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CORROSION RESEARCH CONFERENCE

Theme: Research in Progress

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Extended Abstracts

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1980 NACE Corrosion Research Conference

Chairman: B. E. Wilde
U.S. Steel Corp.
Monroeville, Pennsylvania

Vice Chairman: F. Mansfeld
Rockwell International
Thousand Oaks, California

SESSION 1
Predicting Environment Sensitive Fracture: What We Know and Don't Know
A. Physical Factors

9:00 – 11:00 am, Monday, March 3

Chairman: B. E. Wilde, U.S. Steel Corp., Monroeville, Pennsylvania.

Strain-Rate Effects in Environment-Sensitive Fractures

R. N. Parkins
The University of Newcastle upon Tyne, England

Phenomenologically, it is now reasonably well established that applied strain rate can markedly influence the incidence of environment-sensitive cracking in a number of systems. The strain rates that will, or will not, promote cracking depend sensitively upon the environment as well as the alloy. The effects of monotonic strain rate upon the cracking of high strength Al alloys in water, of Al-Mg alloys in CrO_4-Cl solutions, and of ferritic steels in various solutions will be used to illustrate the interdependence of these parameters. With cyclic loading at low frequencies, strain-rate effects appear to play essentially the same role as with monotonic loading and the limiting strain rate for crack growth is probably the same for both modes of loading, as will be suggested by results from studies on a cast Al-Ni bronze in sea water and a ferritic steel in a CO_3-HCO_3 solution.

There is a need for more research aimed at examining the wider validity of this latter suggestion, which has practical implications both within the laboratory and without, and also for strain-rate effects to be considered in the context of fracture mechanics. In bridging the gap from the latter to the mechanistic side, there is need for precise definition of crack tip strain rates, as opposed to engineering strain rates, which may help in formulating a model that would allow better correlation between observed limiting strain rates for cracking and those calculated involving electrochemical parameters.

Environment Sensitive Fracture: What We Know and Don't Know

R. M. Latanision
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

While it is true that we know quite a lot about the phenomenology of environmentally induced fracture, little is known about the atomic-scale interactions which lead to embrittlement. In some respects, this state of affairs is not surprising since stress corrosion cracking, hydrogen embrittlement, etc., are complex phenomena understanding of which requires interdisciplinary interactions by, for example, materials scientists, surface chemists, mechanical engineers and corrosion scientists. Regrettably, such interactions have never really occurred. In this presentation, emphasis will be placed initially on a brief discussion of phenomenology followed by a more lengthy treatment of those characteristics of metals in electrolytes which, while perhaps not having received attention in traditional thinking on mechanistics, are considered to play a role in the atomistics of environmentally induced fracture and may well affect on our ability to understand and control such phenomena.

Hydrogen Embrittlement of Aluminum Alloys: Fact or Fiction?

D. J. Duquette
Rensselaer Polytechnic Institute, Troy, New York

Environmental embrittlement of precipitation hardened aluminum alloys was reported as early as 1929. In general, the higher the yield strength of the alloy, the more susceptible it is to premature failure. Much of the early work on these alloys was concerned with the effects of liquid phase aqueous environments, particularly those containing chlorides. Under static loading, failure in these solutions is generally intergranular and, due to the preferred orientation of the grain boundaries, the alloys show a marked anisotropy in susceptibility. This behavior has generally been linked with the generic phenomenon of stress corrosion cracking, and numerous mechanisms have been proposed to explain observed results. These mechanisms include all of the classic theories of electrochemical dissolution, film rupture, stress-sorption, etc. Under cyclic loading conditions, the environmentally assisted crack path tends to be transgranular in commercial alloys with some tendency toward mixed transgranular/intergranular under certain environmental conditions in high purity alloys.

Recently, spontaneous crack growth and low ductilities have been observed in Al-Zn-Mg alloys exposed to water vapor. This observation has led to the conjecture that many of the electrochemical models which had been previously proposed were in error and that either molecular adsorption or molecular dissociation to produce hydrogen and subsequently hydrogen embrittlement may be responsible for environmental susceptibility. These hypotheses have led to other experiments where atomic hydrogen, at high fugacity was introduced into the alloy by electrochemical charging. These experiments have been performed under both cyclic and static loading and, at least for the highest strength alloys, generally resulted in degradation of mechanical properties. However, the question has been raised that cathodic charging also increases dissolution due to hydroxide formation. This presentation will address the pros and cons of each model and attempt to indicate under what circumstances hydrogen embrittlement of Al alloys may or may not occur.

Current Understanding of the Embrittling Effects of Hydrogen on Steels and the Remaining Areas of Ignorance

R. A. Oriani
U.S. Steel Corp. Research Laboratory, Monroeville, Pennsylvania

The advance and initiation of a crack in high strength steels under the influence of low activity hydrogen are manifestations of atomic bond weakening by the dissolved hydrogen. The decohesioning by hydrogen occurs very near the crack tip, usually along internal interfaces already weakened by chemical and structural features. The crack advance is bimodal, the plastic tearing component increasing with increasing stress intensity parameter and with decreasing yield strength. The hydrogen-caused decrease of strain to fracture also reflects enhanced decohesion at interfaces where stress is generated by inhomogeneous plastic deformation. In addition to causing decohesion, low activity hydrogen hardens steel by dislocation reactions with the dissolved hydrogen, but steel is also softened by the microvoids the population of which is increased by hydrogen. Hydrogen of very high activity increases all above effects, and also generates internal stresses because of hydrogen gas produced within the microcracks. This causes increased tendency to link up microcracks and thereby cause failure.

To attain predictive capability by the decohesion model, one needs to understand the basic physics of the decohesioning mechanism, the relation between the atomic structure and chemistry of an interface and its resistance to decohesion, the details of how stress is generated at an inclusion interface by plastic deformation, and the effect of hydrogen on dislocation dynamics. To be able to calculate the rate of crack propagation, one must understand all aspects of the transport of hydrogen, the stress distribution at the atomic scale within the plastic enclave, and the plastic collapse of ligaments between decohered regions.

Quantitative Measurements of Local Strain Variations in Welded 304 Stainless Steel

S. R. Bates and E. D. Verink, Jr.
University of Florida, Gainesville, Florida

In recent years, failures of some welded austenitic stainless steels have been observed which have been attributed to stress corrosion cracking (SCC). Recent literature indicates that plastic strains of 2 to 4% are required to nucleate and propagate SCC. Stresses contributing to the nucleation and propagation of SCC include residual stress from welding or cold work as well as applied stress. With regard to residual welding stresses, what has been lacking in the past is the ability to measure the level and distribution of strain on a local level, *i.e.*, areas as small as 10 microns in diameter. Recent developments in scanning electron microscopy have provided the ability to obtain selected area channeling patterns (SACP) from a bulk specimen. In the SACP mode of operation, the electron beam of the SEM is rocked about a point on the specimen surface instead of being scanned over it in a normal fashion. Rocking the beam gives a pattern from a small selected area which carries with it crystallographic information concerning that particular small volume of material. In the SACP process, a series of diffraction lines are obtained. The acuity of the lines is altered by changes in the level of strain in the volume from which the pattern is obtained. Increasing the level of strain decreases the line acuity.

Much of the early work in this field involved the measurement of SACP line width of prestrained specimens. The line widths were measured directly on the photograph of the SACP. Because of the low contrast nature of the SACP process, large statistical variations were observed.

In this work, the line width vs strain were obtained using an *in-situ*, tensile-compression stage. The electronic signal obtained as a result of the SACP was processed using an analog-to-digital converter and a mini-computer to obtain statistically significant data. Local strain levels were determined and compared with the engineering strains measured in standard tensile tests.

Since we have now developed the means of characterizing the local stress state in bulk specimens, we are in the process of applying this technique to the analysis of SCC.

SESSION 2
Predicting Environment Sensitive Fracture: What We Know and Don't Know
B. Electrochemical Factors

1:00 – 5:30 pm, Monday, March 3

Chairman: R. N. Parkins, University of Newcastle, Newcastle Upon Tyne, England.

The Prediction of Environmentally-Controlled Cracking by Electrochemical Techniques

F. P. Ford
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Schenectady, New York

A present need of technology in the field of environmentally controlled cracking is a quantitative prediction capability of the cracking susceptibility for a given alloy/environment system, and the utilization of this knowledge into a design criterion. In a discussion of the problems associated with fulfilling this need, the electrochemical aspects governing the thermodynamic requirements for cracking by various crack advancement mechanisms are reviewed, together with a critique of our present capabilities to predict crack propagation rates. It becomes apparent that, although systems exhibiting severe cracking susceptibility may be predicted relatively accurately, and the theoretical maximum and minimum propagation rates in a given system may be adequately quantified, there are serious restraints on our predictive capabilities for the technologically important intermediate propagation rates in environments which could be classified as "minimally aggressive." The reasons for these shortcomings in our present knowledge are discussed in the light of such matters as the definition of localized chemistries and the variation of the rate determining step in a crack propagation mechanism with such parameters as time and stressing mode.

Finally, the factors which inhibit crack propagation are discussed, in view of the observation that industrial experience is not in agreement with laboratories' predictions of an ever-increasing number of alloy/environment systems capable of presenting a cracking danger over extended design lives.

Concentration and Potential in Stress Corrosion Cracks

T. R. Beck
Electrochemical Technology Corp., Seattle, Washington

It is now well known that concentration and potential within stress corrosion cracks and within corrosion crevices and pits are very different from the surrounding bulk conditions. The solution within becomes concentrated in the salt of the corroding metal and acidic by hydrolysis of this metal salt and by anodic formation of oxides on the walls. Several attempts at mathematically modeling conditions within stress corrosion cracks, crevices, and pits have been described in the literature. The general procedure used has been to solve a system of equations consisting of fluxes for each species, electroneutrality and continuity. Boundary conditions are bulk concentration and potential at the mouth, and electrode kinetic equations at the tip or base and on the walls of the crack or pit. Results of several published models are reviewed and suggested directions for new work are discussed.

Predicting SCC Propagation Rates and Crack Morphologies by Fast Straining Metal Electrode Techniques

J. R. Galvele
Commission Nacional Energie Atomica
Buenos Aires, Argentina

A technique is described by which quantitative evaluation of the SCC parameters can be made. This technique applies only to those cases where the anodic dissolution is the rate determining step in the crack propagation process. The technique is based on potentiostatic straining of metal wires. The strain rates used are in the range of 10 to 300 %/min. This is much faster than the well known slow straining technique developed by Parkins and co-workers, where strain rates of the order of 10^{-6} %/min were used, and much slower than those used by Staehle and co-workers and by Diegle and Vermilyea, in the study of transient repassivation processes, where strain rates of the order of 300,000 %/min were used. When the wire is strained, slip steps are produced on the metal surface, eventually leading to the exposure of bare metal to the solution. The current density on the fresh metal is evaluated and it is compared with the crack propagation rate measured by other techniques. A very good correlation has been found between both values for the following systems:

i. mild steel in nitrate solutions;[1]
ii. mild steel in alkaline solutions;[2]
iii. stainless steel in HCl solutions;[3]
iv. stainless steel in NaCl + H_2SO_4 solutions;[4]
v. stainless steel in NaOH solutions;[5]
vi. Ni alloy 600 in NaOH solutions;[5]
vii. Ni alloy 800 in NaOH solutions;[5]
viii. stainless steel in NaCl + HCl solutions;[6]
ix. yellow brass in Na_2SO_4 + Na_2S solutions.[7]

Besides that the ratio between the current density on the bare metal (i_b) and the current density on the filmed metal (i_s) was found to be very convenient parameter for the evaluation of crack morphology. When i_b/i_s is higher than 10, sharp cracks are found, while when this ratio is lower than 10, only shallow trenches or general dissolution are found.

The theoretical bases for this technique, as well as the present chances of having a credible theory for SCC are discussed.

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Repassivation Rates and Stress Corrosion Crack Propagation

J. C. Scully
The University of Leeds, Leeds, England

Abstract not submitted.

In-Reactor Potential Measurements; Application to Stress Corrosion Behavior

M. E. Indig
General Electric Co., Pleasanton, California

In order to understand and provide predictive capability concerning the corrosion behavior of materials in a boiling water reactor (BWR), it would be desirable to perform *in-situ* electrochemical experiments. However, the environment of a BWR, pure water at 290 C and 1050 psi, results in difficulties in measuring and understanding electrochemical phenomena. For example, Indig and Groot[1] in an environment of pH 10 LiOH at 290 C found that most of the electrochemical reaction that occurred near the corrosion potential was a result of charge transfer reactions involving dissolved hydrogen rather than the corrosion reactions. In this case, the electrical resistance of the electrolyte was not a major limitation. Later in reactor studies, Cowan and Kaznoff[2] found similar behavior where oxygen was the principal gas dissolved in high temperature water. Because of these kinetic responses, evaluation of the corrosion behavior by the linear polarization technique or extrapolation of the cathodic Tafel curve is not possible in high temperature aqueous systems. Further electrochemical difficulties occur during the application of either anodic or cathodic potentials to electrodes in high purity water. The resulting current causes significant chemical changes in the local electrode electrolyte environment which is confounded by the inability to account for the large IR drop.

Perhaps the simplest electrochemical measurements that can be obtained in an operating BWR is the corrosion potential of samples of the reactor structurals and other metal electrodes. The first major *in-situ* measurements of corrosion potential (Type 304 stainless and platinum) were conducted in 1975 at the Dresden-2 BWR. These measurements were part of the studies conducted to understand the contributing factors to a series of pipe cracks that occurred in a 4 inch (10.16 cm) by-pass line in boiling water reactors. The experience gained in the Dresden-2 studies was used to guide subsequent experiments at the Vermont Yankee Boiling Water Reactor. In both of these studies, high temperature Ag/AgCl/Cl^- electrodes were developed so that the corrosion potentials could be related to the standard hydrogen electrode scale and that stress corrosion experiments could be conducted in the laboratory at potentials measured in the reactor. Where possible, simultaneous measurements of the chemical species dissolved in the high temperature water were obtained. The chemical analyses combined with controlled laboratory experiments were used to determine the contribution of the various chemical species to the corrosion potential. For example, at low temperatures, $<$150 C, during the reactor startup, it was found that hydrogen peroxide was a major contributor to the corrosion potential. The H_2O_2 generally caused an increase of $>$0.2 V, above the potential caused by dissolved oxygen. At operating reactor temperature, the potential appeared to be determined mainly by the dissolved oxygen concentration. There were no significant effects from unknown radiolytic species in the piping system tested. One of the major findings of the Dresden-2 studies was that the electrochemical environment of the by-pass line, where stagnation had been postulated, was not different than

that in piping lines where fast flow occurred. Thus, the local by-pass water environment was not the reason for by-pass line cracks. In both of the reactor systems (Vermont Yankee and Dresden-2), the reference electrode/metal electrode potential measurements responded rapidly to system chemical transients, especially pH shifts, and were invaluable in setting electrochemical limits for conducting laboratory experiments from simulated cold-standby to-full power reactor operation conditions.

References

1. M. E. Indig and C. Groot. Corrosion, Vol. 25, p. 455 (1969).
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SESSION 3
Advances in Techniques for Corroding Surface Characterization
A. Spectroscopic

9:00 – 11:00 am, Tuesday, March 4

Chairman: J. B. Lumsden, Rockwell International, Thousand Oaks, California.

XPS and Its Application to Corrosion Research

C. R. Clayton
State University of New York at Stony Brook
Long Island, New York

It has been demonstrated in recent years that X-ray photoelectron spectroscopy has considerable potential as a surface tool to characterize the composition, both qualitatively and quantitatively, of corrosion product layers. A review will be given of the theory and technique of XPS highlighting those details which are most relevant to corrosion research.

Examples of work carried out using XPS will be given based on studies of passive and prepassive films formed on stainless steel under different environmental conditions. This work will include nondestructive variable angle XPS analysis of ultra-thin passive films and ion etch depth studies of thicker oxide layers.

Characterization of Corroding Surfaces by Infrared and Raman Spectroscopy

P. Fabis, J. Keiser, C. Brown, and R. Heidersbach
Department of Ocean Engineering, University of Rhode Island
Kingston, Rhode Island

The complementary techniques of infrared and Raman spectroscopy can be used to obtain structural information about passive films which form on metal surfaces in corrosive media. This information is often unobtainable by any other techniques. The Raman technique has the additional advantage of being applicable to *in situ* examination of metal surfaces as they react in aqueous environments.

This presentation will discuss instrumentation for use in studying corrosion phenomena in both aqueous and gaseous environments. Special chopper circuits necessary for *in situ* elevated temperature gaseous exposures are discussed as well as signal averaging techniques, which, when computer interfaced, allow iterative examination of thinner films than had been possible with previous instrumentation.

The results of a completed study of the anion effects on passive films formed on pure lead in aqueous environments are presented along with current research into gaseous and aqueous exposures of iron-chromium alloys.

Nature of Passive Oxide Films on Nickel Determined by Electrochemical and Spectroscopic Techniques

B. R. MacDougall
National Research Council, Ottawa, Ontario, Canada

The nature of the passive oxide film on nickel has been examined by electrochemical techniques in conjunction with high energy electron diffraction, X-ray emission, and Auger spectroscopies. The influence of time and potential of anodization on the thickness, structure, and breakdown susceptibility of the oxide in both the passive and transpassive regions will be discussed. Conversion of the oxide from a thin, compact film to a thick, porous overgrowth has been observed in neutral borate solution and the kinetics of oxide growth is studied. The relationship between the structure and composition of the oxide and its stability towards Cl^- pitting will be examined. It will be shown that the additional data provided by the electron-optical techniques is often essential for a correct interpretation of the electrochemical measurements.

Auger Electron Spectroscopy Studies of Passive Films and Intergranular Corrosion

J. B. Lumsden
Rockwell International Science Center
Thousand Oaks, California

A number of extremely surface sensitive techniques are now available for studying films on the surface of metals as well as the composition of grain boundaries. This presentation will focus on one of these, Auger electron spectroscopy. After a brief discussion of the principles of the technique, pointing out its advantages and limitations, results will be presented in which Auger spectroscopy has been utilized to study corrosion and corrosion related phenomena. For example, applications will be presented in which this technique has been used to obtain an improved understanding of the effects of alloy additions on passive film stability on iron and stainless steel. This will include studies of pitting mechanisms and the effects of inorganic inhibitors. Other investigations which will be presented and discussed will be those in which Auger spectroscopy has been utilized to obtain grain boundary compositions. These analyses have provided mechanistic information concerning intergranular corrosion, stress corrosion cracking, and hydrogen embrittlement.

Applications of Analytical Electron Microscopy to Corrosion Research

Charles E. Lyman
Materials Engineering Department
Rensselaer Polytechnic Institute, Troy, New York

Microanalysis of thin specimens in the scanning transmission electron microscope (STEM) is an emerging technique capable of performing chemical analysis with a lateral spatial resolution in the range 30-50 nm. Initial investigations used energy dispersive X ray spectroscopy as the primary analysis method. This technique

currently allows detection of elements from Na to U. One of the major results from early work on stainless steels was the direct measurement of the chromium depletion profile in sensitized steels. Several studies of the microchemistry across phase boundaries and grain boundaries have been influential in determining structure-property relationships in metals and ceramics. Electron energy loss spectroscopy can be adapted to STEM instruments easily and affords a method for analyzing light elements, Li and heavier. Although the specimen must be very thin (<500 nm), this technique does allow the identification of oxides, nitrides, and carbides. Microdiffraction from very small regions (<10-20 nm) completes identification of precipitates as well as giving the crystallographic orientation of individual grains and second phases. X-ray spectroscopy, electron energy loss spectroscopy, and microdiffraction techniques together make analytical electron microscopy a powerful tool for corrosion research.

The presentation will discuss the capabilities and limitations of these techniques as well as give examples of studies related to corrosion research.

SESSION 4
Advances in Techniques for Corroding Surface Characterization
B. Electrochemical

1:00 – 5:30 pm, Tuesday, March 4

Chairman: F. Mansfeld, Rockwell International, Thousand Oaks, California.

An Electrochemical Method to the Quantitative Determination of the Reactivity of Grain Boundaries

L. Beaunier, M. Froment, and C. Vignaud
Groupe de Recherche n°4 "Physique des Liquides et Electrochimie" du C.N.R.S. associe a l'Universite Pierre et Marie Curie, Paris, France

Classical tests of intergranular corrosion (Huey, Strauss...) are specially useful when precipitations like carbides in stainless steels involve a variation of the composition near the grain boundaries. In the case of an homogeneous phase, an electrochemical method is proposed which allows obtaining a well controlled general corrosion and a reproducible intergranular attack. For iron, nickel, chromium alloys, this method is based on a potentiostatic attack (H_2SO_4 2N, 25 C) in the transpassive domain. The determination by scanning electron microscopy of the geometrical feature of the grooves (α, opening angle, H depth) leads to establish a model for the selective dissolution of the grain boundaries. From this model, it is possible to deduce the value of a parameter α_0 which characterizes the intergranular corrosion susceptibility of a given alloy. Furthermore, the preferential attack of a grain boundary is interpreted on the basis of the electrochemical kinetics. This allows one to calculate the density of active sites at the emergence of the grain boundary and on the surface of the grains.

This electrochemical method of attack allows studying the effect of segregation phenomena on the intergranular corrosion. Examples will be given in the case of nickel (segregation effects of sulfur and silicon), and iron, nickel chromium alloys (reactivity of the α,γ grain boundaries and α/γ boundaries).

Recent Advances in Impedance Techniques in Corrosion Science

D. D. Macdonald
Department of Metallurgical Engineering
The Ohio State University, Columbus, Ohio

The electrochemical corrosion of metals and alloys in ionically conducting media (solutions, fused salts, etc.) occurs via the passage of charge across the interface. The driving force for this process is an electrical potential difference that is established by the anodic and cathodic partial processes. Accordingly, the electrical and hence electrochemical properties of the system may be described generally in terms of a complex impedance function Z ($j\omega$), where ω is the frequency and $j = \sqrt{-1}$. Only at $\omega = 0$ is the impedance of the interface equal to the polarization resistance, and hence can the corrosion rate be calculated using the Stern-Geary relationship. Because the impedance functions for many corroding systems are characterized by very long relaxation times, it is necessary to use low frequency methods for the measurement of the polarization resistance in order to ensure that the measured "resistance" is unreactive.

Methods for measuring the interfacial impedance of a corroding interface, and its frequency dispersion, will be reviewed. The discussion will include an analysis of both frequency domain and time domain methods, and the advantages and disadvantages of each technique will be presented. Mechanistic information that can be drawn from the frequency dispersion of the complex impedance will be discussed. Where appropriate, the techniques will be illustrated by reference to measurements that have been made on specific corroding systems.

Determination of Surface Inhomogeneities Using a Scanning Probe Impedance Technique

H. S. Isaacs and M. W. Kendig
Brookhaven National Laboratories, Upton, New York

A scanning AC probe technique has been developed to measure the impedance variation of electrode surfaces in electrolytes resulting from heterogeneities. The technique can be applied to all conducting surfaces in conducting liquids. Measurements have been conducted on abraded specimens, partly etched Alloy 600, mixed alloy surfaces, Type 304 stainless steel weld and corroding polymer coated zinc painted surfaces. With all specimens marked variations in impedance were observed.

Electrochemical Noise Measurements in Corrosion Research

Ugo Bertocci
Chemical Stability and Corrosion Division
National Bureau of Standards, Washington, DC

The detection and analysis of wideband noise in the current of an electrode under potentiostatic conditions can give useful information of two different types. If the current fluctuations are the deterministic response of the system to the input noise generated by the potentiostat, the data can be used to obtain the electrode impedance as a function of frequency, giving information concerning the nature and rate of the electrochemical reactions occurring on the corroding electrode. If the current noise, however, is due to stochastic processes occurring at the electrode, it can be employed for detecting the onset of localized corrosion and to study the processes of breakdown and formation of protective films. Examples of these measurements are presented, and some of the problems involved in the experimental analysis of the noise signals are discussed.

Electrical Methods for Appraising Corrosion in Organic Coating/Metal Substrate Systems

John Standish and Henry Leidheiser, Jr.
Lehigh University, Bethlehem, Pennsylvania

The objectives of this study were to determine (a) the nature and exact location of defects and (b) the presence of bulk-phase water beneath polymeric, protective coatings on metals. Such information is useful in a better understanding of the mechanism of loss in corrosion protective character of coating systems.

Alternating current (AC) electrical measurements were used to investigate the properties of polymer coated metals before and during exposure to electrolytes. The coating was the dielectric in a parallel plate capacitor, with the metal substrate serving as one plate and a counter electrode serving as the other plate. An alternating voltage (<1 V RMS) was applied across the coating and the in- and out-of-phase components of the resulting current were determined with a lock-in amplifier. Electrical properties were measured as a function of time of exposure, concentration and type of electrolyte and temperature. The effects of exposure of a coating to an electrolyte were not completely reversible. Coatings having defects showed a characteristic frequency-dependent behavior. Measurements made as a function of temperature identified the presence of small amounts of water placed at the polymer/metal interface. Measurements made with a shielded counter electrode enabled an analysis of the electric properties on a highly localized scale. The electrical properties of different areas of a coating did not change uniformly during exposure to an electrolyte.

Interfacial and Diffusion Effects on Corrosion of Copper and Iron in Oxygenated Acid Solutions as Measured by the Digital Faradaic Impedance Technique

W. H. Smyrl, Sandia Lab., Albuquerque, New Mexico

The digital Faradaic impedance measurement (DFIM) technique is extremely fast and accurate for determining parameters which control corrosion processes. The measurements may be made under steady state conditions, and results are similar to those obtained by other techniques. The most important application promises to be in characterizing corrosion reactions under transient conditions. Results obtained for copper and iron will be discussed.

SESSION 5
Corrosion Processes in Wear

9:00 – 11:00 am, Wednesday, March 5

Chairman: H. Stott, University of Manchester, Manchester, England.

Detection of Corrosive Wear by Electrochemical Measurements

J. A. Richardson, F. H. Stott, and J. E. Breakell
ICI Agricultural Div., Billingham, Teeside, England

Electrochemical techniques have been used to investigate corrosive wear of cast iron during reciprocating sliding in various sulfuric acid environments. Corrosion potential/time data obtained in the absence external polarization and current/time data obtained under potentiostatic control have been monitored continuously during sliding and used as diagnostic tools, providing a guide to the influence of corrosion on wear. Observations show that there are direct correlations between the measured changes in these electrochemical parameters and the types of wear damage sustained by the specimens. During sliding in 60% sulfuric acid, there is a decrease in corrosion potential, probably due to the continued removal of the protective hydrated ferrous sulfate film. In 20% sulfuric acid, there is very little effect of sliding on the corrosion potential. An observed progressive shift in potential in the noble direction is attributed to the presence of exposed graphite on the contacting surfaces following graphitic corrosion of the cast iron in this aggressive environment. Sliding has been carried out in 60% sulfuric acid under potentiostatic conditions at potentials covering the range from complete cathodic protection to anodic protection of the cast iron. Wear of the surfaces and measured currents are strongly dependent on the applied potentials. Some of the advantages and disadvantages of electrochemical measurements in investigating corrosive wear are evaluated.

Electrokinetic Wear Phenomena

T. R. Beck
Electrochemical Technology Corp., Seattle, Washington

About ten years ago, a new wear phenomenon was reported to occur in the hydraulic control valves of commercial jet airplanes. Flow of phosphate ester hydraulic fluids through steel valves caused the generation of electrokinetic streaming currents. These currents are generated at the metering edges of the valves and cause corrosion which gradually increases leakage, requiring valve replacement. Numerous approaches have been investigated to eliminate erosion including changing the valve material, the valve geometry and the fluid composition. The most successful solution to the problem to date has been the addition of certain ionizable compounds to the fluids at a concentration of a hundred or a few hundred parts per million. Adsorption of such ionic species on the steel metering edges of the valves changes the electrical double layer structure and decreases the zeta potential, resulting in smaller streaming current generation. Certain organic additives can also be oxidized in preference to corrosion of the steel. The streaming-current corrosion phenomenon may occur in other situations such as in cavitation, in ball bearings, and on gear teeth.

Electrochemical Aspects of Wear in Slurry Pipelines

J. Postlethwaite
University of Saskatchewan, Saskatoon, Canada

Electrochemical techniques have been applied to the study of erosion-corrosion in pilot plant slurry pipelines to determine the effects of the presence of the suspended solids on: the corrosion rate; the anodic and cathodic reactions; the relative magnitude of the chemical and mechanical aspects of the total wear; and the efficiency of inhibitors normally and to control the corrosion of iron in near neutral aqueous solutions. Results are presented for coal, iron ore and sand slurries at commercial concentrations and velocities.

Fretting Wear of an Austenitic Stainless Steel in CO_2 at Temperatures up to 650 C

D. E. Taylor, R. B. Waterhouse, F. B. Hardisty, and A. Y. Nehru
The Wolfson Institute of Interfacial Technology,
University of Nottingham, England

The paper discusses results from a series of tests, the purpose of which was to assess the effects of a range of experimental variables on the nature and degree of damage produced on fretting a Type 321 stainless steel. Normally loaded annular contact surfaces were torsionally fretted at small amplitude in an environment of dry CO_2 at selected temperatures up to 650 C. Optical, electron-optical, surface profiling and metallographic techniques provided a means of qualitatively assessing the characteristic features of the resultant damage.

Of the experimental variables investigated, amplitude of slip between the surfaces, frequency, test duration, and normal pressure were all shown to influence to a greater or lesser extent the magnitude of surface damage in terms of area coverage. At the highest test temperature (650 C), the type of damage differed significantly from that observed at the lower temperatures which was characterized by a considerable degree of surface plucking. By contrast, the damage at 650 C took the form of a general smearing of material across the surface.

An Evaluation of the Oxidational Parameters of Wear

T. F. J. Quinn, J. L. Sullivan, and D. M. Rowson
The University of Aston in Birmingham, Birmingham, England

This paper shows that the discrepancies between theory and experiment, revealed by previous papers in which the oxidational theory of sliding wear had been applied to steels, are mainly due to the assumption that the oxidational constants obtained from conventional *static* oxidation experiments can be applied to the very different environment which exists at the real areas of contact between sliding surfaces. It is further shown that, although this assumption *may* be valid for the *Activation Energy* for parabolic oxidation (Q_p), it is certainly not true for the accompanying *Arrhenius Constant* (A_p). The paper then describes how friction, wear, and division of heat measurements can be used, in conjunction with the oxidational wear theory, to obtain the best possible values of A_p and Q_p, *i.e.*, values which give *consistent* estimates of the number of contacting asperities (N) at any given moment, the thickness of the oxide film (ξ) formed at these N real areas of contact, and the temperature (T_o) at which the oxide film is formed during a contact. These best possible values of A_p and Q_p are shown to be applicable to a range of similar low alloy steels, thereby indicating that this approach may be used for predicting wear rates relevant to whole ranges of materials with similar oxidation characteristics (as indicated by conventional static oxidation tests).

SESSION 6
General

1:00 – 5:30 pm, Wednesday, March 5

Chairman: R. M. Latanision, Massachusetts Institute of Technology, Cambridge, Massachusetts.

The Nature of Anodic Films on Nickel and Single Phase Nickel-Molybdenum Alloys

V. Mitrovic-Scepanovic and M. Brian Ives
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It is well known that molybdenum improves the resistance to corrosion of stainless steels in acid, neutral and chloride containing media. However, it has not been unambiguously proven whether alloyed molybdenum could make the passive film more stable with or without its incorporation into the passive film. There have been only few reports concerning the passivity of Ni-Mo alloys.

In the present study, electrochemical techniques combined with Auger electron spectroscopy (AES) and dissolution analysis by means of atomic absorption spectroscopy are applied on a single phase Ni-Mo alloy in an attempt to understand the effect of molybdenum on the nature of passive film on nickel in deaerated 0.15N Na_2SO_4 solution (pH 3).

Anodic polarization measurements performed on a series of single phase Ni-Mo alloys (1-15% wt Mo) suggest a negative effect of molybdenum on the corrosion resistance of nickel, by the monotonic increase of passive current density with molybdenum content, at least for alloys with molybdenum content greater than 5% Mo. However, open circuit potential decay and surface reactivity measurements reveal a more stable surface coverage on these alloys than that on pure nickel passivated under the same conditions. Some ESCA evidence confirms the presence of molybdenum in the passive film to be in two valence states (Mo^{4+} and Mo^{6+}). The question that still remains open, and is the main objective of the research in progress, is to understand the structure of the passive film, since there are at least two possibilities:

1. Molybdenum exists in the passive film as a result of anodic oxidation process. There it can form a mixed oxide phase with nickel or exist as a separate oxide phase owing to a much greater thermodynamic stability of molybdenum oxides than that of nickel oxide.

2. Molybdenum is incorporated in the film after being trapped from the solution in the defective nickel oxide due to the fact that molybdenum is active throughout the passive potential region of pure nickel.

The composition-depth profile of anodic oxide films on Ni-10Mo (wt%) formed at various potentials obtained by means of AES and sputter etching will be discussed and compared with data from electrochemical and dissolution rate measurements.

Hydrogen Permeation and Embrittlement in Nickel and Nickel Base Alloys

M. Kurkela and R. M. Latanision
Massachusetts Institute of Technology, Cambridge, Massachusetts

Recent work by Latanision and Opperhauser has shown an association between grain boundary segregation of metalloids like Sn, Sb, P, and S (hydrogen recombination poisons) and susceptibility to hydrogen embrittlement in pure nickel.

In this work, hydrogen permeation was studied using the Devanathan technique. The materials employed in this study were Marz grade nickel, Ni 270, Ni 200, TD nickel, and Inconel 600. Permeation measurements on specimens undergoing plastic deformation showed that hydrogen is transported by mobile dislocations at rates much faster than lattice diffusion. The effects of strain rate, charging conditions, and metallurgical structure on dislocation transport of hydrogen are discussed, and the observed transport rates compared with theoretical predictions. Hydrogen permeation in unstrained specimens was studied as a function of grain size, heat

treatment (annealed and annealed + heat treated conditions), grain boundary segregation (examined by Auger electron spectroscopy), and impurity content. The effect of poisons added to the charging solution were also investigated. Preliminary results show that hydrogen absorption is increased both by poisons added to charging solution and by "built-in" poisons segregated to grain boundaries. These experiments are discussed in detail and relationships between embrittlement susceptibility, permeation behavior, and metallurgical structure are examined.

Corrosion Modeling by Finite Element Method

John W. Fu
Westinghouse Research and Development Center
Pittsburgh, Pennsylvania

Quantitative analysis of the interactive current between cathodes and anodes, which is known to be the cause for many corrosion problems, has not been possible in the past due to the lack of analytical tools. Recently, as the method of finite element analysis is becoming widely known, it is realized that this cathode/anode interaction is essentially a numerical way of solving the Laplace equation which is the governing equation for the potential distribution in corrosion cells and derived from the fundamental requirement of the electroneutrality law. In the finite element analysis, the geometric shape of the corrosive medium is modeled by a finite element mesh and the polarization behaviors of the metals involved are assigned as the boundary conditions to appropriate faces of the element. The result of the finite element analysis gives the potential distribution in the corrosive environment, including the metal/environment interface, which can then be used to calculate the current density on metal surfaces according to the conductivity equation. Potential applications of this method are the cathodic protection system design and the determination of potential distribution in areas where experimental measurements are difficult to perform.

Breakdown of Oxide Films on Steel Exposed to Chloride Solutions

H. E. Townsend, H. J. Cleary, and L. Allegra
Bethlehem Steel Corp., Bethlehem, Pennsylvania

Breakdown of a thin air-formed surface oxide film is the first step in corrosion of steel upon immersion in aqueous chloride solution. By means of visual observation, weight loss, and corrosion potential measurements, we studied oxide film breakdown on steel as a function of chloride and hydrogen peroxide concentration. We also studied the breakdown in air saturated chloride solution of other types of oxide films including: (1) naturally formed oxides on aluminum, stainless steel, and titanium alloys, and (2) oxides of aluminum, chromium, and titanium that were applied to steel substrates by means of RF sputtering. The results are considered in terms of the mechanism of, and critical factors required to avoid, breakdown of thin surface oxides.

A Laboratory Test on Corrosion f Steel in Concrete

Satoshi Ito and Edward Escalante
National Bureau of Standards, Washington, DC

The corrosion of steel in concrete structures such as highway bridge decks where deicing salts are used, continues to be a problem. Because corrosion is usually evident only after considerable damage has occurred, a monitoring system of the corrosion rate of steel rebar in concrete is needed.

In order to develop a measurement method of the corrosion rate of steel in concrete, two experiments were carried out. First, simulated corrosion tests were done in a solution of $Ca(OH)_2$/NaCl, a sand mixture containing $Ca(OH)_2$/NaCl. The mechanism for the onset of the corrosion of steel in concrete were determined. Corrosion was initiated by a drying process which enabled Cl^- ion to be locally concentrated more than 0.2 mol/l, and more than 2 ppm oxygen. Second, corroding mortar covered steel electrodes were prepared, utilizing the corrosion initiating technique as mentioned above. Current and potential step signals were applied to corroding mortar covered steel electrodes and noncorroding ones. From an analysis of the transient response curves in both electrodes, the corrosion current was determined, evaluated, and found to have good agreement with the actual weight loss.