different from the acicular crystals found at pH ~ 10 . A SEM photomicrograph of a typical region is seen in Fig. 8. XPS showed that the surface consisted entirely of NiO . No Ni(OH)_2 or copper phases were identified on the surface nor was any copper phase revealed when the surface was sputtered to a depth of several nanometers. The film was sufficiently thick that strong x-ray diffraction lines were obtained showing the bulk corrosion film to be entirely NiO . The detection limit of additional oxide phases such as Ni(OH)_2 , Cu_2O , or Cu(OH)_2 was $\sim 5\%$ in this case.

The observation of NiO rather than Ni(OH)_2 is still consistent with a precipitation-based mechanism for film formation. The rate of decomposition of Ni(OH)_2 at this pH and temperature has been shown by Swaddle (30) to be very high, and is around two orders of magnitude faster at pH ~ 14 than at pH ~ 10 .

Solution analyses following Monel exposure at pH ~ 14 showed the copper concentration to be about 75 times higher than that of nickel (30,000 $\mu\text{g/liter}$ of copper vs. 400 $\mu\text{g/liter}$ of nickel).

Exposure in gaseous oxygen.—The compositions of corrosion films formed on Monel-400 under aqueous conditions were compared with those formed under gaseous oxidation at the same temperature. Abraded Monel-400 surfaces were exposed at 250°C – 300°C to 0.1 volume per cent (v/o) dry oxygen in argon for 0.3 hr. The resultant XPS spectrum, shown in Fig. 9(a), indicated that NiO and Cu_2O were present on the outer

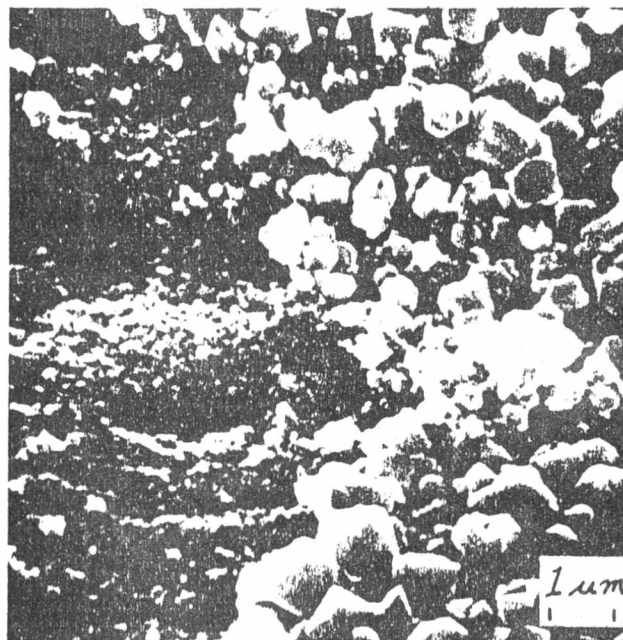


Fig. 8. Scanning electron micrograph of a Monel-400 surface exposed to 1.0M Li(OH) at 285°C for 48 hr.

surface in approximately the 2:1 atomic ratio expected from the alloy composition.

No attempt was made to determine whether the cuprous oxide and nickel oxide formed by gaseous corrosion of Monel-400 are in solid solution or are present as separate oxides, i.e., NiO and Cu₂O. According to Schnal and Muller (31) these oxides are mutually insoluble, and hence one would expect a mixture to form. However, XPS spectra show only one prominent O(1s) line. Since the oxygen binding energy in Cu₂O is different from that in NiO by 0.8 eV (19), one would have expected to see a contribution from both oxygen in Cu₂O and NiO, if separate phases were present. Thus at least on the surface, a mixed cupronickel oxide may be formed.

Discussion

This work shows that, under the experimental conditions used, the aqueous oxidation of Monel-400 is at least partly controlled by a dissolution-precipitation mechanism. At pH ~10, the nickel-rich outer corrosion film is believed to be a result of Ni(OH)₂ precipitation from a solution not yet saturated with respect to any copper species. When the copper does eventually reach saturation in the closed system, it nucleates in localized areas on the hydroxide surface, leaving the major surface coverage as Ni(OH)₂. At pH ~14, the copper-nickel solubility difference is much larger and the resultant corrosion film is composed entirely of a nickel phase (NiO) after 48 hr. Longer exposures would eventually result in saturation with respect to copper species, and again a copper phase would be expected to nucleate and grow at the nickel phase-water interface.

The possibility was considered that nickel enrichment in the surface phase could also arise from a higher outward diffusion rate of nickel ions in the solid lattice. However, the oxide film produced by solid diffusion in the gaseous oxidation experiments on Monel-400 contains copper and nickel in quantities proportional to their concentrations in the alloy. Thus, under these time and temperature conditions, it appears that the relative diffusion rates of copper and nickel are approximately the same and are unlikely to result in surface nickel enrichment. Castle (17) previously studied the oxidation layer of a 50:50 Cu/Ni alloy and after heating the specimen in 13 kPa of oxygen for 0.5 hr at 500°C, the surface layer was found to be somewhat richer in copper than in nickel.

One other possibility which might lead to only a nickel oxidation product on the surface is the prior enrichment of one component of the alloy due to phase separation. Copper-nickel alloys are known to exhibit phase separation in this temperature range (32); however, the analyses of Monel-400 surfaces exposed under hydrogen at 285°C show that if separation does take place its extent is clearly insufficient to explain the major compositional change observed here during oxidation.

Under the oxygen partial pressure and temperature used in the aqueous corrosion experiments, film growth must occur by both solid-state diffusion and by dissolution-precipitation. An oxide of copper appears rapidly as the outermost layers of corrosion films formed at pH ~10 are removed by sputtering. It is believed that this copper is present in the film by virtue of a diffusion process since, as shown above, copper precipitation has not been found to occur in significant quantities even after lengthy exposure. The rising concentration of copper in the composition profile shown in Fig. 7 is likely controlled by the diffusion rate of the ion and possibly by the rate of leaching of copper by the unsaturated solution. On the other hand, while the presence of a significant diffusion process is based on the observation of copper in the underlying oxide layer, the evidence for a dissolution-precipitation process is based on the identification of Ni(OH)₂, a phase which can only form by this mechanism. The occurrence of Ni(OH)₂ in a film thick enough to be measured by x-ray diffraction helps to establish that the precipitated layer is not just a negligibly thin layer formed on top of a layer formed largely by solid diffusion, but rather that it constitutes an appreciable portion of the total corrosion product. At pH ~14, it is clear that the major corrosion process is dissolution precipitation since no copper phases are detected by any means in the film.

Since the composition of the surface products depends at any time on the solution concentrations of copper and nickel, the effects of exposing Monel-400 in a "once-through" autoclave system are expected to be different from those observed for the "closed" system in the present study.

Manuscript submitted Dec. 8, 1975; revised manuscript received March 29, 1976. This was Paper 75 presented at the Toronto, Canada, Meeting of the Society, May 11-16, 1975.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1977 JOURNAL. All discussions for the June 1977 Discussion Section should be submitted by Feb. 1, 1977.

Publication costs of this article were assisted by Atomic Energy of Canada Limited.

REFERENCES

1. S. C. Datsko and C. R. Breden, USAEC, Report ANL-5354 (1954).
2. W. E. Berry and F. W. Fink, Rept. NP-8425, Battelle Memorial Institute, Columbus, Ohio (1958).
3. J. McGrew, S. Frank, and T. Page, Report MND-E-2655, Martin Company Nuclear Division (1961).
4. H. Urata, N. Kawashima, and O. Asai, *Hitachi Rev.*, 10, 19 (1962); *CA*, 61, 11707a (1964).
5. G. C. Wiedersum, *ASME Trans.*, 87, 324 (1965).
6. J. E. LeSurr, P. E. C. Bryant, and M. G. Tanner, *Corrosion*, 23, 57 (1967).
7. E. G. Brush and W. L. Pearl, *ibid.*, 25, 99 (1969).
8. J. E. LeSurr, Report AECL-3778, Atomic Energy of Canada Limited (1970).
9. P. J. Boden, *Corrosion Sci.*, 11, 363 (1971).
10. D. W. Rahoi, R. C. Scarberry, J. R. Crum, and P. E. Morris, *ASME Trans.*, 95, 27 (1973).
11. B. E. Hopkinson, Report 62-WA-274, ASME (1962).
12. J. E. Castle, J. T. Harrison, and H. G. Masterson, in "Proceedings of the Second International Congress on Metallic Corrosion," NACE, p. 822, New York (1963).
13. A. van der Linde, Report RCN-194, Stichting Reactor Centrum (1973).
14. Y. Arai, *Kogyo Kagaku Zasshi*, 64, 600 (1961); *CA*, 57, 5701E (1962).

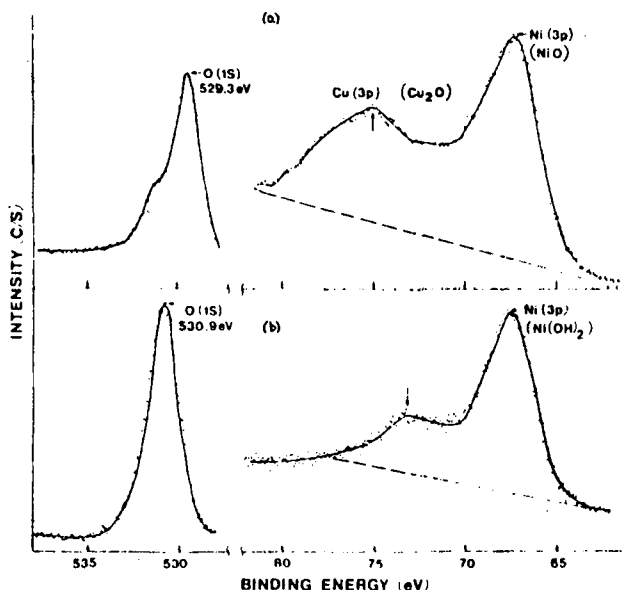


Fig. 9. Comparative XPS spectra of a Monel-400 surface exposed in (a) oxygen and (b) 1×10^{-4} M Li(OH) with an oxygen overpressure. In (b) the shoulder on the Ni(3p) peak indicated by the arrow results from a multi-electron excitation.

15. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. Karlsson, I. Lindgren, and B. Lindberg, "ESCA—Atomic Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Uppsala (1967).
16. L. D. Hulett, A. L. Bararella, L. L. Donnic, and J. C. Griess, *J. Electron Spectry.*, **1**, 169 (1972).
17. J. E. Castle, *Nature*, **234**, 93 (1971).
18. D. J. Hnatowich, J. Hudis, M. L. Perlman, and R. C. Ragaini, *J. Appl. Phys.*, **42**, 4883 (1971).
19. N. S. McIntyre and M. G. Cook, *Anal. Chem.*, **47**, 2208 (1975).
20. G. Schoen, *Surface Sci.*, **1**, 1 (1973).
21. K. S. Kim and R. E. Davis, *J. Electron Spectry.*, **2**, 251 (1973).
22. K. S. Kim and N. Winograd, *Surface Sci.*, **43**, 688 (1973).
23. T. Robert and G. Offergeld, *Phys. Status Solidi*, **14**, 277 (1972).
24. N. S. McIntyre, Unpublished results.
25. N. S. McIntyre and M. G. Cook, "Surface Analysis Techniques for Metallurgical Applications," STP 596, ASTM (1976).
26. C. J. Powell, *Surface Sci.*, **44**, 29 (1974).
27. T. E. Rummery and D. D. Macdonald, *J. Nucl. Mater.*, **55**, 23 (1975).
28. S. Le Bihan and M. Figlarz, *Thermochim. Acta*, **6**, 319 (1973).
29. P. H. Tewari, Private communication (1975).
30. T. W. Swaddle, Private communication (1974).
31. N. G. Schmahl and F. Mueller, *Z. Anorg. Allgem. Chem.*, **332**, 217 (1964).
32. W. M. H. Sachtler and R. Jongepier, *J. Catalysis*, **4**, 665 (1965).