PMTM/A-22

COMISION NACIONAL DE ENERGIA ATOMICA
PRESIDENCIA DE LA NACION

PROYECTO MULTINACIONAL DE TECNOLOGIA DE MATERIALES
(Programa Regional de Desarrollo Científico y Tecnológico - OEA)

INCLUSIONES NO METALICAS

Dr. F. B. Pickering

REIMPRESION DE LA PUBLICACION PMM/A-257 (1978)

Buenos Aires - Argentina
1978

LECTURE 1

SOME OBSERVATIONS ON THE KINETICS OF DEOXIDATION OF STEEL

Introduction

The subject of the kinetics of deoxidation of liquid steel is a major study; consequently this paper will survey the subject briefly and then discuss in more detail those areas which appear to be most worthy of further experimental and theoretical study. Reactions resulting in the formation of gaseous deoxidation products will not be considered.

The "kinetics" of deoxidation could be said to be concerned with the removal of oxygen from liquid steel, the formation of deoxidation products and the behaviour of those products in the liquid steel once they have formed. Thus, the topics to be covered will be:

A) Nucleation of deoxidation products

B) Growth of deoxidation products

C) Floatation and associated phenomena such as:-

(i) Floatation in quiescent baths;

(ii) Effects of convection in the steel bath;

(iii) Collision of inclusions and capture by vessel walls and bath surface.

Most attention will be paid to the floatation of inclusions.

We may write a generalised equation for deoxidation using the deoxidant M:-

$$x[M] + y[O] = (M_xO_y) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The molar free energy change accompanying the formation of the deoxidation product M_xO_y would be given by:-

$$\Delta G = \Delta G^{\theta} + RT\ln \frac{a_{(M_xO_y)}}{a^x_{[M]} \cdot a^y_{[O]}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ΔG^{θ} is the molar standard free energy change accompanying the reaction, and the equilibrium constant, K, for the reaction is given by

$$K = \frac{a'_{(M_xO_y)}}{a'^x_{[M]} \cdot a'^y_{[O]}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$a_{(M_xO_y)}$ is the activity of the deoxidation product in whatever phase (inclusion or slag) it is produced, and $a_{[M]}$ and $a_{[O]}$ are the activities of the deoxidant and oxygen respectively in solution in the liquid steel. Primed symbols indicate equilibrium activities.

Nucleation of Inclusions

Application of homogeneous nucleation theory to the reaction given in equation (1) leads to the establishment of the following relationships[1], assuming that spherical nuclei are formed:-

$$\text{Rate of nucleation, } I = A \exp\left(-\frac{\Delta G^*_N}{kT}\right) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\text{Activation free energy for nucleation, } \Delta G^*_N = \frac{16\pi\sigma^3_{im}}{3(\Delta G_v)^2} \quad . \quad . \quad (5)$$

$$\text{Critical nucleus radius, } r_c = -\frac{2\sigma_{im}}{\Delta G_v} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where A is the 'frequency factor', estimated by Turpin and Elliott[1] for deoxidation reactions, k is Boltzmann's constant, T the absolute temperature, σ_{im} the interfacial energy between the inclusion deoxidation product and the liquid metal, and ΔG_v the free energy per unit volume accompanying the reaction in equation (1), which can be calculated from equation (2).

Using the above relationships, the amount of 'supersaturation' necessary before inclusions will nucleate homogeneously can be calculated [1], [6]. Sigworth and Elliott[2] used the cell:-

Pt, Air|ZrO_2:CaO| O in Fe(Si)|Ag|W

to add oxygen electrolytically to iron-silicon melts containing up to 1% Si. They followed the change in oxygen potential as the oxygen reacted with the silicon, and related the supersaturation necessary to produce homogeneous nucleation to the concentration polarisation of the cell. From these experiments they estimated that the "supersaturation ratio":-

$$\frac{a_{[Si]} \cdot a_{[O]}^2}{a'_{[Si]} \cdot a'_{[O]}^2} \quad ,$$

was of the order of 80 when homogeneous nucleation occurred. This indicates that $a_{[O]}/a'_{[O]} = 9$, if it is assumed that $a_{[Si]}$ remains constant. Alumina, with a higher value of σ_{im} than SiO_2 is more difficult to nucleate homogeneously. Supersaturation ratios of the order of 3×10^6 have been estimated

for the relationship:-

$$\frac{a_{[Al]}^2 \; a_{[O]}^3}{a'^2_{[Al]} \; a'^3_{[O]}}$$

giving $a_{[O]}/a'_{[O]}$ of about 145 for aluminium deoxidation. Further estimates of these ratios are given by Pomey and Trentini[3] and Grethen and Philippe[4].

Supersaturation is caused by locally high deoxidant concentrations near dissolving deoxidant particles, by solute rejection during solidification and by atmospheric oxidation during tapping and teeming. In this connection, it is interesting to speculate on the influence of the size of deoxidant particles on the localised supersaturation, and consequently on the rate of homogeneous nucleation and on the size of the nucleated inclusions. It is perhaps of interest to try to calculate the rate of solution and mixing of different-sized deoxidant particles, to examine whether the size of the deoxidant particles is likely to have a significant effect on nucleation.

Heterogeneous nucleation is a fascinating source of speculation, but data on interfacial energies in relevant systems are very sparse. The possibility of homogeneous nucleation of oxides with low values of σ_{im}, followed by heterogeneous growth of other less-easily nucleated oxides on the substrates thus provided, is interesting. Straube, Kühnelt and Plöckinger[5] reported changes of composition of inclusions with time as iron-manganese melts were deoxidised with aluminium. Very small inclusions of FeO, containing some MnO and Al_2O_3, were observed within 1 second of the aluminium addition. These quickly changed to larger inclusions of a uniform composition containing about 50% Al_2O_3. Later, inclusions comprising a core containing Al_2O_3, FeO and MnO, with a pure alumina outer layer were observed. It may be possible that this phenomenon might be caused by the difficulty of homogeneous nucleation of Al_2O_3, which grows heterogeneously on the substrate provided by the other less stable mixed oxides.

Growth of Inclusions

Turkdogan[6] assumed a transport-controlled model for the growth of stationary spherical inclusions, and predicted the rate of growth, and hence the rate of oxygen removal, by fixed numbers of nuclei. He suggested that there may be an optimum nucleation rate. Large numbers of small nuclei might never leave the melt, whereas small numbers of large nuclei would float out too rapidly, leaving dissolved oxygen in the melt, and hence operating inefficiently, Fig. 1.

Because of the dominating influence of floatation rates, and associated phenomena, on the efficiency of deoxidation, the pursuit of more accurate models than that suggested by Turkdogan is probably unprofitable. Growth by collision, agglomeration and coalescence must therefore be considered.

Floatation and associated phenomena

This is probably the most important area for investigation. Much has been written about it, but few definitive investigations have been made. Although the formation of deoxidation products may be completed rapidly and efficiently, the effectiveness of the deoxidation process will depend on the extent of the removal of the deoxidation products from the melt before the steel solidifies.

(i) Floatation in quiescent baths

Motion of solid spheres in a fluid, neglecting interaction between spheres and with the walls of the container, and assuming a stagnant unstirred fluid, has been the subject of much experimental and theoretical investigation. A reasonable approximation to true behaviour in laminar flow conditions is given, by the application of Stokes' Law[7], as

$$U_t = \frac{2gr^2(\rho_m - \rho_i)}{9\eta_m} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where U_t is the terminal velocity of the sphere, r is its radius, ρ_m and ρ_i the densities of the liquid steel and inclusion respectively, η_m the viscosity of the liquid steel, and g the acceleration due to gravity.

For typical conditions in the deoxidation of steel, flow would probably be laminar so that behaviour at high Reynolds numbers need not be considered. Inclusions may be non-spherical, and shape and rugosity factors have been proposed to account for changes in shape and surface roughness, but it is doubtful if it is worth worrying about a more sophisticated treatment than for simple spheres. If the inclusions are liquid, small spheres behave like rigid solids, but larger liquid spheres will float out more rapidly than the equivalent solids. However, the maximum possible increase in U_t due to this cause would be by a factor of 1.5[8]. Surfactants, i.e. substances which concentrate at the surface of a phase in a heterogeneous system, are known to reduce the terminal velocities of liquid drops and bubbles in fluid phases[9], but this effect is unlikely to be significant in deoxidation systems. There appears to be no foundation for the speculation that an increase in interfacial energy between the inclusion and the liquid steel can cause a more rapid rate of removal due to a reduction in drag on the inclusion. Speculations of this nature were made when it was found that alumina inclusions were apparently floating out of melts more rapidly than silicate inclusions of a similar size[10].

If liquid inclusions become large, for example, inclusions originating from slag entrapment or refractory erosion, their shape will deviate from the spherical and, if they are large and fluid enough, they will break up into smaller droplets.

A rough calculation based on Stokes' Law for deoxidation systems indicates that inclusions of about 10μm diameter would require about 2½ hours to float out of a quiescent steel bath 5 metres deep. If inclusion removal depended wholly on this floatation phenomenon, deoxidation would be a somewhat unsuccessful process. Further, there are many reported anomalies which indicate that undue attention has been paid to the subject of floatation of inclusions caused by differences in density between inclusions and steel. Recent work in Sweden[11] has

suggested that inclusions formed by rare earth elements such as neodymium, which have a density approximately the same as that of liquid steel, are removed more rapidly than similar alumina inclusions, whose density is just over half that of steel. There are possibly other factors which are important in the rare earth experiments, but one point stands out above all others - the melts were inductively stirred. It is, in fact, difficult to imagine a real deoxidation situation in which the steel is completely quiescent.

(ii) Effects of convection in the steel bath

The steel bath may be stirred by natural or by forced convection. Deoxidant additions may be made while the steel is running out of a furnace into a ladle, the steel may be stirred inductively or by the motion of gas bubbles resulting from the carbon-oxygen reaction or introduced deliberately as an inert purge gas, or natural convection currents can stir the liquid steel during solidification of an ingot. The possible results of this stirring could include:-

(a) increased growth rate of inclusions due to increased rates of mass transfer of the reactants;
(b) changes in the rate and pattern of movement in the melt;
(c) changes in the patterns of collision, coalescence and agglomeration of inclusions;
(d) capture of inclusions by gas bubbles - a similar mechanism to that of mineral "flotation" in mineral dressing processes.

It is unlikely that an increase in growth rate due to improved mass transfer is of any significance, especially if the floatation of inclusions can be neglected compared with the effects of motion caused by convection.

Turkdogan[12], in a review paper in 1972, considered factors affecting the collison of inclusions - and, in doing so, mentioned the relevance of work on aerosols. The number of inclusions in a steel bath following the addition of a deoxidant has been estimated to be of the order of $10^{12}/m^3$, so that the picture of clouds of oxide

particles dispersed in a liquid metal is probably much more useful than the more limited view of single spheres floating freely from a melt. Aerosols are dispersions of liquid or solid particles in a gas phase, and in so far as the dispersed phase is more dense than the medium, the analogy with inclusions is imperfect. Emulsions, in which liquid particles are dispersed in a liquid medium, are perhaps a more accurate analogy, particularly when considering the motion of the dispersed particles in vortices. Bearing this in mind, it may be instructive to examine experimental and theoretical studies carried out on aerosols and emulsions[13], [14], to consider how this may assist in understanding the behaviour of deoxidation systems.

Some idea of the size of inclusion dispersions in relation to other disperse systems can be obtained from Fig. 2.

Inclusions in steel fall clearly in the size range group of coarse dispersions, with emulsions and coarsely dispersed aerosols. Fuchs[13] points out that in this group of aerosols, settling under gravity predominates over Brownian motion, i.e. movement due to molecular motion in the medium. Inclusions are formed partly by chemical precipitation and partly by mechanical entrapment, so that attention can be paid to the two methods of forming aerosols and emulsions, namely "condensation" and "dispersion". The former involves precipitation, either by chemical reaction or a physical process such as the condensation of a liquid from a vapour, and the latter method involves mechanical break-up of the bulk condensed phase into small particles or droplets.

To consider the movement of particles in dispersions in convective conditions, it is clear that the prediction of individual particle motion is impossible, and a statistical approach is necessary. If it is assumed that convective transport of the medium is by "eddy diffusion", then the motion of the dispersed particles will be a combination of this eddy diffusion of the medium, of the net motion of the medium, and of the motion of the

particle relative to the medium. There may be intense convection, in which the mean velocity of convection currents is much greater than that of the particles relative to the medium, which may be ignored.

Thus, equations could be postulated to express the "concentration" of dispersed particles as a function of time and distance:

$$\frac{dc}{dt} = D_e \frac{dc}{dx} - u_x c, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where D_e is the "eddy diffusivity", u_x the velocity of the medium in the x direction and c the "concentration" of dispersed particles at time t.

Again, in a well-stirred bath, the particle concentration will remain practically constant throughout the vessel, except in a thin layer close to the walls. Transfer to the walls takes place through this layer by means of a process analogous to molecular diffusion. In considering this transfer to the "walls" of the vessel, no distinction is made for the moment between the walls of the vessel, its bottom or the upper surface of the steel bath. The analogy with convectional mass transfer could then be used:-

$$\frac{dn}{dt} = k_i \, Ac, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where n is the number of particles impinging on the wall surface of area A in time t, k_i is the "impingement coefficient" and c the concentration of dispersed particles in the steel bath. In a system having a distribution of particle sizes, c and n would in fact have some form such as $\int_o^r n(r).dr$, where n(r)dr is the number of particles having radii between r and (r + dr). The use of models such as the film and penetration theories for convectional mass transfer at a boundary to quantify rates of impingement on the wall, may then be foreseen.

This approach might be worth developing, especially for use with model systems, provided some method of determining the rate of impingement of particles on the walls of the vessel could be devised. Stirring of aerosols is known to increase the rate of deposition on the chamber

walls, and the rate increases as the particle size increases. Apparently, the ratio of the number of particles depositing on the vertical walls to the number depositing on the bottom of the chamber increases as the size of the particle decreases[13]. A recent report[15] of radioactive tracer studies, using ^{97}Zr as a tracer during aluminium deoxidation of steel, claims that in the deoxidation of steel in an inductively-stirred melt, more inclusions were deposited on the crucible walls than in the slag at the surface of the melt. The intensity of deposition bears a strong relationship to the stirring patterns produced by the induction stirrer. Sandberg et al[16] have shown that the rate of inclusion removal is increased exponentially as a function of the energy input to an inductively-stirred bath.

In this analogy with aerosols and emulsions, three factors have been ignored:-

(a) collision and coalescence (or agglomeration) of the inclusions;
(b) effectiveness of capture of the inclusions by the walls once impingement has taken place;
(c) the electrical charge which exists on the surface of dispersed particles.

(iii) Collision of inclusions in the melt

The possibility of collision of inclusions, and their consequent coalescence or agglomeration, should be considered if the rate of floatation under gravity or the influence of particle size on capture by the walls are considered relevant to the rate of inclusion removal. Turkdogan[12] paid some attention to this, but there is considerable doubt about the collision behaviour of particles in dispersed systems. Presumably, in quiescent systems, collision only occurs significantly between differently-sized particles, because Brownian motion has relatively little effect on coarsely-dispersed particle motion compared with gravitational floatation. With differently-sized particles, the active collision area is not simply the projected geometrical area of the moving particle because the smaller particle may follow the flow of the medium around the larger particle.

This seems to indicate that collision between inclusions moving in quiescent liquid steel under gravitational floatation conditions is extremely unlikely.

Levich[17] considers the coagulation of dispersions in liquids and gases, and points out that if a velocity gradient exists in the medium, particles of finite radii can collide. Velocity gradients exist close to the wall of a vessel containing a stirred melt, and locally where turbulent motion occurs in the medium. In turbulent flow conditions, the frequency of collisions is likely to increase substantially in comparison with a similar situation in laminar flow conditions. The size of the inclusions is likely to be small compared with the scale of the eddies in the turbulent flow of liquid steel, and it is assumed that all the particles are contained in turbulent eddies. The mechanism of contact of particles is on a scale smaller than that of the eddies. In the case of aerosol particles, where there is a large difference in density between particle and medium, and where the particle is more dense than the medium, the particles will not be contained fully within the eddies so that the number of collisions between particles is further increased. In inclusion-steel systems, this will not be true, and the inclusions can be considered to migrate within eddies through the bulk steel in a random manner. Levich shows that the rate of collision N between particles is then given by a relationship of the form:-

$$N \propto \frac{R^3 . V_m^{\frac{3}{2}}}{\sqrt{\eta_m . L}} . \qquad (10)$$

where R is the radius within which collision will occur if particles approach one another, V_m is the characteristic velocity of the fluid, η_m the fluid viscosity and L is characteristic of the scale of the eddies. R is equal to 2r, if r is the radius of equally-sized particles which do not interact electrically.

(iv) Effectiveness of collision and capture by the walls

When two particles collide, they do not necessarily coalesce, and if an inclusion hits the walls of the

vessel or the slag on the metal surface, it is not necessarily retained by that surface. Kozakevitch and Lucas[18] examined the necessary conditions for the agglomeration of solid inclusions. It was known that although solid alumina (Al_2O_3) inclusions may be very small when formed, they can agglomerate to form large aggregates. Titania (TiO_2), on the other hand, does not seem to form these large aggregates. Kozakevitch suggests that alumina is less easily "wetted" by the liquid steel than titania. Fig. 3 shows the concept of the "contact angle" ϕ in the wetting of the inclusion by the metal in a three-phase contact.

The values of the contact angles in the system iron/gas/oxide at the temperature of liquid steel are about 140° for alumina and 80° for titania. If the liquid metal "wets" the inclusion, it will penetrate between the oxide particles in the agglomerate, forcing them apart.

For liquid inclusions, coalescence would be favoured by low inclusion viscosity and high interfacial energy, σ_{im}, between inclusion and metal. Similar considerations must apply when the inclusion impinges on the walls of the vessel or on the metal surface. Solid inclusions which are strongly "wetted" by the metal will remain below the surface of the melt and will be more likely to be re-entrained by a descending current. These ideas may explain the apparently anomalous behaviour, mentioned earlier, of inclusions formed when neodymium was used as a deoxidant. A further important consideration could be the behaviour of large agglomerates such as alumina clusters in highly turbulent conditions, and their tendency to be transferred to the walls of the vessel. There is evidence that these "agglomerates" in some cases may be very large dendrites, but this does not affect the need to consider their behaviour in the bath and at its surfaces. It would seem that some factor of "effectiveness of capture" would have to be included to make equations (9) and (10) relevant to the measurement of inclusion removal rates. This "effectiveness of capture" factor might then depend

on the physical properties and morphology of the inclusions, and of the surface on which they are impinging.

There is the possibility that an electrical charge may exist on the surface of the inclusions, and the effect this might have on coalescence could be estimated. Kozakevitch[19], in a study of emulsion formation in slag/metal systems, mentions the possibility of an electrical double layer formed at a slag/metal interface - with the cations of the slag arranging themselves along the metal surface, and the slag anions aligning themselves in the double layer in the slag surface. The influence of additions of basic oxides, such as CaO, to acidic oxide inclusions could be to concentrate the cations from the basic oxide at the surface of the inclusions. Sulphide additions to oxides may also modify the structure of the interface. The importance of this effect might be that the electrical characteristics of the inclusion surfaces were altered, but equally, the interaction of the inclusions with the refractory surface of a ladle lining might also be affected, depending on the structure and composition of the refractory surface.

Improved silicon deoxidation in stainless steels as a result of the injection of slag powders of low silica activity has been claimed[20]. The product of silicon deoxidation dissolves at low activity in the injected material, thus lowering the equilibrium oxygen content of the steel, equation (3). The importance of the surface properties of the inclusion in the interpretation of the results of these powder injection experiments should be worth investigating.

(v) Conclusions

The field covered in this review is characterised by many uncertainties, vague assumptions made as a result of a large number of diverse experimental programmes, and a good deal of blind faith. This review does nothing to change this situation, but there seems to be a case for some fairly fundamental experimental work aimed at helping to quantify and classify the indications which have been the result, and will continue to be the result in the

future, of much research work of a more directly applied nature.

The following topics may be suitable for the development of an appropriate research aimed at correcting this situation:-

(a) Factors controlling the motion of dispersed inclusions in stirred baths. For example, convection patterns caused by inductive stirring, gas bubble stirring and different methods of filling ladles and other containing vessels.

(b) The mechanism of deposition of inclusions on vessel walls and on slag-covered metal surfaces.

(c) The morphology and mechanism of growth of inclusions, and of inclusion clusters.

(d) The interfacial characteristics of inclusion/metal systems, with particular attention being paid to the effect of additions of impurities.

(e) The influence of (c) and (d) on (a) and (b).

(f) The relationship of the rate of dissolution of different sizes of deoxidant particles to the effective local supersaturation of the melt, leading to the possibility of homogeneous nucleation of deoxidation products, and the possible effects of convection on this phenomenon.

(vi) References

1. M L Turpin and J F Elliott: JIS I 1966, 204, 217-225.
2. G K Sigworth and J F Elliott: Met Trans 1973, 4, 105-113.
3. G Pomey and B Trentini: p.1 of "Production and application of clean steels", ISI 1972.
4. E Grethen and L Philippe: ibid, p.29.
5. H Straube, G Kuhnelt and E Plockinger: Arch.Eisenhuttenwesen, 1967, July, 509-518.
6. E T Turkdogan: JISI 1966, 204, 914-919.
7. G G Stokes: Cambridge Trans. IX, 1851.
8. J Hadamard: C R Acad.Sci., Paris, 1911, 152, 1735.
9. R M Griffith: Chem.Eng.Sci., 1962, 17, 1057-1070.
10. R Rosegger: Radex-Rundschau No 6, 1958- Iron and Coal Trades Review, 1960, July 15, 131-140.
11. B Kjellberg: Communication in informal seminar at Imperial College, London, April 1973.
12. E T Turkdogan: JISI 1972, 210, 21-36.
13. N A Fuchs: "The mechanics of aerosols", Pergamon, 1964.
14. P Sherman (Editor): "Emulsion science", Academic Press, 1968.
15. N Lindskog: Communication in informal seminar at Imperial College, London, April 1973.
16. H Sandberg, T Engh, J Anderson and R Olsson: Jernkontorets Annaler, 1971, 155, 201-216.
17. V G Levich: "Physicochemical Hydrodynamics", Prentice-Hall, 1962, Chapter V.
18. P Kozakevitch and L D Lucas: Rev. Met. 1968, 65, Sept, 589-598.
19. P Kozakevitch: J Metals, 1969, July, 57-68.
20. T A Engh, H Sandberg, A Hultkvist and L G Norberg: Scand. J. of Met. 1972, 1, 103-114.

LECTURE 2

SOME ASPECTS OF THE FORMATION OF INCLUSIONS DURING DEOXIDATION

INTRODUCTION

Despite the large amount of work reported in the literature on deoxidation[1-4] and inclusion formation[5-9], there is still a need for a basic understanding of many of the reactions which occur during deoxidation. For obvious reasons it is frequently difficult to carry out controlled experiments on commercial casts. A series of controlled laboratory investigations have therefore been made in an attempt to gain a better understanding of the mechanisms of inclusion formation. These have involved:

1. The addition of various deoxidants to pure iron-oxygen melts in order to study the reactions between the added deoxidants and dissolved oxygen, i.e., to study the precipitation of inclusions directly from the melt.
2. The addition of strong deoxidants to iron-oxygen melts containing appropriate initial types of inclusions. This series of investigations was designed to study the way in which reactions occur between less stable oxides and strong deoxidants to form more stable inclusion phases.
3. The heat treatment of inclusions resulting from the investigations already outlined. This was intended to simulate some of the changes in inclusion structure that might occur during the slow solidification of an ingot, and also during possible reheating processes prior to hot working.

EXPERIMENTAL TECHNIQUES

(a) Inclusions formed by deoxidation

The deoxidation experiments were performed at 1600°C in a 51 kg induction furnace having a magnesia lining. The base material used was high purity iron which melted out at about 0.16% oxygen with a very low residual content. An oxygen-rich melt was used so that on adding the deoxidant, a high concentration of inclusions was formed for subsequent examination.

Sampling was performed by drawing off 30-40 gms of the melt into a 6 mm diameter silica tube attached to a rotary vacuum pump. The samples were water quenched to produce a rapid solidification and it was assumed that the inclusions present in the quenched samples were typical of those present in the melt at the time the sample was taken. In order to examine the initial iron-oxygen melts, a suction sample was

taken prior to the addition of deoxidant. After the deoxidant addition, further suction samples were taken over a ten minute period. In studying the reactions between existing inclusions and strong deoxidants, an initial addition was made to form the desired inclusions within the melt. A sample was then taken, followed by the addition of the stronger deoxidant and suction samples were then taken over a ten minute period as before.

An inert furnace atmosphere was not used in these experiments. It was therefore possible to study the effect of atmospheric re-oxidation of the melt on the inclusion composition throughout the sampling period.

(b) Changes in inclusions produced by heating

Specimens were heat treated in a dry argon atmosphere for seven days at 1200^{o}C, and then water-quenched. This allowed the precipitation of phases to occur which was previously prevented by quenching from the liquid state.

Both the as-cast and heat treated specimens were sectioned and prepared for metallographic examination. A representative number of the different types of inclusions were selected to illustrate the types present in each sample and their analyses were determined by electron-probe microanalysis. It should be emphasised that this examination was only aimed at establishing the types and analyses of the inclusions, and not the quantitative assessment of the number or volume fraction of the inclusions.

The deoxidants studied include aluminium, silico-manganese and calcium silicide, as well as more complex proprietory deoxidants such as Hypercal and Calsibar. Two major aspects of the deoxidation processes will be considered in detail. Firstly the composition and morphology of the inclusions resulting from reaction between aluminium and dissolved oxygen will be considered, and secondly the composition and morphology of the inclusions resulting from reaction between silicates and aluminium will be discussed.

THE DEOXIDATION OF IRON-OXYGEN MELTS BY ALUMINIUM

(a) Observations on Inclusion formation

An addition of 0.5% Al was made to the 0.16% O_2 melt,

and suction samples were taken after varying times.

Two seconds after the aluminium addition, spherical, single phased inclusions containing approximately 10% Al_2O_3 were present in the melt, Fig. 1. These oxides also contained up to 10% MnO, which originated from the base melt. This type of inclusion was only observed in the sample taken two seconds after the aluminium addition and appeared to be fully molten at the melt temperature of 1600°C.

In addition to these single-phased particles, duplex inclusions consisting of the spinel, hercynite, within a wüstite matrix were observed at the same time, Fig 2. This type of deoxidation product was again only observed in the sample taken two seconds after the aluminium addition, and was present mainly in the form of clusters, although a few, larger isolated inclusions were also observed. At 1600°C, the spinel was solid and the wüstite phase was liquid, so that these inclusions were capable of partial coalescence. The glassy, single-phased particle in Fig. 2 contained 70% Al_2O_3 and yet appeared to have been fully molten prior to quenching. This is surprising as its composition lies in the (spinel + corundum) phase field at 1600°C, and it should therefore have been completely solid. Another major type of deoxidation product consisted of a central region or core having a spinel-like composition, surrounded by a rim containing 70%-100% Al_2O_3, Fig. 3. These were present in the samples taken two and six seconds after the aluminium addition, and were very similar to those described by Plöckinger[6]. It should be noted that globules of metal occurred at the rim/core junction.

The final type of deoxidation product observed was alumina, which was present in the form of showers, Fig. 4. These were present in the sample taken fifteen seconds after the aluminium addition. Within these showers, the morphology of the alumina was often spherical, indicating that they probably formed via a liquid-oxide phase, and the presence of spherical, glassy alumina inclusions should be noted. In other cases, Fig. 5, the alumina had apparently precipitated directly from the melt with a dendritic morphology, as well as via a liquid mixed oxide. The difference in the morphologies of the alumina particles in the clusters can clearly be seen.

Before discussing these observations, it is necessary to consider the general features of the deoxidation of steel melts by aluminium, and in particular the work of Plöckinger[5][6]. Opinions differ on the precise mechanism of the formation of alumina inclusions, particularly the interpretation of Plöckinger's theory of inclusion nucleation following deoxidation of nominally pure iron melts, containing different manganese contents, by aluminium at 1630°C. Suction samples were taken at various times after the aluminium addition and the compositions of the resulting inclusions were determined by microanalysis. It was observed that the primary deoxidation products underwent a marked change in composition during the course of their formation. Immediately after the aluminium addition, the inclusions were very low in alumina and consisted essentially of iron and manganese oxides. The proportion of the latter depended on the manganese content of the melt. The alumina content of the inclusions then increased very rapidly during the next few seconds until the composition reached that of the spinel, $(FeMn)O.Al_2O_3$. During this period, the inclusions were in a fluid or partly fluid state and possessed good coagulation properties. In addition, microanalysis showed that each inclusion had a uniform composition. This situation persisted for only a short interval and with further increase in time, the large inclusions developed two regions having different compositions. The core of the inclusions contained about 60% Al_2O_3, 40% (FeMn)O, and had, therefore, a spinel-like composition in which the FeO:MnO ration depended on the manganese content of the melt. In contrast, the outer layers consisted of pure alumina.

According to Plöckinger, the solution and distribution of the aluminium in the melt takes a definite although short time. Within a small volume element of the melt, the aluminium content rises rapidly, but not instantaneously, from zero up to a point at which the solubility product for the formation of mixed oxides is exceeded. This occurs with very small aluminium contents and the deoxidation products consist essentially of iron and manganese oxides with relatively small proportions of alumina, e.g. 85% FeO, 10% MnO and 5% Al_2O_3.

With this composition they are liquid at the melt temperature at 1630°C.

As the aluminium content of the melt increases, there is a corresponding increase in the alumina content of the liquid mixed oxides. So long as the inclusions are liquid, conditions are favourable for the homogenisation of their composition. Only when the alumina content increases further up to a value corresponding to that of the spinel does complete solidification of the inclusion occur. After this stage, the inner core region of the large deoxidation products is no longer involved in a reaction with the now aluminium-rich melt, and pure alumina deposits on their surfaces leaving the cores with a constant composition.

According to Plöckinger, the small pure alumina particles present in the form of clusters can also result from the initial mixed oxides by a similar mechanism, whereby the aluminium reduces the whole inclusion, owing to its small size, and not just the surface as with large ones. This, it is suggested, can explain why pure alumina inclusions often have a rounded shape typical of those which have been liquid even though their melting point lies well above the melt temperature. These clusters of small alumina particles can, however, also form directly after the melt attains a high aluminium level without passing through the liquid mixed oxide phase. That a reaction between pre-existing (FeMn)O rich oxides and aluminium, even in the solid state, can give rise to alumina clusters or aggregates has been shown by heat treatment experiments[12][13].

With regard to the observations already described, the first point to emphasise is that the rate at which nucleation and growth of the inclusions occurred was extremely rapid. Within seconds of adding the aluminium, the deoxidation products observed were mainly duplex spinel/wüstite inclusions, and single-phased particles containing about 10% Al_2O_3. These inclusions were fully or partially molten, and floated out of the melt extremely rapidly as shown by the reduction in the total oxygen content of the melt in the 0.015% Mn steel, Fig. 6. Only when the alumina content increased further did complete solidification of the inclusions

occur. After this stage, the inner core of the large deoxidation products was no longer involved in reaction with the now aluminium-rich melt, and the alumina deposited on their surfaces leaving the cores with a constant composition. These results are in agreement with those of Plöckinger.

The clusters of spinel/wüstite inclusions present after two seconds, Fig. 2, were similar in appearance to some of the clusters of aluminium particles present after fifteen seconds, Fig. 4. This indicates that such clusters of alumina might result from the initial mixed oxides by a similar mechanism, whereby the aluminium reduces the whole inclusion owing to its small size. An attempt has been made to answer the question as to whether the spinel, when it has become completely solid, can still react with aluminium in the melt. By inserting a crystalline spinel particle into an Fe-O-Al melt, it was shown that the extent of the reduction reaction zone to form alumina was about 15 μm. This indicates, that in the case of large spinel inclusions, only partial reduction occurred giving inclusions with rim/core morphologies, whereas complete reduction of smaller inclusions can occur to give pure alumina.

The spherical, glassy inclusion shown in Fig. 2 contained 70% Al_2O_3 and appeared to have been fully molten prior to quenching. This is surprising as its composition lies in the (spinel + corundum) phase field at 1600°C, Fig. 7, and it should therefore have been completely solid. It has been suggested by other workers that the local temperature rise caused by the liberation of the enthalpy of formation of alumina is sufficient to raise the temperature of the precipitating inclusions near to or above that of the liquidus, so that they form in a fluid or viscous state. It is very difficult, however, to account for this in terms of heat transfer considerations. The reaction to form liquid alumina at its melting point of 2030°C from solid aluminium at 25°C and oxygen dissolved in molten iron at 1600°C is certainly exothermic as shown by an enthalpy calculation, which indicates an energy release of 241 Kcals per mole of alumina formed. However, if it is assumed that the heat liberated by this reaction raises the temperature of the melt from

which the oxygen came, then this rise in temperature is only 45°C. For the alumina to be molten, there would always have to be a steep temperature gradient from such an inclusion into the melt. For this situation to arise, the rate of heat transfer would have to be lower than the rate of diffusion of aluminium and oxygen to the reaction surface, and this seems improbable. An explanation for the formation of liquid deoxidation products containing 70%-90% Al_2O_3 in terms of the exothermic heat of reaction is therefore unlikely.

It seems more likely that the spherical, glassy inclusion was a metastable reaction product. That is to say, it precipitated as a liquid mixed oxide having an Al_2O_3 content of less than 30%, Fig. 7. The aluminium content of the surrounding melt then increased very rapidly and there was a correspondingly rapid increase in the alumina content of the liquid mixed oxide. Its composition first of all moved into the (spinel + liquid) phase field and then into the (spinel + corundum) phase field. However, because of the very rapid rate of reaction, and/or nucleation inhibition, neither spinel nor corundum was precipitated within the liquid mixed oxide, which on quenching formed a single phased glass. The fact that relatively few glassy, alumina-rich inclusions were observed in comparison with the many spinel/wüstite particles reflects the difference in the ease of formation of these two types of reaction products.

(b) Thermodynamic and Surface Energy Aspects of Aluminium Deoxidation

It has already been stated that, the solution of aluminium in the melt must cause the concentration in every fraction of the volume to increase from zero to a value, which on exceeding the solubility product, will cause inclusions to precipitate. For aluminium, this concentration is small, and if at this moment the precipitation of an inclusion occurs, as a result of nucleation, then this must necessarily consist of a mixed oxide. If nucleation occurs at a later stage however, that is to say with a higher concentration of aluminium, then the inclusions formed will be richer in alumina. Ultimately, when the aluminium content has risen sufficiently high, only alumina can be precipitated. Since, in addition to the process of solution of the deoxidant, the rate of nucleation is also decisive for the initial composition of the precipitated inclusions, various types of deoxidation

products can always occur side by side.

According to Plöckinger's theory,[5][6][10] the liquid mixed oxides precipitate homogeneously. Frohberg and Pötschke[14], and Förster[15] consider that this suggestion is contradicted by nucleation theory and that nucleation will always occur heterogeneously. This implies that solid nuclei of alumina would have to form on to which iron and manganese oxides would then precipitate heterogeneously. Consequently, Frohberg and Pötschke[14] have postulated that solid alumina particles are formed at the surface of the aluminium immediately after its addition to the melt, thus retarding the solution process. However, convection and stirring effects result in a rapid distribution of these surface alumina particles throughout the melt. In regions where sufficient supersaturation exists, iron and manganese oxides precipitate heterogeneously on the alumina, which then dissolves in the mangano-wüstite to form a fully molten oxide. This then reacts with further aluminium in the manner discussed previously.

Förster[15] has carried out similar experiments to Plöckinger, using zirconium instead of aluminium. The inclusions observed shortly after the addition of the deoxidant consisted of a core of zirconia surrounded by mangano-wüstite. This result points to the primary formation of zirconia, which had obviously not dissolved in the liquid FeMnO.

For aluminium deoxidation, the free energy of formation of alumina is greater than the corresponding free energy of formation of liquid mangano-wüstite at 1600°C. Consequently, a liquid mixed oxide is thermodynamically unstable with respect to a solid alumina particle and the latter phase might therefore be expected to form on adding aluminium to an iron melt. Thermodynamic arguments, however, only apply to the initial and final equilibrium states of the system, and give very little information on either the mechanism or kinetics of the actual reaction. Experimental observations have confirmed that liquid mixed oxides do form and a satisfactory explanation for the precipitation of these oxides is therefore required. This assumes, of course, that the mixed oxides nucleate homogeneously and not by heterogeneous precipitation on alumina particles. At the present time the validity of this assumption is uncertain.

For homogeneous nucleation,

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_V)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where ΔG^* = free energy of formation of a nucleus capable of growth

γ = melt/nucleus interfacial energy

ΔG_V = free energy change on transition of a molecule from melt to nucleus

The type of nucleus which forms is the one for which ΔG^* is a minimum. It can be seen from equation (1) that under certain conditions γ^3 can be a more important factor that ΔG_V, that is to say the phase which nucleates is that which has the lowest interfacial energy with the surrounding melt rather than the highest free energy of formation. Although accurate data is lacking, it is known that at 1600°C, the interfacial energy between alumina and iron is greater than that between mangano-wüstite and iron. This suggests, therefore, that on adding aluminium to an iron melt, liquid mixed oxides can form instead of alumina because of their lower interfacial tension with the surrounding melt.

Vorobnev and Levin[11] have suggested that during aluminium deoxidation, the formation of complex nuclei of the $FeO\text{-}Al_2O_3$ type in the liquid state is possible owing to a reduction of the melt/nucleus interfacial energy caused by chemical reaction between the two phases. The compositions of such nuclei are determined by the oxygen content of the melt prior to deoxidation. Their results are summarised in Fig. 8 where lines 1-5 are based on various equations derived by the authors. The areas A-E between the lines represent the areas of formation of nuclei of various compositions. A represents the region of unsaturated metal where the formation of nuclei cannot occur; B is the area of supersaturated metal where the supersaturation is insufficient for the formation of stable nuclei; C is the area of supersaturated metal where only liquid mixed oxides can form; D is the area where liquid mixed oxides and pure alumina can form; E is the area where only alumina nuclei can precipitate. According to these workers, when aluminium is introduced into a melt, the processes

of solution of the deoxidant and deoxidation occur simultaneously throughout the volume of the melt. The concentration of aluminium at any point increases with time from zero. Consequently, the initial state of the system is in area A. With increasing time, the concentration of aluminium at a given point reaches a value which is in equilibrium with the dissolved oxygen (line 1), after which the metal becomes supersaturated (area B). With further increase in the aluminium concentration, the supersaturation of the metal becomes sufficient for the oxide phase to separate. With a sufficiently high concentration of oxygen in the melt, for example, 0.05%, the nuclei which form will be liquid mixed oxides (area C). If the oxygen concentration is less than 0.01% before deoxidation, the oxide phase will separate in the form of alumina (area E).

Finally, the nature of the deoxidation reaction can also be illustrated by the morphology of the alumina clusters. These can be revealed by scanning electron microscopy of deeply etched surfaces. Aggregates of spherical alumina particles probably form via a liquid oxide phase, whilst dendrite morphologies most probably occur by direct precipitation of solid alumina from the melt. The main point emphasised by the structures shown in Figs. 9-12, is that both spherical and dendritic morphologies can occur together in the same aggregate, which illustrates the complex nature of the deoxidation reaction and the formation of the resulting inclusions.

The Reaction between Silicate Inclusions and Aluminium

There is now considerable evidence to show that during steelmaking, the addition of strong deoxidants to the metal in the bath, ladle, or ingot can cause reactions to occur between the existing inclusions and the deoxidising additions[9][12][13][16]. A good example of this is the effect of aluminium on silicate inclusions formed in rimming steels[12]. The addition of aluminium to balance the ingot causes an abrupt change in the inclusions at the rim-core junction, and is the result of both direct deoxidation of the metal, and of reaction between the pre-existing inclusions and the aluminium dissolved in the molten steel. Many

complex reaction products and structures are observed depending on the amount of aluminium used and the time before the inclusion is trapped by the solidifying metal.

In order to understand more fully the reaction mechanisms involved, the addition of aluminium to iron-silicon-oxygen melts containing silicate inclusions has been studied.

In the first series of experiments, the inclusions present in the melt prior to the aliminium addition were liquid silicates containing about 95% SiO_2 and a balance of FeO, Fig. 13. On adding aluminium, complex reaction products were formed consisting of silicate inclusions surrounded by rims of alumina, Fig. 14. These rims were apparently formed as a result of the initial rapid reaction between aluminium and the small amount of FeO in the silicates. This mechanism is supported by the fact that small globules of metal were observed at the silicate/alumina interface. In some cases, however, the quantity of this entrapped metal appeared to be greater than that expected solely from the replacement of the small amount of iron initially present in the silicates. An additional source of entrapped metal may therefore be proposed. After the initial rapid reaction, the resulting rim of alumina defined the position of the original silicate/melt interface. Further replacement of the iron (or silicon) of the silicate by aluminium then occurred inside the rim.

It is possible that this reaction was accompanied by a decrease in volume, as a result of the closer atomic packing in solid crystalline alumina compared with liquid silica. Consequently, voids were formed inside the rim so that iron from the surrounding melt penetrated through the rim in order to fill these voids. This would necessitate pores in the alumina rim, probably caused by the contraction effect.

After the initial rapid reaction therefore, the silicate inclusions were surrounded by rims comprising fine alumina crystals. This is represented schematically in Fig. 15(a). At first sight it appears that the alumina rim might prevent any further reaction. This was not the case, however, for although the reaction rate was very much decreased, the continual replacement of silicon by aluminium occurred by a diffusion-controlled mechanism. In terms of a very simple ionic model, it is suggested that there was an overall diffusion of silicon ions from the silicate

inclusion to the melt and of aluminium ions from the melt to the silicate. This is represented schematically in Fig. 15(b). The important factor was probably the small size of both the Si^{4+} and Al^{3+} ions compared with the relatively larger O^{2-} ions, as shown in Table I, which facilitated their diffusion through the alumina rim. In addition, the diffusion of these ions was also possibly facilitated by the presence of defects within the structure of the rim, that is at alumina crystal boundaries.

TABLE I
Elemental and Ionic Radii

Elemental radius in crystals - A^0	Ionic Radius - A^0
Fe - 1.24	Fe^{2+} - 0.80
Al - 1.43	Al^{3+} - 0.55
Si - 1.17	Si^{4+} - 0.40
	O^{2-} - 1.35

As the reaction proceeded therefore, the replacement of silicon by aluminium caused the alumina content of the inclusion to increase and the alumina rim to thicken. The extent of this reaction obviously depended on the local concentration of dissolved aluminium. Frequently, the Al^{3+} ions penetrating into the silicate caused an enriched concentration of Al_2O_3 in the silicate, from which mullite needles precipitated, Fig. 16.

Heat treatment of silicate inclusions surrounded by alumina reaction rims caused the reaction between aluminium and silica to recommence, although at a much slower rate due to the reaction occurring in the solid state. Consequently, the central silicate phase gradually became smaller and the surrounding rim of alumina became larger. At the same time, more and more metal was deposited between the alumina and the silicate. On completion of the reaction, the final products consisted of rings of alumina crystals, with no silicate present, Fig. 17. Similar formations have been observed in rimming steel ingots after suppression of the rimming action with aluminium[12].

In a second series of experiments, the effect of aluminium on silicate inclusions containing larger amounts of FeO was

studied. These were duplex, liquid silicates consisting of a silica-rich liquid (90% SiO_2) within an iron silicate matrix containing abuut 50% FeO, Fig. 18. On adding the aluminium in this case, the reaction was much more rapid than with the highly siliceous inclusions. Very few silicate inclusions surrounded by rims of alumina were formed. The resulting inclusions, even after only 30 seconds consisted mainly of alumina within an alumino-silicate matrix, Fig. 19. Obviously, therefore, the replacement of silicon and iron by aluminium occurred extremely rapidly and to a marked extent. This was confirmed by analysing the globules of metal entrapped within the inclusions, some of which were found to comprise 70% Si, 30% Fe. It is suggested therefore, that when aluminium reacted with a viscous, highly siliceous inclusion according to the mechanism put forward previously, the replacement of silicon by aluminium and the subsequent diffusion of the aluminium in the silicate were so slow that an aluminous rim was formed. As a result, many reaction products were observed in which mullite had nucleated at the rim and grown into the silicate inclusion. For the iron silicates, however, aluminium reacted with a more fluid inclusion and in this case, the replacement of iron and silicon by aluminium and diffusion of the aluminium within the silicate were much more rapid. As a result, no time was allowed for an aluminous rim to form and the concentration gradients across the inclusion were not as great as in the previous series. Consequently, alumina and mullite were precipitated within the alumino-silicate, rather than only at the surface.

The increased ease of reaction of aluminium with iron silicates compared with highly siliceous inclusions also accounts for the fact that in the latter case, although the entrapped metal globules were found to be slightly richer in silicon than the surrounding matrix, no globules were examined in which the silicon concentration approached anywhere near the 70% level found with the iron silicates.

Fig. 20 shows the morphology of a silicate inclusion surrounded by an alumina reaction rim after deep-etching in bromomethanol followed by examination using the scanning electron microscope. Clusters of spherical alumina particles are also present.

Conclusions

The work which has been described has shown that in the early stages of deoxidation of iron-oxygen melts by aluminium, liquid mixed oxides can be formed which are deficient in Al_2O_3. Subsequent reactions then take place, which are complex in nature, but which can result in the eventual formation of aggregates of alumina inclusions. The morphologies of these reaction products are very varied, and considerable further work is required before the complete sequence of events can be fully understood. The nucleation mechanism is also worthy of further study.

Evidence has also been presented to show that reactions take place between pre-existing silicate inclusions and aluminium dissolved in the molten steel. A suggested mechanism for this reaction has been postulated, but this too requires further work to elucidate the details more clearly. It is accepted that a direct comparison with commercial deoxidation practice is not entirely valid for two reasons:

(1) The initial melt oxygen contents were much higher than those observed during actual steelmaking.

(2) An inert furnace atmosphere was not used so that atmospheric re-oxidation of the melt occurred throughout the sampling period.

Nevertheless, many of the inclusions observed in the laboratory experiments were very similar to those observed during actual steelmaking. This was particularly so in the case of the rings of alumina particles observed in rimming steels treated with aluminium.

References

1. J F Elliott, M Gleiser and V Ramakrishna. "Thermo-chemistry for Steelmaking" Vols. I and II. Addison-Wesley 1963.
2. O Kubaschewski and E L L Evans. "Metallurgical Thermochemistry" Pergamon Press.
3. C Bodsworth and H B Bell. "Physical Chemistry of Iron and Steel Manufacture". Longman, 1972, 2nd Edition.
4. E T Turkdogan. "Deoxidation of Steel". Review paper. International Symposium on Metallurgical Chemistry. University of Sheffield, 1971, The Metals Society.
5. E Plöckinger and M Wahlster. Stahl v Eisen 1960, 80, 659.
6. E Plöckinger. ISI Spec Rep. No. 77, 1963, 51.
7. E T Turkdogan. JISI 1966, 204, 914.
8. P H Lindon and J C Billington. Trans AIME, 1969, 245, 1775.
9. F B Pickering. "Production and Application of Clean Steels". Proc. of Int. Conf. Hungary 1970. ISI Publication, 75.
10. H Straube, G Kühnelt and E Plöckinger. Arch.f.d.Eisen. 1957, July 509.
11. A A Vorobnev and A M Levin. Izv. V,UZ, Chern. Met. 1967, 12, 12.
12. F B Pickering. Jenkontorets Ann. 1964, 148, 845.
13. F B Pickering and P E Waudby - unpublished work, 1971.
14. M G Frohberg and J Pötschke, Freiberger Forschung. 1969, B144, 31.
15. E Förster, Arch.f.d.Eisen. 1967, July, 607.
16. P E Waudby et. al. JISI. 1973, 209, 486.

LECTURE 3

SOME ASPECTS OF THE FORMATION OF SULPHIDE INCLUSIONS IN STEEL

Introduction.

The formation, mode of occurrence and type of the sulphide inclusions observed in steel is an extensive topic, as also are the effects of sulphide inclusions on various physical and mechanical properties. These latter effects will be discussed in later chapters. The object of this chapter is to discuss the formation and conditions of occurrence of some of the many types of sulphides observed in steels, but excluding the zirconium and rare-earth sulphides which will be discussed in more detail in subsequent chapters. Much work has been carried out by controlled research programmes to study the occurrence of sulphides in steels, and this has been supplemented by further information obtained during commercial steelmaking and processing. In addition there have been reviews in the literature relating to sulphide formation (1)-(7).

The sulphide types which will be considered are those based on the elements manganese, chromium, nickel, calcium, copper and magnesium, most of which are observed to occur in steel, although some are relatively rare. The tendency of elements to form sulphide can be shown by the free energy of formation diagram, fig 1. (8)

The relative stability of sulphides, besides depending on their free energy of formation, is also dependant upon the temperature and partial pressure of sulphur and the other elements present. This is very clear in Fig.2, where for example MnO is more stable and readily formed than MnS. However, both SiO_2 and Al_2O_3 are even more stable oxides and being normal deoxidisers in steel will allow the manganese to react with the sulphur, having reduced the presence of free oxygen very considerably. Hence, all these features must be remembered when considering the formation of various sulphides type. It must also be appreciated that Fig. 2 also refers to the conditions for the pure elements, when the activity is unity. In steelmaking this assumption is much over-simplified, as the molten steel must be regarded as a dilute solution of many elements in iron; for many of them the solution is far from saturated and hence activity is clearly not unity, but considerably less. For example, the effect of making manganese a solute element on the free energy of formation of MnS is quite considerable, and has been calculated by Jorgensen (3), Fig. 1.

It is very evident from this that at normal steel solidification temperatures, the tendency to form MnS is only slightly greater than the tendency to form FeS; above 1600°C the tendency is reversed, when the lower manganese activity is considered. Obviously, however, whilst the difference is small at steel solidification temperatures, and concentrations, MnS is the more stable phase at much lower temperatures. In contrast, assuming unit activity of manganese, FeS should never be formed when manganese is present, until all the manganese has formed MnS. As will be shown later, confirming the results of Kiessling[1], this situation is not observed in practice.

Certain elements, such as calcium, magnesium etc, will not be present as pure metals, but will form as oxides, usually in the form of slag during steelmaking. Clearly, the ability of a slag to desulphurise depends very largely upon the relative stability of the sulphide compared with the oxide. Muan and Osborn[8] have shown curves, depicting the differences between the standard free energies of formation of sulphides and the corresponding oxides $\Delta(\Delta G)$; some of these curves are shown in Fig.3. This diagram can therefore be used to estimate the tendency for sulphide to be formed from oxide, but again it must be appreciated that the diagram is based on values for pure elements, having unit activity. However, Fig.3. does show the tendency for sulphide formation relative to oxide formation, and it can be seen that $\Delta(\Delta G)$ is positive for most combinations of a particular metal sulphide and oxide.

Following Muan and Osborn[8], the Ps_2/Po_2 ratio of the gas phase in equilibrium with the condensed oxide and sulphide phases is given by:-

$$\log Ps_2\ (eq) - \log Po_2\ (eq) = \frac{\Delta(\Delta G)}{2.3\ RT} \quad \text{-----(1)}$$

It is clear that the partial pressure of sulphur must exceed that of oxygen in order that the reaction oxide→sulphide can occur. Vacuum melting is one instance in steelmaking where this difference can be increased and may therefore increase the sulphide: oxide ratio. Reference should also be made to the fact that strong sulphide forming elements can be used to desulphurise iron and steel.

Such elements as calcium, magnesium, titanium and rare-earths are possible for this purpose[10], the precipitating sulphide being removed to a slag. A heavily deoxidised melt is clearly necessary for desulphurisation as $\Delta(\Delta G)$ is positive, and is helpful in any circumstances.

As has already been indicated there are a number of different sulphides which can occur in steel, but it is appropriate to consider first those occurring in the Fe-Mn-S system.

Sulphides occurring in the Fe-Mn-S system

Before considering the sulphides in the Fe-Mn-S system, some comment on the three different forms of MnS which are commonly found in steels, is appropriate. Many explanations have been advanced for the mechanism of formation of the different types of MnS [2][3][5-7], namely type I, II and III, typical microstructures of which are shown in Fig.4. The morphology can generally be described as globular, branched rod or idiomorphic for type I, II and III respectively, but Fig.4 illustrates the appearance in a two dimensional polished section. The scanning electron microscope allows a much more informative examination to be made of these sulphide forms, and Fig.5 shows the three types again, examined in both deep etched and fractured samples. The three dimensional effects can be appreciated and the various morphologies are very evident.

Because of the controlling effect of the oxygen in the steel on the mechanism of formation of MnS, it is necessary to consider the quaternary system Fe-Mn-O-S, a part of the liquidus surface of which is shown in Fig.6. Type I MnS have been suggested to form by a monotectic reaction involving the miscibility gap in the quaternary system, those liquid inclusions which form first having the higher oxygen concentration. The presence of oxide associated with type I MnS is shown in Fig.4, and these inclusions are generally found in rimmed or semi-killed steels where the oxygen content of the liquid steel is high and the sulphur solubility low. Type II MnS has often been referred to as a eutectic form, but has more recently been suggested to occur by a co-operative monotectic reaction. This form occurs in steels which have been fairly heavily deoxidised, often by aluminium, so that the oxygen content is low and the sulphur solubility is higher.

This means that the sulphide phase precipitates as a liquid from the last parts of the steel to solidify, i.e. between the dendrites, and has many morphological similarities to a eutectic. Type III MnS has an angular or octahedral form, and their morphology indicates that they precipitate as solid particles from the melt. They have been suggested to be produced by a divorced eutectic reaction, and occur in steels or cast irons which have been very heavily deoxidised. The oxygen content is low, but due to the high aluminium content often used, the sulphur solubility in the liquid steel is lowered so that type III tends to precipitate at a higher temperature than type II. In general however, they form from residual liquid and usually are mono-phased with little or no oxide associated with them. They are often considered to be a fairly pure form of MnS.

The pseudo quaternary system Fe-FeS-MnS-Mn, shown in Fig.7, together with the relevant binaries, is not simple because it presents at the solidus surface a number of interacting and hence interdependent troughs and plateaux. Melford[11] has pointed out that there are several features peculiar to this system, one of which makes the Mn : S ratio at which FeS does not form dependent on the actual sulphur content of the steel. If the Fe-rich corner is examined more closely, Fig.8, in conjunction with the pseudo binary Fe-MnS, Fig.9, several very important points emerge. Because the miscibility gap of the two liquids is cut off from the iron rich corner by a eutectic valley, manganese cannot be used to desulphurise the steel completely. Furthermore, the lowest point in the eutectic valley is at a point T in Fig.7, equivalent to the ternary eutectic. Therefore if free FeS is present in the steel it can contain a molten eutectic liquid at temperatures above 980°C. This of course will tend to make a steel "hot short".

To avoid FeS formation completely - and subsequent hot shortness - the steel composition must lie to the manganese rich side of the maximum temperature in the eutectic valley, i.e. the ridge shown in Fig.8. To the iron-rich side of this ridge, FeS will always be precipitated. Since this ridge lies askew to the Fe-MnS line, the Mn : S ratio necessary to ensure the formation of only MnS is relatively greater at lower sulphur levels than at high sulphur levels.

Hence the Mn : S ratio, much talked about in practice, is not the only guide as to whether FeS formation will be avoided; the sulphur content must also be stipulated. For example increasing the sulphur level by a factor of about 3, from A→B in Fig.8, does not require a proportional increase in the manganese, which only needs to increase from C→D.

Work has been carried out[12] to investigate the effects of varying the Mn : S ratio on the sulphides formed in the Fe-Mn-S system. This work has been carried out at a nominal 0.25%S level in order to obtain sufficiently large sulphides for microanalysis. Typical sulphides found at different Mn : S ratios are shown in Fig.10, ranging from FeS, through duplex FeS-MnS inclusions to almost pure MnS. Microanalysis and dihedral angle measurements of these sulphides showed a number of interesting features. For this level of sulphur, it was found that FeS was still present at a Mn : S ratio of 1.4, but was not present at a ratio of 2.8. It will also be realised from the pseudo-binary FeS-MnS system that the MnS can contain a considerable amount of FeS in solution, and microanalysis, Fig.11, showed that this solubility was a maximum until a Mn : S ratio of about 1.5, thereafter it decreased rapidly reaching a minimum at a Mn : S ratio between 3 and 7. There was always some solubility of FeS in the MnS in the alloys examined, in the as cast condition. An increased amount of FeS dissolved in the MnS will lower the melting point of the sulphide.

It is those sulphides which occur at the grain boundaries on which dihedral angle measurements have been carried out. The relationship between the interfacial tensions and the dihedral angle, Fig.12, has been developed in some detail[12], but it suffices to say that:-

$$\cos\phi = \frac{\gamma_1}{2\gamma_2} \qquad \text{----------(2)}$$

and the limiting condition for this relationship is:-

$$\gamma_1 \leqslant 2\gamma_2 \qquad \text{----------(3)}$$

otherwise $\cos\phi$ would exceed unity, which is not possible. Hence when $\gamma_1 = 2\gamma_2$, ϕ becomes zero and complete grain boundary penetration is possible. To determine the value of 2ϕ - the dihedral angle, a considerable number of individual angles must be measured, and a median value obtained by plotting a cumulative frequency curve.

In doing this, it becomes very clear that a unique angle does not exist, Fig.13, because of the shape of the curve. This is perhaps to be expected because the interfacial tensions will be orientation dependant, and this will vary between various pairs of grains. It is therefore only possible to quote an average median value. The variation found in the dihedral angle for both MnS and FeS at various Mn : S ratios is shown in Fig.14. Both MnS and FeS show a minimum dihedral angle in the Mn : S ratio range 1.5 - 2.0,and the muchlower dihedral angle values of the FeS together with its low melting temperature indicate why FeS will make a steel susceptible to becoming hot short, the FeS being much more able to penetrate between the austenite grains.

The effect of Chromium on the Fe-Mn-S System

The pseudo ternary system FeS-MnS-CrS is shown in Fig.15, from which it can be seen that there is complete solubility between FeS and CrS and both have considerable solubilities in MnS. Experimental studies involved the Fe-Cr-S and Fe-Mn-Cr-S systems. A number of interesting features were observed.

The Fe-Cr-S system has been investigated in much less detail[13] than either the Mn-Cr-S or Fe-Mn-S systems, and there is some doubt concerning the interpretation of the published diagram.

In the Fe-Cr-S system, it was confirmed that there was complete mutually solubility between FeS and CrS. X-Ray diffraction showed that only the FeS structure occurred; thus as no pure CrS was found it is suggested that it requires only a small amount of FeS to be present in the sulphide to stabilise the structure. In the sulphur range 0.25/0.30%, it was found that a Cr : S ratio of approximately 19 was necessary to obtain a maximum chromium content in the sulphide. There also seems to be an extended solubility of CrS in MnS as predicted in the literature [14][15], and complete solubility has been reported[16].

The effect of chromium on the dihedral angle is shown in Fig.16, where it can be seen that there is an initial small decrease in dihedral angle up to a Cr : S ratio of 3, thereafter the dihedral angle increasing rapidly up to a Cr : S ratio of 10, and continuing to increase up to the highest Cr : S ratio examined. It is clear therefore that CrS will not tend, as FeS does, to make the steel susceptible to hot shortness. If the dihedral angles, Fig.17, are related to the ratio, Cr (sulphide)/Cr (steel),

then the Cr-rich sulphides become clearly differentiated from the Fe-rich sulphides containing Cr, the dihedral angle for both phases decreasing with increasing ratio but the higher chromium sulphides showing a much greater dihedral angle than the lower chromium sulphides.

The sulphides were found to occur either interdendritically or at grain boundaries, because they solidified after the matrix. At the higher chromium contents, whilst the CrS could solidify before the matrix, it did contain FeS and a eutectic reaction is involved at the CrS side of the Fe-CrS pseudo-binary. Thus it was found that a sulphide, similar in character to MnS-type II was generally observed. Kiessling and Lange[1], have also observed that in the (MnCr)S crystal structure, considerable metal ion vacancies can exist. This is a particularly important feature, because these vacancies would clearly tend to cause an apparent increase in the sulphur contents of the sulphide when subjected to analysis. The level of these vacancies, is indicated in Fig.18, from which it will be seen that the vacancies in the (Mn, Cr)S can occur in concentrations up to 25% of the metal atom fraction. Thus the composition of (MnCr)S containing a maximum vacancy concentration would be 19.9 wt % Mn, 35.5 wt % Cr and 44.6 wt % S. This is an apparent increase in sulphur from the stoichiometric 36.7 wt % to 44.6 wt %, whilst still maintaining the (MnMe)S structure. This compares with the sulphur content of 45.7 wt % in Cr_2S_3. It is very clear therefore, that both the analyses of the sulphides and determinations of their structures are necessary to decide whether the crystal form is of MeS or the Me_2S_3 type of sulphide which has been reported by some workers[17][18]. The highest concentrations of sulphur in the inclusions observed in the investigation of inclusions in the Fe-Cr-S and Fe-Cr-Mn-S systems[19] were 44 wt % and 42 wt % respectively, but in all cases X-Ray diffraction confirmed the absence of the Me_2S_3 structure. These higher than stoichiometric sulphur levels were therefore the result of metal ion vacancies.

Typical the sulphides found are shown in Fig.19, the sulphide colour darkening on changing from FeS to CrS and then to MnS, although the difference between chromium and manganese rich (MnCr)S is small.

It also becomes apparent from the analyses that the tendency to form metal ion vacancies increased with the presence of chromium in the sulphide, and decreased with presence of manganese in the sulphide, reaching a maximum of 20% in the 0.12%Mn steel. This may be compared with theoretical maximum values of 23% in the Fe-Cr-S system and 25% in the Mn-Cr-S system. The results of many analyses of Mn-Cr-Fe sulphides are shown in Fig.20, from which it can be seen that there appears to be complete solubility between MnS and CrS, as reported by other workers[16]. The extent to which equilibrium has been achieved in the work shown in Fig.20, however, has not been established by extensive annealing studies.

It will be recalled that in the Fe-Mn-S system it was necessary to define both the sulphur level and the Mn : S ratio at which only MnS would be formed, because the maximum in the eutectic trough was not parallel to the Fe-MnS pseudo-binary system. In the Fe-Cr-S system this situation did not occur, and therefore it did not appear likely that variations in the sulphur level normally found in steel would have any marked effect on the Cr : S ratio at which only CrS would be formed. In the Fe-Mn-Cr-S system however, the peculiarity of the Fe-MnS psuedo-binary system might have been expected to have an effect, but the analyses did not appear to differentiate between the various sulphur levels.

The analyses of the sulphides found in these systems can be shown in such a way to illustrate how it is dependent upon the ratio of the sulphide forming metals. The effect of varying the Cr : S ratio upon the %Cr in both (MnCr)S and (FeCr)S is shown in Fig.21, the solid lines referring to the chromium content and the dashed lines to the (manganese + iron) contents. It is clear that manganese is a stronger sulphide former than chromium and in the case of (Mn.Cr)S the curves level out so that increasing Cr : S ratio does not continually increase the chromium content of the sulphide. On the other hand, with the manganese contents used, the (Fe.Cr)S reverts to (Mn.Cr)S before any maximum in the chromium content of the sulphides is observed.

If the chromium content of the sulphides is plotted as a function of the Cr : Mn ratio, Fig.22, unique curves are obtained for the (MnCr)S and (FeCr)S. The independent variable not included is sulphur, from which it can be concluded that the

sulphur content of the steel at these levels does not materially affect the chromium content of the (MnCr)S, but is only dependent on the Cr : Mn ratio. The same argument holds true for the chromium and iron contents of (FeCr)S. The effect of the Mn : S ratio in the steel, and the sulphur content of the steel, upon the manganese content of the (MnCr)S is clearly shown by the dashed lines in Fig.22(a).

The effect of chromium on the dihedral angle of sulphides at grain boundaries is shown in Figs. 23 and 24. The effect of varying Cr : S ratio, Fig.23, shows an increasing dihedral angle with increasing Cr : S ratio, but the effect of varying Mn : S ratio appears not to affect greatly the dihedral angle. There is however a slight indication that for a particular chromium content, increasing the Mn : S ratio increases slightly the dihedral angle. The effect of the ratio of chromium in the sulphide : chromium in the steel, Fig. 24, shows two distinct curves indicating manganese levels of 0.14/0.27% and 0.97% respectively. For both manganese contents, the dihedral angle of the sulphides decreases with increasing ratio of chromium in the sulphide : chromium in the steel.

Summarising the general surface energy effects of the sulphides present in the Fe-Cr-Mn-S system, it appears that the dihedral angle increases in the order FeS, MnS, CrS, (Mn.Cr)S, and that the effect of the sulphide : austenite interfacial energy is more responsible for this than is any possible effect of the alloy composition on the grain boundary surface energy of the austenite itself.

The Effect of nickel on the Fe-Mn-S system

Whilst this system has not been studied in detail, the effects of nickel seem to be small. This is not perhaps surprising because nickel has a lower sulphide forming tendency than iron.

Steels in the slow cooled condition were examined, containing 0.25%S, up to 0.30% Mn and up to 12% Ni. Within these composition limits a maximum of 0.6% Ni was found in solution in the FeS, and none was found in the MnS. The effect of nickel on the dihedral angles of both (FeMn)S and (MnFe)S was also small, causing some increase in the angle value with increasing Ni : S ratio,

Observations on other Sulphides found in Steels.

(i) Calcium Sulphide

Calcium sulphide is not infrequently found in steels, and is often commonly associated with slag entrappment[20]. CaS occurs therefore as one phase together with a complex oxide. Two examples of a form in which it normally occurs are shown in Figs.25 and 26. The CaS shown in Fig.25 is present as a peripheral phase, which may have resulted from precipitation on a pre-existing inclusion, or be due to a surface reduction of the oxide by sulphur, CaS forming in preference to an aluminium or silicon sulphide. The X-Ray spatial images show the concurrence of calcium and sulphur, together with manganese, forming a (CaMn)S, which is the more common form.

The CaS is seen more clearly in Fig.26, where the sulphide and calcium-aluminate of the low melting point $12CaO.7Al_2O_3$ type, appear to have formed together. The two optical photographs show an important feature of CaS. In the case where the sample was prepared in the absence of water, the phase has a similar contrast to MnS, but when prepared with water, it blackens even to the extent of becoming darker than the oxide. Again the concurrence of calcium and sulphur is shown in the X-Ray images.

It should also be mentioned that CaS can also be formed by calcium bearing additions, as will be shown in a subsequent chapter, but this is unusual as the main aim of these additions is to modify pre-existing oxides.

(ii) Magnesium Sulphide

This can occur in steels to which magnesium has been deliberately added, and the particular example shown in Fig.27, has precipitated in association with Ti(CN) in a steel of the alloy 600 type containing 75%Ni. MgS, like CaS, reacts with water, but more rapidly, and must therefore be prepared in the absence of water. Whilst the addition of magnesium to this particular steel improves its hot working characteristics, MgS is detrimental from the point of view of corrosion because it rapidly disintegrates in an aqueous environment. The X-Ray images in Fig.27, show the concurrence of magnesium and sulphur in relation to the Ti(CN).

(iii) Copper Sulphide

Copper sulphide Cu_2S is reported[22] only to occur in the Fe-Mn-S system, when the manganese content is very low and the copper and sulphur contents are high. Indeed, there are few references to it occurring in steel. There is, however, one favourable situation for its formation. During the reheating and scaling of steel, particularly mild steel, where the residual copper level is sufficiently high, or where it is a copper-bearing steel, enrichment of this element, together with others, can occur such that a Cu-rich phase containing in excess of 90% Cu is precipitated immediately beneath the scale and at surface grain boundaries. If the heating atmosphere is such that the steel can pick up sufficient sulphur, then the high copper and sulphur contents can result in the formation of Cu_2S, as shown in Fig.28, although FeS is also very likely to form. Cu_2S, unlike copper, does not wet or penetrate the grain boundaries and will therefore inhibit hot shortness.

(iv) Titanium bearing Sulphide

In steels, there is little published evidence that titanium sulphides occur in steel, but the possibility does not seem to have been systematically investigated. However, a titanium carbo-sulphide, Y-phase, is observed, and occurs most frequently in titanium stabilised austenitic stainless steels, frequently associated with Ti(CN), Fig.29.

Summary and Conclusions

This consideration of sulphides in steel has not been intended to summarise the very considerable literature on manganese sulphide, nor to consider the modification of MnS to produce inclusion shape control. These topics will be discussed in later chapters. However, some new observations on the dihedral angle of various sulphides which can occur in alloy steels, has been presented together with some observations on the effect of steel composition on the composition of iron and manganese sulphides. The effect of chromium on iron and manganese sulphides has been dealt with in some detail, and may be relevant to sulphides in various types of stainless steels. Finally a brief discussion of the occurrence of calcium, copper and titanium sulphides in steel has been presented.

References

1. R.Kiessling and N.Lange. ISI Publication No.100,1966
2. C.E.Sims Trans AIME 1959, 215,367.
3. T.J.Baker and J.A.Charles JISI 1972, 210,702.
4. W.Dahl et al. Stahl u.Eisen. 1966, 86,796.
5. D.C.Hilty and W.Crafts. Proc.Elect.fee.Steel,Conf.AIME,1953,121.
6. P.P.Mohla and J.Beech. Brit.Foundryman. 1968, Dec, 453.
7. H.Frederiksson and M.Hillett. JISI. 1971, 209,109.
8. A.Muan and E.F.Osborn. "Phase equilibria among oxides in Steelmaking" Addison-Wesley. 1965.
9. C.Jorgensen. Royal Institute of Technology, Institute for Ferrous Metallurgy, Stockholm, Internal Report.
10. C.Bodsworth and H.B.Bell "Physical Chemistry of Iron and Steel Manufacture". 1972 Longman.
11. D.A.Melford - private communication.
12. W.J.M. Salter. PhD Thesis, University of London, 1965.
13. R.Vogel and R.Reinbach, Arch.f.d. Eisenhuttenwesen. 1938,7,457.
14. R.Kiessling and C.Westman. JISI 1966, 204,37.
15. R.Kiessling et al. JISI 1967, 205, 531.
16. R.Payet and R.Leveque. Rev.de Met. 1967, July/Aug.653.
17. F.K. Lotgering. Phil. Res. Rep. 1956, 11,190.
18. C.W.Kovach et al. Trans. ASM. 1968, 61,575.
19. W.J.M.Salter - unpublished work.
20. F.B.Pickering - "Production and Application of Clean Steels". ISI. 1972, 75.
21. W.J.M. Salter and F.B. Pickering. JISI. 1969, 207,992
22. H.Morrogh JISI. 1946, 154, 399.

LECTURE 4

THE CONSTITUTION OF NON-METALLIC INCLUSIONS IN STEEL

Synopsis

A review has been presented of some of the more salient features associated with the constitution and occurrence of some of the more commonly occurring types of non-metallic inclusions in steel. The main types considered are sulphides, oxides, silicates, calcium aluminates and the less common selenides and tellurides The composition, crystal type and solubility effects of the various phases have been described, together with relevant information concerning their mode of occurrence, plasticity etc.

Introduction

The influence of non-metallic inclusions in steel on the properties continues, as indeed it has been for many years, to be a major study by many metallurgists. In fact it has been stated[1] that steel should be considered to be a cermet, containing a small volume fraction of non-metallic material. It seems therefore that the non-metallic inclusions must be regarded as an integral part of the steel, and in studying their effects the microstructure of the inclusions must be examined in the same detail as has been the microstructure of the metal matrix.

In general, non-metallic inclusions in steel fall into two major categories, namely oxides and sulphides, although several other minor types of inclusions may also be present. In this chapter, attention will be concentrated on the oxides and sulphides. Inclusions may also be classified into three main groups according to their mechanism of formation:-

(i) Primary inclusions which form by reactions in the liquid steel, and thus precipitate directly as solids or liquids from the steel before or during solidification.

(ii) Secondary inclusions which precipitate from the steel during cooling and solidification, and which also may be liquids or solids.

(iii) Exogenous inclusions, which may be defined as mechanically entrained inclusions as distinct from the indigenous inclusions formed by a chemical reaction or precipitation sequence integral to the steel[2]. Exogenous inclusions occur in many forms, but are generally characterised by their large size, sporadic occurence, often irregular shape and complex constitution and microstructure. Usually they are oxides, resulting from slags or refractories. However, exogenous inclusions may undergo reactions with the steel, and they may also act as heterogenous nuclei on which indigenous inclusions may precipitate.

By virtue of their method of formation, non-metallic inclusions are seldom, if ever, equilibrium products. Consequently the composition of an inclusion is often only the merest guide to its constitution in terms of the assemblage of phases of which it is comprised, which in turn defines its microstructure. For example, a complex silicate may be, and often is, glassy or non-crystalline in the as cast condition, but if present in a large ingot or casting may have had time to crystallise into several distinct phases. A similar crystallisation of the glassy silicate may occur when the ingot is reheated prior to hot working. In addition, the composition, and hence the constitution of an inclusion, may alter during reheating or

slow cooling, by reaction with the steel This can occur in both sulphides and oxides, and in some cases the reaction is so extensive as to change entirely the composition from a silicate to alumina[3]. It can be appreciated therefore that the detailed microstructure of an inclusion may not be constant, and yet it is this microstructure and associated constitution which affects the properties of the steel.

Sulphides in Steel

Sulphides in steel generally comprise one or more of the phases, FeS, MnS, CaS. Frequently there can be extensive solid solution of other elements in the sulphide[4]. In recent years, considerable attention has also been focussed on sulphides of titanium, zirconium and the rare-earth metals[5,6], in an attempt to minimise the detrimental effects of certain types of MnS inclusions on mechanical properties.

(a) Iron Sulphide - FeS

Iron sulphide, FeS, occurs in steels deficient in manganese. Melting at 1190°C, and forming a eutectic with gamma iron at 988°C, fig. 1, the high solubility of sulphur in molten iron but low solubility in solid iron causes the FeS to precipitate as a eutectic during solidification, the melting point of which is further lowered to 940°C by the presence of oxygen. Thus FeS tends to form at grain boundaries and gives rise to the well known hot shortness effects[7,8]. In fact, in oxide scales on sulphur bearing steels, the binary FeO-FeS eutectic is often clearly observed[4]. FeS has a characteristic coloration, making it relatively easy to identify even in the absence of micro-analysis, and is anisotropic, having a hexagonal structure. It has an extended homogeneity range and is best defined as $Fe_{(1-x)}S$ where x can assume values up to 0.18[9]. The lattice therefore contains metal vacancies, and it is not surprising that considerable solid solubility has been found with chromium[10], with titanium[11]

and with vanadium[12]. Kiessling[4] reports some conflicting data on the solubility of manganese in FeS, but the FeS-MnS phase diagram indicates limited solubility of MnS in FeS but a fairly extensive solubility of FeS in MnS, fig. 2. The fact that there is a sharp decrease in the solubility of FeS in MnS with decreasing temperature results in the precipitation of FeS laths as a Widmanstatten structure in MnS. Examples of this effect have been observed in cast irons[13], and in steels[14]. In general, a Mn:S ratio of about 4 is required in order to replace FeS by the higher melting point MnS, with a consequent elimination of hot shortness. However, it has been shown[15] that in the Fe-Mn-S system, in order to avoid FeS formation the steel composition should be to the manganese rich side of the maximum temperature in the eutectic trough. This maximum temperature lies on a ridge at an angle to the Fe-MnS tie line, so that the Mn:S ratio required to prevent FeS formation is relatively larger at low sulphur contents than at high ones. It has also be shown that the penetration of the grain boundaries by FeS[16], as indicated by dihedral angle measurements, is much greater than that by MnS and more-over seems to be greatest at a Mn:S ratio of $\sim$1.5, at which FeS still forms.

Returning to solubility effects in FeS, a recent investigation[17] has confirmed the evidence of Vogel and Reinbach[18] that there is complete solid solubility between FeS and CrS, despite the apparent dissimilarity in lattice types[4]. However Kiessling[4] does indicate that the CrS structure is related to hexagonal symmetry, and it is perhaps not surprising that mutual solubility with FeS is extensive. The evidence suggests[17] that, as for the case of FeS, CrS has a metal vacancy structure. On the basis of crystal structure similarities, it might be expected that many rare earth sulphides would dissolve in FeS, as also would TiS, ZrS and NbS[4]. Nickel has a very low solubility in FeS, of the order of 1%[16].

(b) Manganese Sulphide - MnS

Manganese sulphide is the normal form of sulphide in many steels, and depending on the Mn:S ratio of the steel and the rate of cooling, it can contain variable and often large amounts

of FeS in solution in the as cast state. Diffusion may then occur during subsequent reheating, to produce MnS which is virtually free from iron. The form of the MnS in cast steels is very dependant upon the degree of deoxidation of the melt. In general, as the degree of deoxidation increases the sulphide morphology changes from the characteristic globular type I, through the "eutectic-like" type II to the angular type III. A high degree of deoxidation is not the sole criterion for forming type III MnS, as other elements are also necessary[19]. In particular carbon seems to be very effective in promoting the angular type III MnS, and this form is common in many cast irons and high C-Cr steels[20].

Many explanations have been given for the mechanism of formation of these different MnS morphologies[2] [19] [21-24]. Because of the controlling influence of oxygen on the formation of MnS, it is necessary to consider not only the Fe-Mn-S ternary system, fig. 3, but also the Fe-Mn-S-O quarternary system, fig. 4. A recent interpretation of the reactions involved indicates the following modes of formation:-

(i) Type I MnS occurs by precipitation from the molten steel by a monotectic reaction, the MnS formed first having a higher oxygen content than that formed at a later stage during solidification. The inclusions form by the rejection of liquid rich in sulphur and oxygen, and even when the matrix of the steel is solid they are still liquid, and occur in the interdendritic regions. Because of their formation via an oxygen rich liquid, type I MnS is frequently associated with oxide but there is little clear evidence that the MnS contains oxygen in solid solution. The oxygen is generally assumed to occur as MnO in a ternary eutectic with iron and MnS.

(ii) Type II MnS has traditionally been regarded as a

eutectic form, but is now regarded as a co-operative monotectic in which the MnS is precipitated as a liquid. The morphology however, which is in the form of branched rods or fan-like structures constrained between adjacent dendrites, has many similarities with a eutectic, and it would only require the melting point of the steel to be depressed by alloying for a true eutectic to occur. The role of deoxidation in moving the alloy composition nearer to the Fe-MnS psuedo-binary edge of fig.4 can readily explain the observed microstructure.

(iii) Type III MnS has an angular nature, which has been shown to be of octahedral form, in keeping with the f.c.c. structure. Again the particles precipitate interdendritically, and their morphology indicates that they are precipitated as solid from the residual melt. There is some uncertainty as to their mechanism of formation, some workers believing them to be a divorced eutectic brought about by the depression of the freezing point of the steel by the alloying elements so necessary for their formation[19], whilst others[21] consider that the eutectic in the Fe-MnS pseudo binary is moved by the alloying additions nearer to the iron corner of the diagram in fig. 4 so that the type III MnS forms as a solid pro-eutectic constituent. Some support for the latter mode of formation is provided by the fact that in cast irons and 1% C-Cr steels[20], the type III MnS is frequently in the form of skeletal or "anchor" shaped particles, typical of a primary crystallisation, and that the skeletal crystal gradually fills in to assume the octahedral form. Mohla and Beech[23] show clear evidence for this, and a similar sequence of crystallisation for octahedral chromite inclusions has been illustrated by Waudby[25]. A recent paper[19] has however

identified certain objections to this hypothesis, namely the lack of any elimination of type III MnS by flotation and the inability to change type II to type III merely by increasing the sulphur content. Again it has not been possible to show positively that type III MnS contains less dissolved oxygen than either types I or II.

Manganese sulphide is readily deformed during hot working. It has the ability not only to deform less readily than the steel matrix[26, 27] but also the plasticity relative to the matrix increases with decreasing hot working temperature and decreases with increasing deformation. There is some uncertainty regarding the relative plasticities of types I, II and III MnS. Some work has indicated that they all deform to virtually the same extent when the differences in particle size and matrix plasticity are taken into account[28], but there is a widely held opinion[21] [26] that the plasticity increases as one moves from type I to type III. It has been suggested that this is due to oxygen in solution hardening type I MnS[26], but in view of the lack of positive evidence for this it may be that the MnS is dispersion strengthened by very small oxide particles. The low plasticity of type I MnS is utilised in the production of free cutting steels, in which type II MnS is most detrimental, but this very generally accepted observation may be open to some doubt[29]. Also open to doubt may be some of the plasticity data on type II MnS, due to the fact that the initial morphology is vermiform rather than equiaxed, but there is little doubt that during hot deformation the type II MnS forms arrays of nearly coplanar ribbons which are most detrimental to transverse mechanical properties.

Being f.c.c. in structure, many sulphides are extensively soluble in MnS. Kiessling[4] [30] [31] has shown both the solubility of varying alloying elements in the first transition period in MnS, fig. 5, together with the effects produced on the hardness of the MnS, fig. 6. The additions which harden MnS appreciably might be expected to decrease its plasticity, but there is no apparent relationship between the hardness and the

melting temperature. Although the effects shown in figs. 5 and 6 were observed on synthetic sulphide melts, experience on inclusions occurring in steels has confirmed the general solubility effects which are indicated[32]. For example, nickel has been observed to have a very limited solubility in MnS in steels. Also, chromium, the partial ternary diagram for which is shown in fig. 7, has been found to produce a much more extended solubility range between MnS and CrS than indicated by figs 5 or 7, as shown in Fig. 8. This tends to be in agreement with the work of Payet and Leveque[33], who found complete solubility between MnS and CrS. The presence of large amounts of chromium in MnS also produced a metal vacancy structure in the MnS, up to 20% vacancy concentration being observed[32] which is in good agreement with the 25% vacancies observed by Kiessling[4]. So great was the metal deficiency that the composition approximated closely to that of the double sulphide $MnS.Cr_2S_3$, observed by some workers[4], [34] [35] [36], but no X-ray evidence for this spinel type double sulphide was obtained. It should be noted however that a relatively low manganese content, ~3%, can virtually eliminate chromium from solution in the MnS[33]. Frequently the chromium rich MnS, for example in stainless and C-Cr steels, is idiomorphic type III in morphology. This is not due to any increase in the melting point of the sulphide, the reverse actually being the case, but rather due to the general effects discussed previously.

It has also been shown that CaS and MnS are isomorphous and both calcium and magnesium can dissolve in MnS, but there does not appear to be complete mutual solubility[20] [37]. This is to be expected in view of the great difference in ionic size between calcium and manganese. Up to 19% Ca can replace Mn in MnS.

The dihedral angle of MnS is much greater than that of FeS[16] and thus there is little tendency for MnS to penetrate along grain boundaries. The replacement of manganese by chromium in MnS causes a marked increase in the dihedral angle,

and a similar but smaller effect is observed for the small solubilities of nickel in MnS.

(c) Calcium Sulphide - CaS

Calcium sulphide is a much more stable phase than MnS, and thus should form preferentially to MnS when calcium bearing deoxidants are used. Because CaS is less stable than CaO, the steel should preferably be deoxidised by aluminium prior to the calcium addition. There are many difficulties associated with the use of calcium, because of its very low solubility in steel and its high vapour pressure (1.6 atmospheres at 1600°C)[38], but the more recently developed barium containing calcium deoxidants have tended to overcome these problems.

When calcium is added effectively to steel, the stable CaS can be formed as isolated idiomorphic particles. It is however relatively uncommon to form pure CaS in steels, and frequently the CaS contains manganese[20] [39] or even magnesium[4] in solid solution. The most common mode of occurrence of CaS is as a peripheral phase around inclusions comprising one or more forms of calcium aluminate[4] [20] [39].

Contrary to one view expressed in the literature[40], CaS and MnS do not form a complete solid solution series. There is considerable agreement[20] [37] that calcium is more soluble in MnS than is manganese in CaS, although at temperatures above 1200°C there is some indication of more extensive, and possibly complete solid solution[37]. A summary of the observed mutual solubilities of CaS, MnS and FeS in 1% C-Cr steels is shown in Fig. 9.

It is reported that CaS is less readily deformed than MnS during hot working[4], and thus does not form the elongated sulphides which are detrimental to mechanical properties. There is no data on the plasticity of CaS in steel, and because the CaS may well be supported by associated calcium aluminates, this

could well give a low apparent plasticity. CaS does however have a very high melting point of about 2500°C.

(d) Other Sulphide Phases in Steels.

Kiessling[4] has reviewed available data on many sulphides, and it is not possible in the present paper to summarise all this information. Attention instead will be focussed on those sulphides formed by the recently developed inclusion shape control additions[5][41].

(i) Zirconium Sulphide.

Zirconium forms a more stable sulphide than manganese and thus tends to displace manganese from MnS to form inclusions of the type (Mn Zr)S[41] which are much less plastic than MnS and thus do not elongate into undesirable stringers. There is evidence[42] that with large zirconium additions, a ZrS phase with a hexagonal structure can be formed. However, it has been shown that with too great a zirconium addition, undesirable phases from the point of view of mechnaical properties, i.e. ZrC and $Zr_4C_2S_2$, can be formed[41] [43]. The plasticity of the (Mn Zr)S decreases as more zirconium dissolves in the MnS, up to a maximum of about 12% Zr replacing manganese[44]. With this maximum replacement of manganese by zirconium, the sulphide is completely undeformable. No quantitative data on the plasticity of (ZrMn)S appears to have been determined. In order to achieve this optimum sulphide inclusion shape control, the zirconium must be added in sufficient quantity to combine with the nitrogen in the steel and yet leave sufficient to give adequate reaction with the sulphur.

The interesting feature is that eutectic type II sulphides are not formed, and it may be that the zirconium so increases the melting point of the MnS that isolated sulphides are formed, possibly directly from the melt during solidification. In general, however, the (Mn Zr) is believed to follow metal solidification. Various authors[45] have claimed to show zirconium sulphides in

steel, but the positive identification of these phases may be open to question.

(ii) Titanium Sulphide

It has been known for some time that titanium additions, for example to stainless steels, could prevent the formation of MnS, but little systematic work has been done on this subject in contrast to the attention given to zirconium additions. Considerable use has been made of titanium additions in the U.S.S.R., but only recently have steels microalloyed with titanium been introduced commercially in Europe.

Titanium can form a number of sulphides, which have hexagonal structures, and several of which are of the general form $Ti_{(1\pm x)}S$ with either metal or sulphur vacancies[46]. In this it resembles zirconium, but the data shown in fig. 5 indicates that it dissolves to a smaller extent in MnS than does zirconium. Because of its greater affinity for nitrogen than for sulphur, enough titanium must be added to combine with the nitrogen and leave sufficient for sulphide modification, and to achieve predictable recoveries the steel should preferably be killed prior to the titanium addition. The mechanism by which titanium alters the sulphide morphology seems to be uncertain and direct substitution for manganese is not yet proved, although such substitution would probably be small. A titanium sulphide may form, but most probably a carbo-sulphide is formed of the Y-phase type[47]-[51], namely $(FeMnTi)_2(CS)$. This phase exhibits very little plasticity when present in titanium stabilised stainless steels, but may cause embrittlement if it forms at grain boundaries, as does the zirconium carbo-sulphide.

Mention may also be made of the possible use of hafnium to modify MnS, but little is known of its sulphides which will probably parallel in general terms those of zirconium. Similar effects might also be expected from vanadium and niobium additions, which also form $M_{(1\pm x)}S$ sulphides, but their stability is not

great and there is no real evidence that they occur in current structural steels containing small niobium or vanadium additions.

(iii) Rare Earth Sulphides

The rare-earth lanthanides have high affinities for oxygen, carbon, nitrogen, hydrogen and especially sulphur, cerium sulphide being even more stable than calcium sulphide. All the lanthanide sulphides and oxy-sulphides have melting points higher than 1800°C[4], and should therefore be ideal for producing modification of manganese sulphide to a non-deformable type, even at the highest hot working temperatures. Recent work[44] has shown that in steels treated with rare-earths, there are several different forms of rare-earth sulphide. The major sulphide appears to be MeS containing sulphur vacancies, which has a tendency to segregate into bands. Other work,[52] believes the major phase to be Me_2S_3 when full modification is achieved.

Care is required in using rare-earth additions, due to their reactivity and variable recovery, coupled with the tendency to segregate, which may offset any benefit from the sulphide modification. The steels should be deoxidised prior to the rare-earth addition. As far as is known, the mechanism of sulphide modification by rare-earths is one of replacing the MnS by the rare-earth sulphide, although Kiessling[4] states that there should be some mutual solubility between rare-earth sulphides and the sulphides of manganese, iron and calcium. Currently there does not seem to be any clear evidence for the rare-earth metals replacing manganese in MnS[53].

Recent evidence[41] indicates an optimum rare earth : sulphur ratio of $\sim$ 2.0 for inclusion modification, but above this optimum ratio deleterious carbides or even low melting point intermetallic compounds, Fe_5Ce or Fe_2Ce, are formed as interdendritic segregates which persist during hot working.

Because of their not too great affinity for nitrogen, the

rare-earth additions can be used for sulphide modification in steels which owe their properties to vanadium nitride precipitation, in which case neither zirconium nor titanium can be used.

Oxides in Steels

Oxides in steels occur in four main types, namely simple metal oxides, silicates of many various forms, spinels and a variety of calcium aluminates.

(a) Metallic Oxides

(i) Iron-Manganese Oxide - (FeMn)O

The predominant oxide of iron or manganese in steel is (FeMn)O, which occurs in rimming steels. FeO (Wüstite) and MnO (Manganosite) form a continuous series of solid solutions. FeO forms as spherical particles by the precipitation of a liquid FeO rich phase in the miscibility gap of the Fe-O system, fig. 10, and occurs either as large particles in Fe-O alloys containing more than 0.16% O_2 or as a network of globules between the iron dendrites in lower oxygen alloys. Frequently, the Wüstite particles contain iron particles within them[54] [55], probably due to the rejection of iron from the liquid FeO during cooling. At lower temperatures, $\sim 560^{\circ}C$, FeO should breakdown to iron and Fe_3O_4 by a eutectoid reaction, but this reaction is seldom observed in inclusions.

MnO occurs as a translucent idiomorphic or dendritic phase[55], which precipitates directly from the liquid metal because of its high melting point of $1850^{\circ}C$, but the more normal occurrence is of the (FeMn)O solid solution which is usually a single phased globule. Occasionally however, a two phased inclusion is observed in which a central MnO rich phase is surrounded by a peripheral FeO rich phase. These are non-equilibrium inclusions in which the solid MnO phase

formed whilst the metal was still molten has acted as a nuclei for subsequent precipitation of a more FeO rich phase during solidification. The cooling conditions have been such that diffusion to form the solid solution indicated by the equilibrium diagram has not occurred to the required extent.

(ii) Silica - SiO_2

Silica can occur in three forms[56] quartz, tridymite and cristobalite. Quartz is rarely observed except in exogenous inclusions of sand or refractory origin, but tridymite has been observed as lath-like crystals in exogenous[56] and also in certain highly siliceous deoxidation products[57]. The occurrence of cristobalite has often been reported [3] [56] [58] [59] to occur as dendrites or rosettes within highly siliceous deoxidation or exogenous products. More recently however, it has been shown that these phases are not crystalline, but are a very highly siliceous liquid phase[60]. In fact, the more general mode of occurrence of silica is as a highly siliceous, very transparent spherical particle. The solubility of silica for many of the other oxides common in non-metallic inclusions in steel is very limited, and thus frequently a glassy, highly siliceous phase is associated in complex inclusions with a wide variety of other phases.

(iii) Alumina - Al_2O_3

The crystalline form of alumina, corundum (α - Al_2O_3), is the usual form observed. It can occur in a number of morphologies, but because of its high melting point (2050°C) it is always as a primary crystallisation. Generally, when formed by deoxidation it is observed as clusters or groups, which have been shown to comprise one particle [3] [61] [62] and to occur as:-

(a) A dendritic form showing a very large skelatal network,[61] [63] [64] [65] which usually forms at high degrees of supersaturation.

(b) A globular cluster[64] [65], often occurring at low supersaturations, in which the individual particles appear to be sintered together. This latter form has been shown to be produced by the simple sintering of alumina particles[66], but other authors believe they can occur by simple collision between isolated particles in the molten steel[67]. More recently, this type of alumina aggregate has been shown to originate also from nozzle blockage deposits[68] [69].

Isolated alumina inclusions are less common than clusters, but can occur in the as cast condition possibly due to the mechanical fracture of the clusters. In the hot worked condition, isolated particles are often observed due to dissemination of the particles within the alumina stringers, which themselves originate from clusters.

Quite massive alumina particles have been observed to originate from refractory erosion[59], and alumina is a frequent constituent of multiphased particles of exogenous origin. Also, because alumina is solid at steelmaking temperatures, it can act as a nucleus for deoxidation products in which case it may not be related to the constitution of the deoxidation product itself[59]. Finally, alumina 'rings' can be formed by the reaction between dissolved aluminium in the steel and pre-existing less stable (FeMn)O or silicates[3][70]. These are typical of aluminium treated semi-killed steels. Space does not permit the consideration of the liquid $FeO-MnO-Al_2O_3$ phases which form intermediate to the Al_2O_3 during the deoxidation of steel by aluminium, but reference should be made to the relevant literature[71-73].

Corundum is hexagonal and has complete mutual solubility with other oxides of the M_2O_3 type. This is rarely observed in steels due to the very great deoxidising power of aluminium.

The β-Al_2O_3 form has not been reported in steels, but the γ-Al_2O_3 has many similarities with the spinels which will be considered later, and also with the most alumina-rich calcium aluminate, $CaO.6\ Al_2O_3$.

(iv) Other Oxides

The inclusions formed by deoxidation with chromium are complex[74]-[77]. In chromium steels, the main oxide is the spinel chromite, $FeO.\ Cr_2O_3$, but with increasing chromium content a distorted spinel structure is obtained. With more than 9% Cr, Cr_3O_4 is observed and disproportionates into Cr_2O_3. Recent studies have tended to confirm the above general sequence[78], and indicate that for deoxidation of Fe-O melts by chromium, the following sequence is observed:-

$$\underset{\text{Spinel, } Cr<2.5\%}{FeO.\ r_2O_3} \longrightarrow \underset{\substack{\text{Distorted Spinel,}\\ 2.5\%<Cr<8.0\%}}{(Fe\ Cr)\ O.Cr_2O_3} \longrightarrow \underset{\substack{\text{Distorted Spinel,}\\ Cr>8.0\%}}{(Cr\ Fe)O.Cr_2O_3}$$

An investigation of titanium oxides[79] has shown that four titanium oxides can occur in Fe-O melts deoxidised by titanium, namely TiO, α-Ti_2O_3, Ti_3O_5 and TiO_2 (rutile). In addition ilmenite ($FeO.TiO_2$) and a spinel were also observed, and a number of these frequently occur as spherical but polycrystalline inclusions. Of these, three forms of titanium oxides have been observed in steels, especially in titanium stabilised stainless steels or titanium treated carbon-manganese steels[80]. TiO_2 occurs as a spherical, relatively non-deformable phase. Ti_2O_3 occurs as small clusters, and is very characteristically twinned as well as exhibiting clearly identifiable pleochroism. Ti_3O_5 is rather similar to Ti_2O_3 but shows characteristic twinning or faulting under polarised light.

(b) Spinels - $MO.\ M_2O_3$

Spinels are a common phase in non-metallic inclusions in steel, and cover a number of specific spinel phases in particular, although extensive mutual solubility occurs between all the spinels[56]. The specific spinels which are commonly found are

Hercynite ($FeO.Al_2O_3$), Galaxite ($MnO.Al_2O_3$), Chromite ($FeO.Cr_2O_3$), Chrome Galaxite ($MnO.Cr_2O_3$) and Spinel ($MgO.Al_2O_3$). The spinels $FeO.Al_2O_3$ and $MnO.Al_2O_3$ can occur as direct deoxidation products[81], forming small plates or clusters of particles rather similar to alumina in general form. Galaxite in particular is often observed in deoxidation products formed by incomplete aluminium deoxidation of a previously killed silicon steel, and often forms dendrites within a globular silicate in the as cast condition[3]. As when other non-deformable inclusions occur within a plastic silicate matrix[82], the presence of galaxite in a silicate tends to decrease its plasticity during hot working, by a mechanical support mechanism. Hercynite, on the other hand, is frequently observed together with FeO during the deoxidation of Fe-O melts by aluminium, but is not a common phase in steels due to the presence of manganese which invariably leads to the formation of galaxite. Recent work[83] has also enabled the interfacial energy between hercynite and FeO to be established (873 dynes/cm^2 at 1150°C).

In chromium and stainless steels, the chromite spinel is very frequently observed either as isolated angular idiomorphs, or as groups of such crystals or skeletal networks. The skeletal crystals are simply the early stage of formation direct from the melt, infilling of the skeletal structure resulting in octahedral chromite particles[83]. Chromite dendrites are also observed to precipitate from silicates formed at very high temperatures[59].

Spinel, ($MgO.Al_2O_3$), inclusions usually form from slag particles which have reacted with aluminium in the steel. They thus are invariably associated with calcium aluminates, the MgO in the slag forming $MgO.Al_2O_3$ which can be present either as angular particles or as dendrites within the calcium aluminate inclusion[4] [20] [59]. Occasionally groups of, or isolated, spinel particles are observed. There is virtually no mutual solubility between $MgO.Al_2O_3$ and the calcium aluminates.

As can be seen from some of the relevant phase diagrams, spinels often exhibit a wide range of solubility about the stoichiometric composition, figs 11-13. Kiessling[4] has shown that hercynite and galaxite most frequently occur on the Al_2O_3 side of stoichiometry, and a similar effect was observed for spinel itself, $MgO.Al_2O_3$, fig. 14[20].

(c) Silicates

Such a wide variety of silicate inclusions occur in steels that it is not possible in this review to discuss all the types which are observed. Attention will therefore be concentrated on some of the more common silicate types.

(i) Iron-Manganese Silicates

The relevant $FeO-MnO-SiO_2$ phase diagram is shown in Fig. 15. The iron and manganese silicates are frequently formed by deoxidation reactions and can show (FeMn)O globules or dendrites in a glassy or crystalline silicate matrix. Depending on the composition of the silicate, eutectics between (FeMn)O and the olivine solid solution series, $2(FeMn)O.SiO_2$ can be observed, or primary laths of fayalite, $2FeO.SiO_2$, or Tephroite, $2MnO.SiO_2$, can be formed. The mono-silicate Rhodonite, $MnO.SiO_2$, is but infrequently observed and the unstable counterpart Grunerite, $FeO.SiO_2$, has not been reported. With higher SiO_2 contents in the silicate, two glass phases representing compositions within the miscibility gap are sometimes observed[84]. Depending on the cooling rate, the type of inclusion in which there is no (FeMn)O phase may be either crystalline or glassy. Reheating the glassy form for hot working can then result in the crystallisation of the silicate phases.

(ii) Aluminium Silicates

Aluminium silicates are seldom encountered in steel because of the invariable presence of iron and manganese. The $Al_2O_3-SiO_2$

phase diagram is shown in fig.16 from which it can be seen that Mullite, 3 Al_2O_3.2 SiO_2, is the only silicate phase present. This phase can frequently be seen as needles in an otherwise glassy silicate matrix in certain deoxidation products, but more usually where reaction has occurred between iron-manganese silicates and aluminium dissolved in the steel[59][85], or in inclusions of an exogenous origin resulting from refractory erosion.

(iii) Calcium and Magnesium Silicates

The CaO-SiO_2 phase diagram is shown in fig.17. Many calcium silicates can form, but apart from being constituents observed in slag inclusions, they are seldom observed in steels. Kiessling[56] however reports that a CaO.SiO_2 type of inclusion is common in steels deoxidised by calcium silicide, but this observation may be open to doubt as the calcium is very difficult to introduce into the steel, and invariably some aluminium will also be present in the silicate. In fact, deoxidation silicates resulting from calcium bearing deoxidants frequently contain MnO and Al_2O_3 in the calcium silicate, and are often glassy in nature. They can however form a number of silicate phases if they crystallise during reheating.

There are two silicates of magnesium, enstatite MgO.SiO_2, and forsterite, 2 MgO.SiO_2. Neither occur with any frequency in steels, but may be present in complex erosion products involving slag attack[56].

(iv) Complex Silicates

Many of the silicates which occur in steels are complex, comprising the oxides SiO_2, FeO, MnO, Al_2O_3, CaO and MgO in varying combinations. These silicates can be either glassy or contain varying assemblages of crystalline phases depending on their composition, mode of formation and approach to equilibrium. In addition, the inclusions may contain particles of a pre-existing solid phase on which they have nucleated, or phases from the refractory materials which are the source of many exogenous

inclusions. It is not likely that these mechanically included particles will be in equilibrium with the main body of the inclusion. The origins of these complex silicates may also be very varied in that they may form due to deoxidation by complex deoxidation alloys, or by sequential or simultaneous deoxidation by single element deoxidation alloys. They may also result from erosion of refractories with or without the assistance of slag attack, or they may be simply due to mechanical entrapment of such steel making additions as mould fluxes, exothermic feeder head compounds, etc. Finally they may result from atmospheric oxidation of liquid metal streams.

Because of the great variability in these complex silicates, an attempt will be made to systematise the silicate phases which may be formed in terms of a few major types. The ternary phase diagrams to which many of the inclusions may be referred are $FeO-SiO_2-Al_2O_3$, $MnO-SiO_2-Al_2O_3$, $CaO-SiO_2-Al_2O_3$ and $MgO-SiO_2-Al_2O_3$. These are shown in figs 18-21. It can be seen that there are a number of groups of common phases:-

(a) The pyroxenes which comprise rhodonite ($MnO.SiO_2$), enstatite ($MgO.SiO_2$) and the iron mono-silicate, grunerite ($FeO.SiO_2$) which requires some manganese to stabilise it. In these phases there is considerable mutual solubility, as there also is with diopside $CaO.MgO.2\ SiO_2$ which may be regarded as a solid solution of $CaO.SiO_2$ and enstatite. These phases form characteristic lath-like crystals.

(b) The olivines, which comprise forsterite ($2\ MgO.SiO_2$), fayalite ($2\ FeO.SiO_2$) and tephroite ($2MnO.SiO_2$) but not di-calcium silicate because of the large ionic size of Ca^{++} These phases all show complete mutual solubility and can dissolve up to 50% CaO. They crystallise in a typical lath-like habit, but often a remnant skeletal structure is apparent.

(c) The garnets, which comprise spessartite (3 MnO.

$Al_2O_3.3\ SiO_2$), almandine ($3\ FeO.Al_2O_3.3\ SiO_2$), pyrope ($3\ MgO.Al_2O_3.3\ SiO_2$) and grossularite ($3\ CaO.Al_2O_3.3\ SiO_2$). Neither the Magnesium or Calcium garnet phase appear on the liquidus projection of the relevant ternary system. All these phases however show virtually complete mutual solubility, and crystallise in a characteristic feathery habit.

(d) The felspars which comprise anorthite ($CaO.Al_2O_3.2\ SiO_2$) and manganese anorthite ($MnO\ Al_2O_3.2\ SiO_2$) and which can extensively dissolve in each other and take into solution quantities of FeO or MgO replacing MnO or CaO.

(e) The cordierites which comprise the phases cordierite ($2\ MgO.2\ Al_2O_3.\ 5\ SiO_2$) and its iron and manganese equivalents, all of which show extensive mutual solubility.

All these phases have been identified in complex silicates together with other silicates such as gehlenite ($2\ CaO.Al_2O_3.SiO_2$) and ackermanite ($2\ CaO.MgO.2\ SiO_2$). However, to identify a specific phase in a complex silicate simply on the basis of micro-probe analytical results requires care due to the often extensive mutual solubilities and the wide spread of composition about stoichiometry. Similarly the identification of a glassy phase with a named crystalline phase simply on the basis of composition, should be avoided.

(d) Calcium Aluminates

Calcium aluminates are common inclusions in many basic electric arc steels[20] [39] and can be produced by a number of mechanisms such as reaction between basic slag inclusions and aluminium dissolved in the steel[20] [59], deoxidation with calcium silicide and aluminium, or the use of the complex barium

containing calcium-aluminium deoxidants, and modification of alumina inclusions by the barium containing calcium-aluminium deoxidants.

Much work has been published on the effects of the use of calcium deoxidants[40] [86-92], and in some cases the results show discrepancies. The object of much of this work has been to replace alumina clusters and stringers by less injurious widely disseminated calcium aluminates and, as already discussed, to modify the sulphide inclusions. Calcium, when added as aluminium containing calcium silicide, or calcium-aluminium-manganese alloys is a difficult addition to control, particularly in carbon and low alloy steels. The reasons for this are the very low solubility of calcium in liquid steel[38], its high vapour pressure of 1.6 atmospheres at 1600°C, and the fact that many calcium alloys have a low density and thus float to the top of the ladle and react with air. The calcium is thus often lost by vaporisation and reaction before it has time to dissolve and act as a deoxidiser.

It has been observed that calcium is more predictable as a deoxidant in stainless steels [86] [87] [88], the reason apparently being that nickel, and aluminium and silicon, considerably increase the solubility of calcium in steel[38]. It seems advisable to pre-deoxidise the melt prior to the calcium addition. More recently the use of barium and silicon in the calcium deoxidation alloys has been shown to lower the activity of calcium and its vapor pressure so that better control over the addition is achieved[40]. It is also suggested that aluminium and calcium added together cause calcium aluminate films to be formed around the dissolving deoxidant, and having a relatively low melting point the calcium aluminate film collapses and so allows the calcium and aluminium to diffuse into the steel. On the other hand if the calcium and aluminium are added separately, solid films of CaO and Al_2O_3 form around the calcium and aluminium rich areas respectively and retard diffusion of the deoxidants.

Recent work[93] has shown that when aluminium bearing calcium silicide is added to an iron-oxygen melt, the calcium rapidly boils off before it can participate in the reactions. Consequently only alumina or aluminium silicates are formed depending upon the aluminium content of the deoxidant. Large amounts of calcium silicide are required before calcium aluminium silicates or calcium aluminates are formed. On the other hand the barium containing deoxidants can readily give calcium aluminates containing up to 30% CaO.

In order to obtain a more reproducible recovery of calcium, the calcium deoxidant may be added after a prior aluminium deoxidation. The calcium can then modify the alumina inclusions, causing the aggregates to be replaced by calcium aluminates. In fact the calcium addition seems to be protected by the prior aluminium addition for the reasons already outlined. Because CaO is even more stable than Al_2O_3, and has a lower solubility product, some CaO will be precipitated, probably on the surface of the alumina particles. Both oxides are solid at steelmaking temperatures and any reaction to form calcium aluminates might be expected to be slow. As shown from the CaO - Al_2O_3 phase diagram, fig. 22, some of the calcium aluminates have low melting points and thus a liquid layer probably forms on the surface of the alumina particles which acts as a sink which dissolves both Al_2O_3 and CaO, thus allowing modification to form calcium aluminate to proceed rapidly.

As shown in fig. 22, a series of calcium aluminates can be formed, and work has been done to investigate the range of compositions for each of the calcium aluminate phases[20]. The results are shown in fig.23, from which it can be seen that there can be quite appreciable departures from stoichiometry. It has also been shown that calcium aluminates can crystallise from very low silica melts. As indicated by Fig 20, the higher the Al_2O_3 : CaO ratio in the calcium aluminate, the greater the SiO_2 content of the silicate melt with which it is in equilibrium[20].

Very little quantitative data has been obtained on the plasticity of the various calcium aluminates during hot working. However, there are indications that CA_6, having a γ-Al_2O_3 structure, forms clusters of particles rather like alumina or spinel and is equally non-deformable. The calcium rich aluminates also polish more readily in stainless steel, and thus give rise to fewer line defects, whereas the harder more refractory spinels, alumina and calcium aluminates may be more detrimental in this respect[94].

Other Inclusions

A group of inclusions, which together with the manganese sulphides, are most important in free machining steels are those produced by additions of lead, selenium and tellurium.

(a) Lead

Lead, whilst having some degree of solubility in liquid steel, may be regarded as virtually insoluble in solid steel. In the as cast condition, it has been shown[95] to occur as separate particles which apparently form from the last liquid to solidify in the interdendritic regions, but not necessarily in contact with the MnS. In the hot rolled condition, however, a very intimate association is observed between the lead and the MnS, there being lead tails at the ends of each sulphide inclusion. When tellurium is added, thephase PbTe can replace lead. It has also been noticed that there can be a close association between lead and complex silicate inclusions.[96]

(b) Selenium

Selenium is chemically similar to sulphur and there is complete mutual solid solubility between MnS and MnSe[4]. Thus the inclusions in a low sulphur steel treated with selenium are MnSe but with increasing sulphur content more towards Mn(SeS). MnSe is reported to be much softer than MnS.

As for the α-MnS structure, the α-MnSe phase has extensive solubility ranges for various substitutionally dissolved elements replacing manganese. A study of these effects[4][97] has shown that the solubility of the first period transition metals in MnSe, and their effects on the hardness, parallel closely the effects observed in MnS, compare figs.24 and 25 with Figs. 5 and 6.

(c) Tellurium

The addition of Tellurium to a leaded high sulphur steel can produce a complex series of phases which co-exist in association with each other.[98] Besides MnS, in which it is reported that there is a small solid solubility of Te[27], the phases PbTe, MnTe and FeTe can be formed. PbTe has a wide range of composition on either side of stoichiometry[99-101] which extends probably from about 20% Te to more than 50% Te. There is also complete solubility between PbTe and PbS at temperatures above 800°C, but very restricted solubility below 400°C,[102] so that in steels heated for rolling some sulphur might be expected to dissolve in the PbTe. PbTe melts at 922°C and forms a eutectic with iron at about 870°C.[103] Consequently there are some low melting point constituents which might give rise to hot working problems, particularly as the minimum melting point in the PbS-PbTe system is at about 875°C.[102] It has been shown that MnTe can depart from stoichiometry on the manganese-rich side,[98] and there are suggestions that MnTe can dissolve small amounts of sulphur and chromium.[27] MnTe usually occurs as tails to the MnS particles in much the same manner as does lead. Iron telluride shows some departure from stoichiometry on the iron-rich side, and there is no evidence of solubility for manganese,[98] nor does there appear to be much sulphur solubility in the metal tellurides. Kiessling has indicated[4] that there would not be expected to be much mutual solubility between sulphides or selenides and tellurides.

The addition of selenium with lead further complicates the situation, as a lead selenide, PbSe, can be formed[104] which produces low melting point eutectics with lead. The phase relationships between the sulphides, selenides, tellurides and lead, however, require much further work before they can be fully understood.

Conclusions

In this survey of some of the constitutional aspects of the non-metallic inclusions which are commonly found to occur in steel, it has not been possible to do more than highlight what are thought to be some of the more salient features with respect to current steel technology. For further more detailed information, and for examples of the common morphological forms of different

inclusion phases, reference must be made to the many detailed monographs[4][27][56][99][105-108] and to some of the original papers to which reference has been made.

It seems clear however, that a study of the way in which the constitution of the inclusion phases, and the thermo-mechanical treatments of the steels, influence the detailed microstructures of the inclusions, and the inter-relation between these micro-structures and the effects of the inclusions on the properties of the steel, is indeed an enormous and forbidding task. Yet significant progress has been made, and continuing work will no doubt further this. So far, only some of the more readily investigated phenomena are understood. The appreciation of the control of inclusion constitution and morphology, whilst being advanced continually, is not yet sufficiently detailed to allow the metal-ceramic composite which is steel to be designed with a high degree of predictability, at least from the point of view of the non-metallic phases.

References

1. R Kiessling, ISI-BISRA Conference, September 1968, Abington, England.

2. C E Sims, Trans.AIME, 1959, 215, 367.

3. F B Pickering, Jernkon.Ann. 1964, 148, 845.

4. R Kiessling and N Lange, ISI Publication No.100, 1966.

5. M Korchynsky and H Stuart, "High Strength Low Alloy Steels" Lond-Scandinavian Conference, Nurenburg, 1970.

6. J H Little and W L M Henderson, "The Effect of Second-phase Particles on the Mechanical Properties of Steels", ISI, 1971, 183.

7. A Hultgren and B Herrlander, Trans.AIME, 1947, 172, 493.

8. A M Portevin and R Castro, JISI 1953, 132, 240.

9. G Hagg and I Sucksdorf, Z.Phys.Chem. 1933, 22, 444.

10. J Philibert et al. Metallurgia 1965, 72, 203.

11. R Vogel and G W Kasten, Arch.f.d.Eisen, 1948, 19, 65.

12. R Vogel and A Wustefeld, Ibid. 1938/39, 12, 261.

13. R E Lismer and F B Pickering, JISI 1952, 170, 263.

14. H C Chao et al. Trans. ASM 1964, 57, 885.

15. D A Melford, Private communication.

16. W J M Salter, PhD Thesis, London University, 1965.

17. W J M Salter, Private communication.

18. R Vogel and R Reinbach, Archf.d.Eisen 1938, 7, 457.

19. T J Baker and J A Charles, JISI 1972, 210, 702.

20. W J M Salter and F B Pickering, JISI, 1969, 207, 992.

21. W Dahl et al. Stahl v Eisen, 1966, 86, 796.

22. D C Hilty and W Crafts, Proc.Elec.Fce. Steel Conference, AIME, 1953, p.121.

23. P P Mohla and J Beech, The Brit.Foundryman, 1968, Dec. 453.

24. H Fredriksson and M Hillert, JISI 1971, 209, 109.

25. P E Waudby, Private communication.

26. T J Baker and J A Charles, JISI, 1972, 210, 680.

27. R Kiessling, ISI. Publication No.115, 1968.

28. J R Blank, Private Communication.

29. D M Keane, Seminar presented at Sheffield Polytechnic, 1974.

30. R Kiessling and C Westman, JISI 1966, 204, 377.

31. R Kiessling et al, JISI 1967, 205, 531.

32. F B Pickering and W J M Salter - to be published.

33. R Payet and R Leveque, Rev.Met. 1967, July/Aug, 653.

34. L Passarini and M Baccaredda, Atti.Accad,Lincei. 1931, 14, 33.

35. F K Lotgering, Phil.Res.Rep. 1956, 11, 190.

36. C W Kovach et al. Trans.ASM 1968, 61, 575.

37. R Kiessling and C Westman, JISI 1970, 208, 699.

38. D L Sponseller and R A Flinn, Trans.AIME, 1964, 230, 876.

39. C P Church et al, J.Met. 1966, 18, 62.

40. D C Hilty and V T Popp, AIME Electric furnace Conference Proceedings, 1969, 27, 52.

41. J H Little and W L M Henderson, "The Effect of Second Phase Particles on the Mechanical Properties of Steels", ISI, 1971, 183.

42. V S Kovalenko, Stahl in English, 1964, 2, 136.

43. V L Meyer et al. Thyssen-forschung, 1971.

44. J Arrowsmith, Private communication.

45. H Kaneko et al. J.Japan.Inst.Met. 1963, 27, 299.

46. F Jellinek, Archiv.Kemi. 1963, 20, 447.

47. J F Brown et al. Metallurgia, 1957, 56, 215.

48. K Wetzlar and G Lennartz, D E W Tech. Ber. 1961, 1,.15.

49. C Frick et al. Arch.f.d. Eisen, 1960, 31, 419.

50. O Khop, Metallurgia, 1958, 57, 137.

51. H Kudielka and H Rohde, Z.Kmst. 1960, 114, 447.

52. L Luyckx et al. Met.Trans, 1970, 1, 3341.

53. G Rowntree et al. JISI 211, 83.

54. R E Lismer and F B Pickering, JISI, 1952, 170, 48.

55. F B Pickering, Iron and Steel, January 1957, 2.

56. R Kiessling and N Lange, ISI Spec.Rep. No.90, 1969.

57. F B Pickering - unpublished work.

58. E L Morgan et al. JISI, 1968, 206, 987.

59. F B Pickering, "Production and Application of Clean Steels". ISI, 1972, 75

60. M Hillert and L Hillert, J.Mat. Science 1970, 610.

61. K Torsell and M Olette, Rev.de.Met. 1969, 2, 813.

62. H Knuppel et al, Stahl u Eisen, 1965, 85, 675.

63. R A Rege, E S Szekeres and W D Forgeng, Met. Trans. 1970, 1, 2652.

64. P E Waudby, PhD Thesis, Sheffield Polytechnic, 1974.

65. P E Waudby, Seminar presented at Sheffield Polytechnic 1973.

66. D A Melford - private communication.

67. V Lindborg and K Torsell, Trans.Met. Soc. AIME, 1968, 242, 94.

68. A Kohn et al, "Production and Application of Clean Steels", ISI, 1972, 92.

69. J W Farrell and D C Hilty, Elect.Furnace Conf. Proc. AIME, 1971, 31.

70. P E Waudby - unpublished work.

71. E Plockinger and M Wahlster, Stahl u Eisen 1960, 80, 655.

72. H Straube et al, Archf.d.Eisen, 1967, July 509.

73. E Plockinger, ISI Spec.Rep. No.77, 1963, 51.

74. H Wentrup and B Knapp, Tech.Met.Krupp 1941, 4(11), 237.

75. D C Hilty et al, Trans. AIME 1955, 203, 253.

76. J Chipman, Trans.ASM 1934, 22, 385.

77. H M Chen and J Chipman, Trans. ASM 1947, 38, 70.

78. P E Waudby and G K Allan - unpublished work.

79. F B Pickering, JISI 1955, 181, 147.

80. F B Pickering - unpublished work.

81. R E Lismer and F B Pickering, JISI, 1952, 172, 381.

82. F B Pickering, JISI, 1958, 189, 148.

83. P E Waudby - unpublished work.

84. R E Lismer and F B Pickering, JISI, 1955, 179, 159.

85. P E Waudby et al, JISI, 1973, 211, 486.

86. E J Dunn, New Tech, 1962, 743.

87. A Schoberl et al, Radex Rundschau 1965, 6, 722.

88. A Schoberl and W Holsgruber, Ibid., 1962, 2, 501.

89. A Schoberl et al, Ibid, 1964, 5, 251.

90. M Wahlster et al. Ibid. 1969, 2, 478.

91. E Plockinger et al. Ibid. 1969, 2, 508.

92. J Schoop and K-K. Aschendorf. Ibid. 1969, 2, 495.

93. P E Waudby - unpublished work.

94. J C C Leach, "Production and Application of Clean Steels", ISI, 1972, 105.

95. J R Blank and W Johnson, Steel Times 1965, 191, 110, 148, 176.

96. F B Pickering, JSI Spec.Rep. No.77, 1963, 11.

97. R Kiessling et al. JISI 1967, 205, 531.

98. W J M Salter and F B Pickering, JISI 1967, 205, 973.

99. M Hansen, "Constitution of Binary Alloys", 1958, McGraw Hill.

100. H Endo, Sci.Rep. Tohoku Univ. 1927 16, 209, 1927.

101. V M Goldschmidt, Geochem Verteil 1926 (VII), 1927 (VIII).

102. M S Darrow et al. Trans.Met.Soc.AIME 1966, 236, 654.

103. F Wald and R W Stormont, Trans.Met.Soc. AIME, 1968, 242, 72.

104. D N Seidman, Trans.Met.Soc.AIME, 1966, 236, 1361.

105. T R Allmand, "Microscopic identification of inclusions in Steel", BISRA London 1962.

106. E M Levin et al. "Phase diagrams for Ceramists", Amer.Cer. Soc. Columbus Ohio, 1964.

107. F Trojer, "Die oxydischen Kirstallphasen der Anorganeschen Industri-produkte", 1963, Stuttgart Schweizertbartsche Verlagsbuchhandling.

108. A Muan and E F Osborn, "Phase Equilibrium among Oxides in Steelmaking", 1965, Reading Mass. Addison-Wesley.

LECTURE 5

SOME ASPECTS OF THE PLASTICITY OF INCLUSIONS DURING THE DEFORMATION OF STEEL

INTRODUCTION

During any form of hot or cold working, the inclusion content, size and type has an effect on the ease of deformation and also on the mechanical properties of the steel.[1-10] Of these, the fatigue properties[1-2] and the transverse ductility and impact behaviour are often the most sensitive to these detrimental effects. The behaviour of an inclusion during hot working depends very much on the plasticity of the inclusion itself, the relative plasticity of the various phases within the inclusion, and the plasticity of the inclusion relative to that of the steel matrix. The frictional forces at the inclusion/matrix interface also play a part in the deformation of the inclusion, as does the temperature of hot working.

Thus the plasticity of the inclusion, compared with the plasticity of the steel matrix, has a strong influence on the behaviour of the steel. If the steel matrix and the inclusions are not deforming together during all the steel-working operations, the inclusions will be a potential source of future defects in the finished product. In contrast, inclusions may also enhance steel properties, such as machinability, by their ability to participate in the plastic flow of the steel phase. If much more was known about the behaviour of the different inclusion types during different steel forming operations, the composite product of steel/inclusions could be more closely tailored to the different mechanical working operations, such that considerable advantages could be achieved[3]. For example, it is well known that at low temperatures, silicate inclusions are relatively non-plastic and fracture rather than deform, but at higher temperatures they become very plastic and frequently can have the same or greater plasticity than the steel matrix in which they are embedded[11]. The fracture and/or plasticity of the silicates during hot working largely controls their morphology and distribution, and therefore their effect on the properties of the steel. There is, however, relatively little quantitative data available on the plasticity of inclusions, but

what is available clearly shows that in the case of silicate inclusions, there is a temperature, θ_c, above which the plasticity increases markedly, Fig.1. It has also been shown[3] that this temperature is quite sensitive to the composition of the silicates. The aim of this chapter, therefore, is to describe some of the main features controlling the plasticity of silicate inclusions and the formation of voids and cracks. In addition, brief consideration has been given to work on the deformation of manganese sulphide inclusions.

FACTORS CONTROLLING THE FRACTURE OF SILICATES

The mode of fracture of silicate inclusions at low temperatures during hot working is governed to some extent by the initial shape of the inclusion. In as-cast material, the silicates are usually spherical and frequently fracture along the direction of maximum shear stress, i.e. at 45° to the rolling direction, Fig.2(a). It is fairly common to find that they fracture more or less diametrically, but fracture may also occur away from the diameter and the smaller fragments frequently rotate so as to present a streamlined shape to the flow of the metal, Fig.2(b). In other circumstances, small fragments can be observed to chip off the main silicate inclusion, and to spread out down the direction of flow of the metal, Fig.2(c), forming a discontinuous stringer of the broken silicate fragments. The presence of second phase particles within the silicate can also have a pronounced effect on the mode of fracture. For example, the presence of spinel or wüstite particles, which are fairly common second phases within silicates, causes fracture to occur along the interface between the silicate matrix and the second phase particles, Fig.2(d). There is no reason to suppose that alumina particles within an alumino-silicate would not behave similarly, although no direct evidence for this has been obtained. Duplex silicate inclusions containing less plastic second phases tend to fracture at lower deformations than single-phased glassy or crystalline particles. The presence of these cracks in silicates, which are not easily filled by metal flowing into them at the low deformation temperature at which they form, is undoubtedly a source of crack initiation during testing or in service.

In general, however, the rolling of an ingot is commenced at a high temperature at which the silicates are quite plastic, so that initially they deform into ellipsoids or elongated, continuous stringers. In rod, bar or billet they are usually cylindrical in section, but in flat rolled products such as plate or strip they take the form of oblate or prolate ellipsoids, or plate-like particles. As the hot working temperature decreases, the silicates frequently become less plastic and even brittle. This is particularly the case in thin section material for which the finishing temperature is low, as in controlled rolled plate steels. If this occurs, the elongated cylinders or plates of silicate begin to crack transverse to the deformation direction, Fig.2(e). At first these cracks are too narrow for the metal to flow into them but if the deformation is further prolonged, or if the material is reheated for further deformation, then metal can fill the spaces between the broken fragments, which themselves move further apart, Fig.2(f). The presence of second phase particles acts in a similar way to that already described for spherical silicates, cracking occurring at the interface between the silicate and the second phase. In a duplex silicate which has been plastically deformed, however, the less plastic phases invariably become segregated towards the inclusion/metal interface, and may even protrude into the metal, Fig.3(a). In such a position they experience very large forces owing to the flow of the metal, particularly at low temperatures when the silicate itself is not deforming. This, together with cracking at the silicate/second phase interface, can cause the harder second phase particles to be torn away from the silicate, Fig.3(a), and disseminated along the flow direction of the metal, giving rise to a discontinuous stringer of the second phase particles which is not associated with the original silicate, Fig3(b).

FACTORS CONTROLLING THE PLASTICITY OF SILICATES

It is evident from Fig.1, that temperature has a major effect on the plasticity of silicates. Other factors, however, are also important.

(a) Reduction During Hot Working

Plasticity values for inclusions relative to the steel are usuad.y greater at low reductions than at high reductions.[3] This has been shown by various workers for wustite[4,9] and sulphide inclusions[5],

and has been confirmed in work for alumino-silicate inclusions. The reasons for the effect are not clearly understood; there is great difficulty in comparing the plasticity of a small amount of inclusion to that of a large amount of steel matrix at very high reductions. A probable explanation of the observed effects is that with large deformations, the inclusions become thinner and thus offer less resistance to the flow of the metal than do the more spherical inclusions present at low deformations. The question is further complicated, however, by the fact that the surface area of the inclusion available for the frictional forces to act upon increases as the reduction increases, but the major part of that surface is parallel to the flow of the metal. Frictional forces, viscous flow in boundary layers at the surface of the inclusion, and interfacial forces at the steel/inclusion interface need to be considered in a full elucidation of this effect.

(b) Particle Size

There is fairly general agreement[3,4,5,9] that small particles are less readily deformed than larger ones. The evidence is mainly confined to (FeMn)O and MnS inclusions, but the results of recent investigations indicate that, in general, the same effect also applies to silicates. The explanation generally accepted at the present time is that the surface area on which frictional forces can operate is less for small inclusions than for large ones, and so the total deforming forces are also less. In addition, it is observed that small particles only start to deform at lower temperatures and higher deformations, when presumably the deforming forces are large.

(c) Composition

There can be little doubt that the composition of the silicate has a major influence on the minimum temperature at which plasticity is observed, i.e. in Fig.1. Kiessling[3] has shown schematically that increasing CaO, FeO and SiO_2 in the silicate increases the temperature, θ_c, at which plasticity is observed, whilst increasing MnO in the silicate decreases that temperature. However, these are generalisations which must be treated with care, and the true picture is much more complicated. For example, it has been shown[13]

that silicates based on $2MnO.SiO_2$ become plastic at higher temperatures than those based on $2FeO.SiO_2$. It has also been shown that the replacement of FeO by MgO in iron silicates increases the temperature at which plasticity is first observed, Fig.4.

The above brief summary indicates that the picture with regard to composition is not simple, and in fact there is not very much evidence available on which a simple hypothesis may be formulated. Nevertheless, sufficient evidence is available to show several interesting features. In the first place, it is clear that the silicates do not have to melt, as has sometimes been suggested, for them to show appreciable plasticity. The temperature at which the plasticity index increases rapidly can be as low as 825°C for some silicates, and none of the common silicate inclusions melt at such a low temperature. However, it would be expected that the temperature at which a silicate softened sufficiently to exhibit measurable plasticity would be related to the melting temperature, and the data shown in Table 1 are taken from the published literature (5)(12)(13).

The values of the solidus temperatures are not very well known, but the liquidus temperatures can be estimated with more accuracy from published equilibria[14]. For compositions close to those of tephroite ($2MnO.SiO_2$) and fayalite ($2FeO.SiO_2$), the solidus values are taken as those for the binary eutectic comprising the olivine as one phase. The liquidus values for inclusion types 3 and 4 in Table 1 have been taken from the $FeO-MgO-SiO_2$ ternary system, or the $FeO-SiO_2$ binary, with appropriate small adjustments for the minor amounts of MnO and Al_2O_3 present. The solidus temperatures are interpolated from the relevant data from the appropriate binary systems. The data for inclusion types 5-8 in Table I does not give the ratio of FeO:MnO in the (FeMn)O component, and the liquidus values are taken from the $FeO-MnO-SiO_2$ ternary system on the assumption that the FeO:MnO ratio is unity. The solidus values are the average values between those in the $FeO-SiO_2$ and $MnO-SiO_2$ binary systems.

It can be seen from Fig.5 that for the majority of the data, there is a clear relationship between the average liquidus-solidus temperature and the temperature for the first observable plasticity. Two of the observations marked with asterisks (inclusion types 3 and 6 in Table I) do not conform to this relationship and are for inclusions which were duplex, that with 20% SiO_2 containing wustite, and that with 50% SiO_2 containing trydimite.(5) Both these phases are relatively non-plastic, and would invalidate observations on the matrix silicate. The two observations for higher SiO_2 contents from the same work (inclusion types 7 and 8 in Table I) would undoubtedly be for glassy silicates, and thus conform to the general relationship.

It therefore appears, on the basis of the above evidence, that the minimum temperature for observed plasticity is related to the melting points of the inclusions. From the limited data so far available, this seems to be most easily described by a linear relationship. The evidence also indicates that duplex inclusions containing a hard, non-deformable phase behave differently and this effect will be discussed later.

Of particular interest to commercial steelmaking practice are the observations on inclusion type 9 in Table I. These are from inclusions resulting from the addition of an aluminium-silicon alloy (60% Si, 40% Al) to iron-oxygen melts. This alloy has been used to control the balancing reaction in the ingot mould during the commercial production of balanced steel plates. The average composition of many of the inclusions thus formed lie in the low melting point region of the $FeO-Al_2O_3-SiO_2$ phase diagram.(15) As a result, the inclusions are extremely soft and deformable above about 1050°C, and are elongated into long thin stringers during hot work Fig.6(a). Similar inclusion stringers have been shown to cause lamination defects in balanced steel plates deoxidised with this aluminium-silicon alloy. Because of their low solidus temperatures ($\sim$1080°C), some of the inclusions are partially melted during rolling at higher temperatures, Fig.6(b).

If the indications from Fig.5 are valid, then there will not be any simple effect of a given oxide such as CaO, MgO, Al_2O_3, SiO_2 etc. dissolved in the silicate, on its plasticity. Rather the effect of the dissolved oxide will depend on how it affects the melting point, which may be either raised or lowered depending on the original melting point and composition of the silicate. Also, should the presence of the additional oxide give rise to a second phase, this will completely alter the plasticity characteristics, especially if the second phase is of the non-plastic type. Consequently it does not seem possible to generalise as to the effect of variations in composition on the plasticity of silicates.

Recent work[11] [16] has shown that the softening temperature is clearly related to the SiO_2 content for silicates in the $(FeMn)O-Al_2O_3-SiO_2$ system containing occasional small amounts of CaO. Also, using a model relating the deformability or plasticity index (ν) to the ratio of the flow stress of the inclusion to that of the steel matrix[17], and Newtonian flow for glassy silicate inclusions during deformation, it is suggested that the change in behaviour of the inclusions will occur when the flow stress of the inclusion is equal to that of the matrix[11]. This situation seems to occur at some critical viscosity of the inclusion, i.e. about $10^{7.5}$ poise, and it is suggested that a temperature at which the viscosity reaches this critical value will correspond to the temperature at which there is the very sharp change in the plasticity index. It should be emphasised that this particular analysis refers to glassy silicate inclusions[18], and crystalline inclusions do not apparently follow this general pattern. In fact it might be suspected that in a crystalline silicate the critical temperature for inclusion plasticity may, as described earlier, be more related to the melting temperature. It has also been suggested[18] that hot hardness data may be useful in order to determine the plasticity index of inclusions.

(d) Second Phase Particles

Certain effects produced by a second phase within the silicate have already been described in relation to the fracture of the inclusions, and it has been suggested that a second phase within the silicate alters the plasticity. In fact the presence of a hard, undeformable phase such as alumina, spinel or silica (trydimite or cristobalite) within a silicate can act as a supporting framework which decreases the apparent plasticity. This is particularly the case if the second phase is present as a dendritic skeleton, Fig.6(c). Also, when deformation has taken place, it is found that the more plastic silicate is usually squeezed out to either end of the non-plastic phase, Fig.6(d), or occurs as thin connecting strings between two or more particles of the hard phase, Fig.6(e).

FACTORS CONTROLLING THE NUCLEATION OF VOIDS AT INCLUSIONS

It is well known that voids of a conical form are frequently nucleated at the ends of inclusions during rolling, particularly if the inclusion is behaving non-plastically. A typical example of such a void is shown in Fig.7(a). A similar conical void is shown in Fig.7(b) after deeply etching the specimen in bromo-methanol followed by examination with the scanning electron microscope. Rudnik[7] has suggested that there can also be V-shaped cracks, with the closed ends pointing in the direction of rolling, and has illustrated a stress system leading to the formation of such cracks. However, careful preparation of the sections usually shows that the effect ascribed to a crack is due to incorrect polishing in which metal has flowed into the conical void, Fig.7(c). Similarly, the cracks described by the same worker running between fractured surfaces of elongated silicates are also due to polishing causing flow of metal into what is actually a void between the fractured blocks. It is possible, however, by using the stress system described by Rudnik, to explain the creation of the conical voids at the ends of the inclusions. Frictional forces tend to act around the inclusion surface, as shown schematically in Fig.8(a), the forces acting tangentially to the surface of the inclusion. As

a result of these forces, cracks are initiated as shown. Not only are there the frictional forces, but also the forces imposed by the flow of metal, Fig.8(b). The resultant of these forces tends to widen the crack at its base nearest the inclusion so that the surface of the crack is normal to the resultant force, Fig.8(c). This creates the conical void.

Sometimes, particularly if the temperature decreases during rolling, a void may be created whilst the silicate still exhibits some degree of plasticity. The forces deforming the silicate are greatest at the surface of the inclusion, so that the surface layers are deformed relative to the centre of the inclusion. A fish-tail effect is produced, partly filling in the conical void, as shown in Fig.8(d). Often, however, this fish-tailing effect can be observed without any void at all.[4]

More recently, a mechanism of void formation at the interface between the inclusion and the steel matrix during hot deformation has been proposed on the basis of the formation of prismatic dislocation loops around the inclusion.[19] It has been possible using this mechanism to derive a relationship describing the stress required to exceed the inclusion/matrix interfacial strength so that voids will be formed, in terms of the inclusion size, strain and parameters describing the array of dislocations around the inclusion. This work has then been followed up by the development of a theory to predict the critical non-metallic inclusion size in iron to cause void formation during hot working,[20] and the results appear to accord well with experimental observations. In iron, it is predicted by the theory that inclusions greater in size than 2-3 μm diameter will cause void formation at the inclusion-matrix interface.

PLASTICITY OF SULPHIDES

As already shown earlier, the size and shape of the inclusions are of major importance and their harmful influence becomes especially pronounced if they are elongated normal to the direction of principal stress. Thus in wrought steels the minimum toughness is invariably encountered in the short transverse direction, and Baker and Charles (21) have shown that the resistance to crack propagation in this direction is related to the inter-inclusion spacing, which is

dependent upon the inclusion length per unit area.

Although the deformation behaviour of silicates is reasonably well established, this is not true for sulphides. One of the reasons for this is that they can be precipitated from the molten steel in three different morphologies, types I, II and III.[22] The deformation behaviour of type II and type III MnS has received far less attention than that of type I. The three different morphologies have been compared qualitatively, however, the deformability apparently increasing progressively from type I to III. The results of a recent investigation into the behaviour of type I and type III MnS inclusions during rolling are summarised in Fig.9. Since both these types have an equiaxed morphology, they are amenable to quantitative plasticity measurements, but this is not the case with type II sulphides which are not equiaxed in the as cast condition. Significant differences occur between the results of different workers, Fig.9. These differences, it was concluded, were not due to the influence of the matrix, but were caused by differences in the properties of the various MnS types. Type I MnS, besides having a different morphology from the type II and III sulphides, is frequently associated with an MnO-MnS eutectic phase. The plasticity of the type I MnS increases from 1200 to 900°C and this is indicated by the measured mean values of ν . However, the true relative plasticity is obscured by the behaviour of the eutectic phase which is highly deformable at 1200°C, but non-deformable at lower temperatures. Thus, at high oxygen contents, the characteristic sulphide behaviour may become dominated by that of the eutectic, and the normal increase in plasticity with decreasing rolling temperature may be reversed. The free-cutting steel used by Baker et al,[21] had an oxygen content of 0.029%. If this was all present as the simple MnO-MnS eutectic, the volume fraction of eutectic would be about 0.6%. The steels used by Moore[23] contained up to 0.06% oxygen corresponding to a eutectic volume fraction of 1.3%. According to Baker et al[21], this undoubtedly accounts for the observed differences in plasticity and the observed sharp increase in ν at about 1100°C i.e. typical oxide behaviour consistent with the melting point of the eutectic.

Although the presence of the eutectic may account for some of the differences in plasticity between the type I and type II MnS below 1200°C, it cannot account for the difference at 1200°C. No determined compositional differences between the various sulphide types have been established which could account for their observed differences in deformation. There is, however, considerable circumstantial evidence to indicate that the type I are strengthened by the presence of oxygen in solid solution.

According to Fig.9, the relative plasticity of the type III sulphides of Baker et al[21] is close to that of the single phase sulphides studied by Maunder and Charles[24]. The sulphide type in the latter investigation was not specified but they appeared globular and were assumed to be type I. The steel from which they were precipitated was deoxidised with silicon and aluminium and they contained little dissolved oxygen. Their composition was therefore probably similar to the type III MnS of Baker et al[21], thus resulting in similar deformation behaviour in spite of having different as-cast morphologies and quite different matrix compositions.

The influence of temperature on the deformation of MnS inclusions in steel can also be seen in Fig.9. The relative plasticity of both the type I and type III MnS increases as the rolling temperature decreases from 1200°C, but whereas with the type III the trend continues to 800°C, with the type I a maximum is encountered at 900°C. The increase in the relative plasticity with decreasing temperature reflects an increased rate of hardening of the matrix relative to that of the MnS. The change to a decreased plasticity below 900°C is apparently due to the transformation of austenite to ferrite.[21]

It has been suggested that in order to minimise the harmful effects of sulphide inclusions on fracture properties, their elongation during rolling should be kept to a minimum. Whatever MnS morphology is present in the cast steel, the lowest relative plasticity is encountered at rolling temperatures of 1200°C and above. Thus, provided there are no deformable oxide or silicate inclusions present, the minimum inclusion elongation and the maximum toughness should be obtained by maintaining as high a rolling temperature as possible. This procedure is employed

in the production of free-cutting steels, but in the rolling of medium strength structural steels attention is now being devoted to ensuring that the finishing temperature is below 800°C. Significant improvements in strength are achieved by this 'controlled rolling' technique, but it is to be expected that this steel will have much inferior short transverse toughness compared with rolling at higher temperatures, unless there is a very low volume fraction of sulphide, or the sulphides are of modified composition and properties.

Another factor determining the inclusion elongation and the short transverse toughness is the rolling reduction. There is, however, a limit to the improvement which can be obtained by lowering this, since a minimum degree of deformation is necessary to break down the ingot structure in order to obtain a uniform microstructure, to remove microshrinkage and improve the overall strength and ductility. However, it is considered that some improvement in short transverse ductility will be achieved by limiting the degree of deformation, using continuously cast slab or billet as the starting material. The present trend towards employing largeringots results in increased elongation and lower finishing temperatures, and is probably a contributory cause to the present lamellar tearing problems.

Finally, the type III, and also the type II as-cast morphology should be avoided. Unfortunately, increasing the oxygen content to greater than 200 ppm, in order to achieve type I sulphides, increases the total volume fraction of inclusions and results in problems of oxide and silicate elongation. A more promising way of producing less deformable globular sulphides is therefore by the addition of elements which form more stable sulphides than manganese, e.g. Ti, Zr, Ca, Mg and the rare earth elements, i.e. by inclusion shape control.

References

1. H.N.Cummings et al. Trans. ASM 1957, 49, 482.
2. P.H.Frith. "Fatigue tests on Rolled Alloy Steels made in the Electric and Open Hearth Furnaces". ISI Spec. Rept. No.50, 1954.
3. R.Kiessling. "Non-metallic Inclusions in Steel". Part III, ISI Publication No.115, 1968.
4. F.B.Pickering. J.I.S.I., 1958, 189, 148.
5. E.Scheil and R.Schnell. Stahl n Eisen, 1952, 72, 683.
6. T.Malkiewiz and S.Rudnik. J.I.S.I. 1963, 201, 33.
7. S.Rudnik. Ibid. 1966, 204, 374.
8. J.A.Charles and I.Uchiyana. Ibid. 1969, 207, 979.
9. I.Uchiyana and M.Sumita. Trans. Nat. Res. Inst. Metals, 1965, 7 (6), 233.
10. H.C.Chao and L.H.Van Vlack. Materials Res. and Standards, 1965, December, 611.
11. S.Ekerot. Scand. J. of Met. 1974, 3, 21.
12. P.E.Waudby, Steel Times Annual Review, 1972, October 147.
13. F.B.Pickering. Jern. Ann. 1964, 148, 845.
14. A.Muan and E.F.Osborn. "Phase Equilibria among Oxides in Steelmaking". 1965, Addison-Wesley.
15. P.E.Waudby and F.G.Wilson. International Symposium on Metallurgical Thermo-Chemistry. "Applications in Ferrous Metallurgy". Sheffield University, 1971.
16. S.Ekerot and B.I.Klevebring. Scand. J. of Met. 1974, 3, 151.
17. B.Sundström. J. of Composite Materials, 1970, 5, 277.
18. B.I.Klevebring. Scand. J. of Met. 1974, 3, 102.
19. B.I.Klevebring and R.Mahrs. Scand. J. of Met. 1973, 2, 310.
20. B.I.Kevebring et al. Met. Trans. 1975, 6A, 319.
21. T.J.Baker and J.A.Charles. J.I.S.I. 1972, 210, 690.
22. T.J.Baker and J.A.Charles. J.I.S.I. 1972, 210, 702.
23. C.Moore. M.Met.Thesis 1968, University of Sheffield.
24. P.J.H.Maunder and J.A.Charles. J.I.S.I. 1968, 206, 705.

TABLE 1

AVERAGE MELTING TEMPERATURES FOR DIFFERENT SILICATE INCLUSIONS

Inclusion Type	Composition of Silicate Inclusion wt. %	Minimum Plasticity Temperature °C	Solidus Temperature °C	Liquidus Temperature °C	Average Melting Temperature °C
1	70 FeO, 30 SiO_2	~940	1 180	1 210	1 195
2	71 MnO, 29 SiO_2	~1 020	1 250	1 350	1 300
3	59 FeO, 3 MnO, 3 Al_2O_3, 32 SiO_2	~970	1 180	1 300	1 240
4	48 FeO, 4 MnO, 5 Al_2O_3, 34 SiO_2, 8 MgO	~1 070	1 220	1 350	1 285
5	20 SiO_2, 80 (Fe, Mn)O	~850	1 240	1 330	1 285
6	50 SiO_2, 50 (FeMn)O	~900	1 240	1 660	1 450
7	75 SiO_2, 25 (FeMn)O	~1 200	1 240	1 700	1 470
8	85 SiO_2, 15 (FeMn)O	~1 250	1 240	1 700	1 470
9	45 SiO_2, 15 Al_2O_3, 40 FeO	~825	1 080	1 150	1 115
10	5 FeO, 50 MnO, 45 SiO_2	~1 000	1 250	1 400	1 325

LECTURE 6

THE PLASTIC DEFORMATION AND FRACTURE OF NON-METALLIC INCLUSIONS IN STEEL

1. Introduction

In steels produced by tonnage steelmaking processes, the non-metallic inclusions must be considered as an integral part of the steel itself[1], and it has been shown[2] that every metric tonne of such steel contains 10^{12}-10^{15} oxide inclusions and even more sulphide inclusions. During the hot working which is applied to all steels except castings the inclusion morphology and distribution is greatly modified, and in the modified form the inclusions frequently exert a marked influence on the mechanical properties. Inclusions can be classified into two basic types, other than by their composition, origin or constitution, namely into those which deform during hot working, and those which are largely undeformable. By varying such parameters as the hot working temperature and/or reduction, some inclusion types can be made to appear deformable at some temperatures but undeformable and even brittle at other temperatures, or even at the same temperature if the constitution and degree of crystallinity of the inclusions is altered. There are considerable differences between the major inclusion types which are present in steels. MnS for example is much less plastic relative to the steel at high temperatures than at low temperatures[3][4], a factor of which advantage is taken in the hot rolling of free cutting steels. On the other hand, most silicates are much less plastic at low temperatures than at high temperatures,[5] and usually show a temperature at which there is a sharp transition from non-plastic or brittle behaviour to plastic behaviour. Kiessling[

has indicated that this temperature is increased by increasing SiO_2, CaO or FeO, but decreased by increasing MnO. This is a simplified concept and Waudby[7] has shown that in many cases there is a relationship between the plastic-non plastic transition temperature and the melting temperature of the silicate. As will be shown later, this is still a simplified concept. In addition, some inclusions such as alumina, spinels and the more aluminous calcium aluminates are undeformable even at the highest hot working temperatures.

2. Some Effects of Inclusions on Mechanical Properties

It is well known that the non-metallic inclusions markedly influence the mechanical properties of steel, and not always detrimentally. Whilst inclusions rarely are of dimensions which exceed the critical size for the propagation of a running crack, even inclusions of a sub-critical size may be responsible for growth of a defect under cyclic stressing, or in corrosive environments, so that it may exceed the critical defect size. Also, a concentration of inclusions ahead of a propagating crack may accelerate failure. Brooksbank and Andrews[8] have shown that internal stresses can readily be generated around inclusions, and Kiessling[2] has shown that these can alter the properties of the matrix around the inclusion and even cause local yielding. The volume of such a yielded region depends on both the volume fraction of the inclusions and the number per unit volume. Co-planar or co-linear distributions of inclusions can therefore lead to yielded planar regions, which can markedly affect the toughness or ductility, particularly in the through thickness direction in flat hot rolled products. It is well established that the inclusion separation is related to crack opening displacement fracture toughness measurements[9], and that the volume fraction of inclusions, and their shape with respect to the stress direction controlsboth the toughness and ductility[10]. The effect of localised high volume fractions can readily be appreciated, particularly if present as elongated ribbons or filaments, and this leads to lamellar tearing during welding[11]. The presence of such a distribution of inclusions can lead to a marked loss of cold formability, particularly during bending thin flat rolled products[12].

Fatigue properties are also influenced by the inclusions present, particularly in high strength steels, and increasing the volume fraction has clearly been shown to decrease the fatigue life of bearing steels.[13] In this case, the type of inclusion is also important, non-deformable inclusions particularly if they act as stress raisers being particularly detrimental.[14][15] Spinels, alumina and aluminous calcium aluminates are thus more detrimental than many silicate types, whilst sulphides can be actually beneficial and if they encapsulate the detrimental inclusion types, can completely offset the detrimental effects.[8][13]

Apart from influencing lamellar trearing during welding, the liquation of sulphides can form hot tears in weld metals and heat affected zones[16], the sulphide size being important from this point of view. Sulphides, by acting as hydrogen traps, can however be beneficial from the point of view of minimising hydrogen cracking in weld heat affected zones, and hairline cracking in general[17]. Another property in which sulphides are very beneficial is machinability,[6][18] and it is often reported that large, slightly elongated MnS particles give better machinability than small highly elongated particles. In some circumstances, calcium-aluminium-silicates also improve machinability.[19][20]

Inclusions can also promote the tendency for pitting corrosion in many types of steels, and the volume fraction, number of inclusions, and inclusion shape will markedly influence the corrosion effects observed. Elongated inclusions can be tunnelled out during pickling and lead to line defects in subsequently processed materials.[21] Similarly, hard undeformable inclusions have been shown to lead to undesirable polishing defects in stainless sheet, particularly if the inclusions occur as continuous or discontinuous stringers[21]. Adjustments of the deoxidation technique to provide smaller, more randomly distributed, softer and more plastic inclusions greatly improves the polishability of stainless steel.

It can be seen from this brief survey of the effects of inclusions on steel properties, that the type, shape, size and distribution of the inclusions is of the utmost importance. These inclusion parameters are controlled by the composition of the inclusions, which determine the plasticity of the inclusions, their tendency to elongate or to fracture, and their dissemination during hot working. The hot working parameters, such as temperature, strain, strain rate, type of deformation, etc, also influence the way the inclusions deform into elongated stringers, break up, and are disseminated throughout the steel. The creaction of voids during hot working, either at the inclusion-matrix interface, at the ends of non-deformable inclusions, between the phases comprising an inclusion or between cracked inclusion fragments is also important from the point of view of the properties of the steel, and is particularly influenced by the inclusion composition and constitution, and by the hot working conditions. The appreciation of the importance of inclusion plasticity and fracture has led in recent years to attempts to control the plasticity, particularly of sulphide inclusions, by inclusion shape control employing additions of zirconium, titanium, calcium or rare earths (cerium)[10,12,22,23,24]. Much of this work has been confined mainly to sulphides, although the use of calcium to eliminate alumina stringers has also been studied. There has however, been little work which applied the principles of inclusion shape control, by either chemical control of the composition, constitutional control by thermal effects or mechanical control by the introduction of second phase particles, to silicate inclusions. Some of these effects will be considered later, with particular reference to silicates, but it is suggested that some of the principles outlined and observations made, may be applicable to inclusions in general.

3. The Assessment of Inclusion Deformation and Plasticity

It is not possible to determine the absolute plasticity of inclusions 'in situ' in the steel, and so it has been customary to assess the inclusion deformation by comparison with that undergone by the steel matrix itself. The ratio of the inclusion deformation to the steel matrix deformation is termed the relative plasticity ( ). A common method used by many workers[5][26][27] has been to determine the aspect ratio of the deformed inclusions in longitudinal sections, and to compare this with the aspect ratio of the deformed metal specimen itself:-

$$\nu = (a/b)_i / (a/b)_m \qquad \text{----------(1)}$$

where $(a/b)_i$ = aspect ratio of inclusion

and $(a/b)_m$ = aspect ratio of metal specimen

This method assumes that initially spherical inclusions are deformed into ellipsoids, which at high deformations may not be the case.

The extension of this concept to use true strain has been advocated by other workers[3][27][28][29], in which case:-

$$\nu = \epsilon_i / \epsilon_m = \beta \ln\lambda / \ln H \qquad \text{----------(2)}$$

where :-

ϵ_i = inclusion true strain
ϵ_m = matrix true strain
λ = inclusion aspect ratio after deformation
H = matrix reduction ratio
β = a constant which is 0.5 for plane strain in rolling or 0.67 for cylindrical strain in rod drawing.

Again this assumes that initially spherical inclusions deform into spheroids of constant aspect ratio in longitudinal section, which is only true for small deformations. Nevertheless, this method has proved most useful for determining inclusion relative plasticities, and it has also been shown[3] that the inclusion true strain, ϵ_i, can be related to projected length of inclusion in the longitudinal plane by :-

$$\epsilon_i = \ln P_i/P_o \qquad \text{----------(3)}$$

where P_i = projected inclusion length per unit area after deformation.

and P_o = projected inclusion length per unit area before deformation.

This allows use to be made of automated quantitative television microscopy, but is conditional upon there being an initial distribution of equal sized spherical inclusions, of constant volume fraction. This condition is rarely met in practice, but it is possible to correct the results for variations in volume fraction by dividing the projected length by the measured area fraction of inclusions.

From the relationship between inclusion strain and matrix strain, the relative plasticity can be calculated, see equation (2), Fig.1. Much of the published data uses the simple ratio $\nu = \epsilon_i/\epsilon_m$ that is the chord of the curve in fig.1 at the appropriate values of ϵ_i and ϵ_m. This leads to a misconception, in that it simply averages the value of ν from $\epsilon_m = 0$ to the actual value of ϵ_m used for the measurement of ν. If the inclusion ceases to deform at some intermediate value of ϵ_m, the value of ν is still finite, and so the inclusions still exhibit apparent plasticity when in fact they have ceased to be deformed. Thus the same value of ν can be obtained from inclusions having very different curves of ϵ_i against ϵ_m.

A more realistic value of is obtained from the tangent to the curve in fig.1, i.e. $d\epsilon_i/d\epsilon_m$. This valuevaries with ϵ_m, but is a maximum at $\epsilon_m = 0$, when it also equals the value obtained from the chord of the curve. The value of ν at $\epsilon_m = 0$ may be termed the initial maximum relative plasticity, and is used in the discussions to be presented later.

Consideration also requires to be given to the three dimensional shape of the deformed inclusions. Whilst in rod rolling or drawing, the assumption of cylindrical strain may be legitimate, and inclusions deform into prolate spheroids, in flat rolling it is often not justified to assume plane strain deformation of the inclusions, which in fact undergo considerable lateral spread[30]. This lateral spread has been known for many years, and indeed is clearly shown by many lamellar tearing phenomena. It would appear best, therefore, if the relative plasticity, , can be measured in three dimensions. Moreover, at high strains the deformation and thus the shapes of the inclusions become very irregular, and they do not exhibit constant aspect ratios. In fact a 'pinch and swell' affect is often observed, fig.2, and the measurement of the aspect ratio in such cases is virtually meaningless.

3. Factors affecting Inclusion Plasticity

(a) The effect of inclusion and matrix strength

One of the more important factors which controls the relative plasticity of an inclusion is the strength of the inclusion relative to the matrix.[25][31][32] A relationship between ν and the ratio $\sigma_i/\sigma_m = \beta$ is shown in fig.3, where σ_i and σ_m are the flow stresses of the inclusion and matrix respectively. This indicates that the inclusions may still show significant plasticity even when $\beta \sim 6$, i.e. the inclusion has six times the strength of the matrix. On the other hand, some workers[31] have shown that ν becomes zero at values of $\beta \sim 2$, and Sundstrom[32] showed this to be the case theoretically, assuming the inclusion and matrix to work harden at the same rate, which is most unlikely. Under these conditions the relative plasticity, ν, was given by :-

$$\nu = \epsilon_i/\epsilon_m = \frac{2\sinh(1-n)}{1-n} \Big/ 2 + \left(\beta^{\frac{1}{n}} - 1\right) \quad \text{-----(4)}$$

where ϵ_i = inclusion true strain

ϵ_m = matrix true strain

$\beta = \sigma_i/\sigma_m$ = flow stress of inclusion/flow stress of matrix

and n = work hardening exponent of both inclusion and = matrix (assumed to be the same).

Due to dynamic recovery and recrystallisation during hot working operations, it is clear that the value of n will vary widely, and the effect of varying values of this work hardening exponent on the relative plasticity of the inclusion, ν, is shown in fig.4. At low values of n, appropriate to high temperature deformation and little work hardening, the plasticity tends to zero at $\beta \sim 2$, in agreement with Zeisloft and Hosford[31], but at lower temperatures where there will be a higher value of n, the analysis more nearly fits the results of Unkle[25], i.e. ν tends to zero at $\beta \sim 6$. This difference in behaviour can also be related to the nature of the inclusion-matrix interface.

(b) The effect of the inclusion-matrix interface

It is now appreciated[33] that the bonding of the inclusion-matrix interface plays an important role in controlling the plasticity of the inclusion. The value of β at which ν tends to zero is ~ 2 for interfaces which are poorly bonded, but is in excess of 6 for well bonded interfaces. This clearly reveals the importance of the interfacial bond, and with a well bonded interface strain can be effectively transferred to the inclusion which is therefore constrained to deform even at high values of its flow stress relative to that of the matrix. On the other hand, with a poorly bonded interface, the strain is not readily transferred to the inclusion and some relative sliding occurs at the matrix-inclusion interface so that the matrix deforms around the inclusion, rather than the inclusion itself deforming. In addition,

the degree of interface bonding is important in controlling the de-cohesion which can occur during deformation, and the formation of cavities at the ends of non-deformable inclusions. At higher inclusion strengths, i.e. values of σ_i , the effect of the interface bonding is very important, as it largely controls whether hard inclusions will deform. At low σ_i values however, the effect of such bonding on the inclusion plasticity is relatively unimportant. Since most inclusions are relatively weakly bonded to the steel matrix, it is probable that the mathematical models[32][34] are not representative of the behaviour of inclusions in steel, especially as the work hardening rate of inclusion and matrix are assumed identical.

One further factor concerning the strength of the inclusion on its ability to deform, irrespective of either the value of $\beta = \sigma_i/\sigma_m$ or of the degree of bonding of the interface, is the absolute value of σ_i itself. This may be said to be the inherent ability of the inclusion to deform[33], and for very high values of σ_i the inclusion will be inherently non-plastic irrespective of the other factors discussed.

(c) The nature of the Inclusion

From the point of view of their deformation and fracture characteristics, inclusions may be categorised as :-

(i) Inherently plastic inclusions such as MnS, which show a gradual change in plasticity over a wide range of temperature, fig 5. In the case of MnS, the plasticity relative to the steel decreases with increasing temperature.

(ii) Non-crystalline glassy inclusions which behave rigidly at low temperatures but become plastic at some characteristic critical temperature. Typical inclusions of this type are glassy silicates which become plastic at a critical viscosity at the non-plastic - plastic transition temperature. It has been shown theoretically that this critical viscosity occurs at a temperature corresponding to the normal working viscosity range for glass manufacture,[35,36] i.e. 10^6-10^8 poises (10^5-10^7 Nsm^{-2}).

(iii) Crystalline ionic solids typified by crystalline silicates, spinels, sesquioxides and certain calcium aluminates. These show no plasticity and often behave in a brittle manner until reaching their solidus temperature when they assume fluid behaviour. The non-plastic - plastic transition thus approximates to the solidus temperature.

The effect of various oxides in the glassy non-crystalline and the crystalline silicate inclusions is often very different. For example increasing the MnO content of glassy iron-manganese silicates lowers the non-plastic - plastic transition temperature, whilst in crystalline silicates the transition temperature is raised because MnO increases the (FeMn)O - Olivine eutectic temperature. The original classification of the effects of various oxides[6] is therefore very much simplified, and in fact depends both on whether the inclusion is crystalline or glassy, and also on the composition of the inclusion. An oxide addition in many cases can either increase or decrease the solidus temperature depending on the composition of the inclusion in the equilibrium system.

The softening temperature of glassy non-crystalline silicates is commonly several hundred degrees lower than the corresponding crystalline solidus temperature. Thus the non-plastic - plastic transition temperature for any given silicate

composition will depend on whether it is crystalline or glassy, and CaO can have a very marked effect in this respect. It is possible therefore to predict the effect of various oxides on the non-plastic - plastic transition temperature for crystalline silicates (and other oxides) from a knowledge of the phase diagrams. In the case of glassy silicate phases, the prediction of the effect of various oxides on the non-plastic - plastic transition temperature is more complex. However, a qualitative assessment can be made from a knowledge of the behaviour of glass forming or modifying oxides on the viscosity. For example, CaO at concentrations less than $\sim$ 30% can lower the viscosity of the glass by breaking down the SiO_4 networks. On the other hand oxides such as Al_2O_3 and Cr_2O_3 may have variable effects depending on the basicity of the silicate glass. In a basic silicate they may reinforce the network structure and increase the viscosity, but in an acid silicate they may break down the network and decrease the viscosity.

Care should be taken in using single values of the plasticity index, particularly the initial maximum relative plasticity, to predict the way in which inclusions will deform. This is because the value of ν decreases with increasing matrix strain, see fig. 1 and fig. 6. For example a fluid silicate may have a much higher value of ν at low values of matrix strain than does MnS, but at high matrix strains it will be the MnS which forms the more elongated inclusions.

Various other factors in the nature of the inclusion will also influence the relative plasticity by their effect on the inclusion flow stress, σ_i :-

(i) The inclusion may be solid solution hardened, which will increase σ_i and decrease ν . This is possibly the reason why type I MnS, which may contain oxygen in solution, are less plastic than type III MnS[3,4]. Similarly, solid solution hardened has been reported in MnS by elements replacing manganese[37], fig. 7,

and also in selenides[37]. It is observed for example that chromium rich MnS in stainless steels exhibit lower plasticity than MnS in low alloy steels, and that zircomium or calcium[38] dissolved in MnS also decrease the plasticity. In fact these latter two effects are the basis of sulphide inclusion shape control.

(ii) Second phase particles present in the inclusion may cause mechanical support and lower the inclusion plasticity. An alternative possibility for the decreased plasticity of type I MnS is that it is precipitation hardened by fine MnO precipitates, and it has recently been shown that fine FeS precipitates can form in MnS[39]. These effects may alter the relative plasticity in different ways, depending on the nature and composition of the precipitates. Alternatively, the inclusion may contain more massive precipitates of a second phase, such as dendrites of alumina or spinel in a silicate matrix. These can be completely non-deformable and produce a true mechanical support. During the hot deformation of such inclusions the more plastic phase may be stripped from the less deformable phase, leaving separated particles of the harder phase as a disconnected stringer. If such particles are angular, they can act as potent stress raisers. A similar effect can be seen in the case of hard phases such as silica precipitated at the periphery of a glassy silicate, or in the case of alumina-rich reaction rims around inclusions. During deformation the peripheral phase may reduce the plasticity of the inclusion as a whole, fig. 8a, but when it is broken at higher deformations it can lead to angular fragments in a very plastic matrix, and the plastic matrix may be stripped from the harder fragments, figs 8 (b) and (c).

(d) Particle Size

Various authors have shown that small particles have reduced plasticity, or do not deform relative to larger particles[5,27,40] fig. 9. A recent analysis of this effect has been made in terms of the energy required to create the new interface as the particles deform. The energy required to create the new interface, per unit volume, is given by:-

$$\frac{E}{V} = \frac{4\gamma E_i}{a} \quad \text{Sinh}\,\epsilon_i \qquad \text{---------- (5)}$$

where γ is the surface energy per unit area
ϵ_i = inclusion true strain, and
a = initial inclusion diameter.

This relationship can be shown graphically in terms of the energy required as a function of inclusion strain for different initial inclusion diameters, fig. 10. For initial inclusion diameters $> 5\mu m$ the surface energy effects are unimportant, but for inclusions of initial diameter $< 1\mu m$ the energy required can be prohibitively high. Small inclusions are thus reluctant to deform, and it is observed that the cut off below which they do hot deform is 2-3μm, fig. 11. This is rather larger than would be predicted theoretically from equation (5), and probably indicates other mechanisms which may be involved, such as inclusion rotation. It is observed that above about 15μm initial diameter, particle size has little effect on inclusion plasticity. This effect of particle size suggests that inclusion shape control by inclusion size control may be possible, and indeed the smaller sulphides produced during continuous casting of small sections confirm this possibility.

(e) Temperature, strain and strain rate effects

Temperature has a most important effect on inclusion relative plasticity by influencing the relative strength ratio of the inclusion to the matrix. This can, depending on the inclusion characteristics, cause ν to increase or decrease with increasing

temperature. For example, MnS shows a decreasing ν with increasing temperature whereas silicates do not become deformable until some critical temperature is exceeded. At the highest temperatures, ν decreases again in the case of the glassy silicates because at those temperatures the silicate viscosity decreases less rapidly than does the flow stress of the steel, σ_m. Thus a maximum value of ν is observed just above the non-plastic - plastic transition temperature for glassy silicates, fig. 12.

With increasing matrix strain, ϵ_m, there is a reduction in relative plasticity, ν, as the inclusion becomes more elongated. This is probably due to an initial shear of the inclusion under the relatively large couple acting at its extremities, followed by rotation to produce a more streamlined form. This, together with the thinning of the inclusion as deformation proceeds, leads to a smaller deforming couple in a lower differential velocity gradient across the inclusion. The effect is also seen in fig. 12, and some workers have attributed it to work hardening of the inclusion.

Theoretically, increasing the strain rate should increase the flow stress of the matrix, σ_m, thus decreasing the ratio σ_i/σ_m and increasing the relative plasticity of the inclusion. It has been observed that this is not the case, at least for changes in strain rate of ~ 2, possibly because σ_i is more sensitive to strain rate than is σ_m. A theoretical analysis of the effect of increasing strain rate indicates that it should increase the non-plastic - plastic transition temperature of glassy silicates and decrease their initial maximum relative plasticity. There are however no systematic data on these effects.

(f) Hydrostatic Pressure

Hydrostatic pressure can render brittle materials to be quite deformable, and this has been referred to in explaining the high plasticity of MnS in steel compared with its brittle behaviour when isolated from the steel matrix[26]. Such hydrostatic

pressure can be developed during rolling, and although the effects of such pressure has not been extensively discussed in the literature, or investigated, it would be expected to increase the relative plasticity. Such factors as specimen thickness, strain rate, rolling load and roll diameter, all of which affect the magnitude of the hydrostatic pressures developed, would also be expected to influence the plasticity of inclusions.

4. The Mechnisms of Inclusion Deformation and Fracture

Considerable work has been published on the deformation of MnS inclusions[3, 4, 9, 12, 22, 29, 29], but much less has been done on silicates and alumina[5, 6, 7, 27]. The observations which will be referred to are concerned mainly with silicate inclusions of the $FeO-MnO-SiO_2$, $MnO-Al_2O_3-SiO_2$ and calcium bearing types, together with some consideration of non-deformable Al_2O_3 inclusions.

(a) Non-crystalline glassy silicates

At low temperatures below the non-plastic - plastic transition, these inclusions are rigid and do not deform. In general, it is observed that spherical glassy silicates are also reluctant to fracture, possibly due to the absence of phase interfaces or cleavage planes. There is much evidence to show that the metal-inclusion interface decoheses, giving rise to the well known conical voids at the ends of the inclusion, fig. 13 (a), which are characteristic of all non-deformable inclusions. It is possible that these spherical inclusions rotate during the deformation of the steel under the action of the couple generated by the shear strain rate gradient.

Above the non-plastic - plastic transition temperature, the lower viscosity of the glassy silicates allows them to deform readily, and with increasing matrix strain they continue to elongate, albeit at a reducing rate. At very high matrix strains, inclusions which are close together tend to join up[3,9]

as the metal between them necks, fig. 13 (b). As the inclusions elongate, an irregular deformation occurs because the laminar flow becomes unstable under the action of perturbations in the flow pattern[34]. This gives rise to "pinch and swell" effects, fig. 2, which are clearly observed in scanning electron micrographs, figs. 14 (a) - (d), and in transmission electron micrographs of extracted inclusions using a 1MeV microscope, fig. 14 (e). Eventually at the highest temperatures or strains the thinner sections rupture to form holes, and the edges of the ruptured regions thicken and spheroidise due to surface energy effects, fig. 14(b). This can lead to the formation of smaller, spheroidised particles which are disseminated throughout the metal.

As the deformation temperature decreases, the glassy silicates which were plastic at higher temperatures, become non-plastic as they pass through the transition temperature, and begin to fracture. If the inclusions have been only slightly deformed before the temperature falls below the transition temperature, they tend to become crushed, to crack generally and to shear, fig.15(a). The sheared fragments frequently separate as metal is intruded between them, fig.15(b), and the fragments rotate to achieve a streamlined flow effect fig.15(c). It is observed that it is often the thinner ends of elongated glassy inclusions which show the crushing effects, and the fact that some of the crush cracks are arrested before passing through the entire inclusion, fig.15(a), tends to indicate that even below the non-plastic-plastic transition temperature there is still some plasticity residual in the glassy silicates which allows blunting of the crack tip. In the case of very elongated glassy silicates which are deformed further below the transition temperature, these begin to break up by the formation of transverse fractures, fig.15(d), possibly due to the shearing action generated by the compressive rolling forces. This is clearly shown by scanning electron micrographs, figs 15(e) and (f), and it can be seen that rotation of the fractured blocks also occurs. An interesting feature of glassy silicates deformed at temperatures well above the transition temperature is their ropy appearance, which is indicative of a swirling effect due to internal plastic flow within the silicate glass.

(b) Crystalline Silicates

Observations have been made on the fracture characteristics of various crystalline silicate inclusions of the rhodonite, tephroite, spessartite and cordierite types. Crystalline silicates can form directly in the as cast condition, or can be produced by de-vitrification of glassy silicates during heating prior to rolling or during the rolling process. It has been observed that hot deformation frequently enhances the devitrification or crystallisation of glassy silicates. The morphology of the silicate crystals is frequently that of interlocking laths of the silicate within the original inclusion, be it either spherical or elongated. The whole inclusion may comprise silicate crystals, or these may be embedded in residual glass, or in a eutectic which comprises one or more silicates and/or (FeMn)O. As has been described previously, the crystalline silicates only become plastic (or fluid) at their solidus temperatures, and in the case of eutectic structures such temperatures are lower than the melting point of the crystalline silicates themselves. Thus it is often observed that crystalline silicates occur in a fluid matrix within the inclusion.

In the as cast condition, the spherical crystalline silicates fracture when rolled at temperatures below the non-plastic-plastic transition. The usual conical voids are produced, and the fractured fragments rotate to produce a streamlined effect and are disseminated as stringers, fig.16. Providing the temperature is high enough, metal may intrude into the cracks, see fig.16(a). When rolled at high temperatures above the transition temperature, such inclusions melt and behave in a fluid manner. However, as the temperature of rolling decreases, the elongated fluid silicates often crystallise and it is observed that when the inclusions comprise entirely of silicate crystals, fracture tends to occur along the crystal boundaries. Initially voids are formed at the silicate crystal boundaries which are clearly shown by transmission electron micrographs using a 1 MeV microscope, fig.17(a). These voids are analogous to the cavities produced at metal grain boundaries during hot working. It is probable that they form by grain boundary sliding, and as fracture progresses the voids link up and complete fracture occurs on the silicate crystal boundaries, fig.17(b). The crystals appear to slide off along their boundaries, fig.17(c), until they become completely separated, fig.17(d), and when the temperature is low enough metal is not intruded between the silicate crystals.

At higher temperatures or large matrix strains, the individual silicate crystals become completely separated, forming a discontinuous stringer of silicate laths which often have rotated to present a streamlined profile to the metal flow, fig.17(e).

In many cases however, the inclusion does not consist entirely of silicate crystals, and especially when deformation has caused partial crystallisation in deformed inclusions the silicate crystals occur in a fluid or plastic matrix. The low viscosity matrix then thins down between the silicate crystals, fig.18(a), and eventually tears apart, fig.18(b), thus allowing the crystals of silicate to slip off each other, fig.18(c). The fluid silicate between the crystals frequently forms a eutectic structure on subsequent cooling. Eventually the individual silicate crystals, with their accompanying fluid tails, become isolated from each other, fig.18(d), and the optical microstructure may show a discontinuous stringer which gives the misleading impression that the elongated silicate has been mechanically fractured in a brittle manner, fig.18(e).

(c) Duplex Inclusions

The duplex inclusions which were examined comprised (FeMn)O particles of very low plasticity in a plastic non-crystalline or a eutectic (FeMn)O-silicate matrix. In the as cast condition, and after deformation at low temperatures, fracture was often observed along the phase interfaces, fig.19(a) with the usual formation of conical voids and the rotation of the fractured fragments. Erosion of the less plastic fragments occurs, fig.19(b), to form long stringers, and intrusion of metal may occur into the cracks, or the fractured particle may contain very many voids or discontinuities.

Deformation at higher temperatures above the silicate non-plastic-plastic transition temperature often shows the effect of mechanical support of the inclusion by the more rigid phase, fig.19(c), but with increasing deformation the plastic silicate becomes stripped off from the rigid undeformable particles, figs.19(d) and (e), and the plastic silicate often ruptures to produce discontinuous stringers, fig.19(f). This effect is clearly shown by scanning electron microscopy, fig.20. The plastic silicate may, if it was actually liquid at the deformation temperature, form a eutectic on subsequent cooling, fig.20(c). These effects clearly illustrate the differential plasticity between the phases in duplex inclusions, and generally are similar to those already described where an inclusion is duplex but comprises a

a crystalline silicate within either a plastic non-crystalline silicate or a fluid silicate liquid.

(d) Rigid Inclusions

By far the most common rigid inclusion is alumina, which is non-deformable even at the highest metal deformation temperatures. Similar effects are observed with the more aluminous calcium aluminates, or with spinels, and sometimes with very highly siliceous inclusions. The effects which will be described refer to alumina, which can occur in two major forms in as cast steel, namely dendritic and sintered globular aggregates.

A typical dendritic alumina particle is shown in fig.21(a), and deformation at all temperatures results in the fragmentation of the dendrite by the fracturing of the dendrite arms, fig.21(b), so that the particles are spread out into a dessiminated stringer. At low strains, the thinner necks where the dendrite arms branch are broken, but later the whole dendrite becomes fragmented, fig.21(c).

A typical sintered globular alumina aggregate is shown in fig.22(a). If such an aggregate is well sintered, it has been observed to resist fracture until matrix strains in excess of 1.0. When fracture does occur, it takes place predominantly at the sintered boundaries of the alumina particles comprising the aggregate, fig.22(b), and also to a more limited extent across the sintered grains themselves, fig.22(c) The more loosely sintered aggregates completely disintegrate and become widely disseminated, but the more highly sintered aggregates tend to form dense stringers comprising polyhedral alumina particles, figs. 22(d) and (e). In alumina stringers produced from both dendrites and sintered globular aggregates, depending on the temperature at which the metal has been deformed, the stringer may be riddled with cavities between closely adjacent particles, or at the ends of more isolated particles, or metal may have been able to intrude between the particles and so eliminate in large measure the cavities.

5. Concluding Observations

The preceding discussion of the factors which influence the plasticity and mechanisms of deformation and fracture of non-metallic inclusions in steel has shown how the control of these factors can markedly alter inclusion morphology and distribution. This is of great importance, as it has also been shown how many of the properties of steel are controlled by the morphology, size and distribution of the inclusions. Consequently, if it is required to tailor the inclusions so as to minimise their detrimental effects and utilise their beneficial effects to the full, detailed consideration must be given to the plasticity of the inclusions and the way in which they fracture and are disseminated throughout the steel during hot working. For example, whilst controlled rolling of high strength low alloy steels can optimise the basic microstructural features to obtain good general toughness and ductility with high strength, the controlled rolling process can produce a very undesirable inclusion morphology and distribution which leads to low through thickness ductility and toughness and susceptibility to lamellar tearing. Consequently there has been the need to introduce techniques for the shape control of both sulphide and aluminous inclusions, mainly by controlling their plasticity.

Various possibilities exist for controlling inclusion plasticity and fracture. The composition of the inclusions can be adjusted by the steelmaking and deoxidation process to obtain specific plasticity characteristics, but due cognisance should be taken of the very different characteristics of inclusions of the same composition in the glassy non-crystalline and in the crystalline conditions. Particularly, it must be appreciated that the non-plastic-plastic transition temperature is much higher for the crystalline silicates than for glassy silicates. The particle size of the inclusions, as influenced by the solidification conditions is also important, and it is possible to control to some extent the particle size either by composition control or by the use of such processes as continuous casting. Cooling rate also can influence the constitution of the inclusions in terms of the phases which they comprise.

The processing variables during hot working are also very effective in controlling inclusion plasticity, both for sulphides and silicates. In the case of glassy silicates, the temperature with respect to the non-plastic-plastic transition will be important, and it should be borne in mind that during hot working the temperature may decrease through the transition range. Thus glassy silicates may first be plastically elongated, and later may be fractured. Much more work is required to define the effect of composition not only on the plasticity of glassy silicates, but also on the transition temperature. Moreover, originally non-crystalline glassy silicates may have their deformation and fracture behaviour significantly altered if they crystallise either during soaking for hot deformation, or during the deformation itself. In the latter case, the effect of the inclusion strain and the strain rate could be most important. During hot working, at temperatures below their solidus, crystalline silicates fracture, or if embedded in a plastic silicate matrix, the plastric matrix may thin down thereby allowing the crystalline fragments to separate and be disseminated into a stringer. The temperature at which this occurs, and the total deformation applied to the steel, will determine the extent to which dissemination occurs. Moreover, the temperature and strain will determine to what extent voids are produced between fractured fragments and/or at the ends of inclusions. Such voids can have most detrimental effects, and every effort should be made to ensure that the processing succeeds in closing them by welding or by intrusion of metal into the cracks.

In many cases, the presence of long elongated inclusions is detrimental to mechanical and other properties. It is the function of the current technology of inclusion shape control to reduce the plasticity of inclusions and thus prevent highly elongated morphologies.

Whilst it can be appreciated that apart from changing the composition of the inclusions by the steel making practice, the actual mechanical processing can produce a measure of inclusion shape control, it must also be borne in mind that mechanical support by crystalline silicates or by the more rigid non-deformable inclusions in otherwise plastic inclusion matrices may also present, or delay, inclusion elongation. The effects of many of the phenomena which have been described are, however, difficult to control in terms of producing effective control of the inclusion morphology and distribution. Considerable further work is required before they are fully understood, but the current stage of of understanding allows certain general principles to be used when considering the best way of effectively utilising processing to ensure the least detrimental effects from the inclusions which are indigenous to the steel. In using the information currently available on the plasticity and fracture of inclusions to the optimum however, the particular properties required from the steel, and the effect of inclusions on these properties must be fully appreciated.

References

1. R.Kiessling. I.S.I.-B.I.S.R.A. Conference. Abington, England, 1968.

2. R.Kiessling and H.Nordberg. "Production and Application of Clean Steel" I.S.I. 1972, 179.

3. T.J.Baker and J.A.Charles. J.I.S.I., 1972, 210, 680.

4. W.Dahl et al. Stahl u Eisen 1966, 86, 796.

5. F.B.Pickering. J.I.S.I. 1958, 189, 148.

6. R.Kiessling. I.S.I. Publication No.115, 1968.

7. P.E.Waudby. Steel Times Annual Review, 1972, Oct, 147.

8. D.Brooksbank and K.W.Andrews. "Production and Application of Clean Steel". I.S.I. 1972, 186.

9. T.J.Baker and J.A.Charles. "The Effect of Second Phase Particles on the Mechanical Properties of Steels" I.S.I. 1971, 79.

10. F.B.Pickering. "Towards Improved Ductility and Toughness" Climax Molybdenum Company Conference, Kyoto, 1971, 9.

11. J.C.M.Farrar et al. "The effect of Second Phase Particles on the Mechanical Properties of Steels" I.S.I. 1971, 171.

12. M.Korchynsky and J.Stuart. "High Strength Low Alloy Steels" London-Scandanavian Conference, Nuremberg; 1970.

13. S.Enekes "Production and Application of Clean Steels" I.S.I., 1972, 215.

14. R.F.Johnson and J.F.Sewell. J.I.S.I., 1960, 196, 414.

15. J.D.Murray and R.F.Johnson. I.S.I. Spec. Rep. 77, 1963, 110.

16. T.Boniszweski and R.G.Baker. J.I.S.I. 1964, 202, 921.

17. J.Hewitt and J.D.Murray. Brit. Weld. J. 1968, 15 (4), 151.

18. E.M.Trent. I.S.I. Spec. Rep. 94, 1967, 11-77-179.

19. H.Opitz and W.Konig I.S.I. Spec. Rep. 94, 1967, 35.

20. A.Wicker. Radex-Rundschau, 1965, 432.

21. J.C.C.Leach "Production and Application of Clean Steel" I.S.I. 1972, 105.

22. J.H.Little and W.L.M.Henderson. "The Effect of Second Phase Particles on the Mechanical Properties of Steels" I.S.I. 1971, 183.

23. D.C.Hilty and J.W.Farrell. "Inclusions and Their Effects on Steel Properties" British Steel Corporation Conference, Leeds, 1974, Paper No.4, to be published.

24. L.Meyer. "Micro-Alloying '75". Proceedings of International Conference, Washington 1975.

25. H.Unkle. J.Inst. Metals. 1937, 61 (2), 171.

26. E.Scheil and R.Schnell Stahl u Eisen 1952, 72, 683.

27. T.Malkiewitz and S.Rudnik. J.I.S.I. 1963, 201, 33.

28. P.J.H.Mannder and J.A.Charles. J.I.S.I. 1968, 206, 705.

29. K.Gove and J.A.Charles. Met. Tech. 1974, Sept., 425.

30. G.Wardle and J.C.Billington. Private Communication, 1977.

31. R.H.Ziesloft and W.F.Hosford. Trans. ASM 1969, 62, 297.

32. B.Sundstrom. J. of Composite Materials, 1970, 5, 277.

33. S.Ashok. PhD Thesis, Cambridge University, 1976.

34. N.C.Gay. Tectonophysics. 1968, 5 (3), 211.

35. S.Ekerot. Scand. J. of Met. 1974, 3, 21.

36. F.B.Pickering and S.W.Robinson, to be published.

37. R.Kiessling and N.Lange I.S.I. Pub. No.100, 1966.
38. W.J.M.Salter and F.B.Pickering. J.I.S.I. 1969, 207, 992.
39. T.M.Banks. "Inclusions and their effects on Steel Properties" British Steel Corporation Conference, Leeds, 1974, to be published.
40. I.Uchiyama and M.Sumito. Trans. Nat. Res. Inst. Metals Japan. 1965, 7 (6), 233.

LECTURE 7

INCLUSION SHAPE CONTROL

THE NEED FOR INCLUSION SHAPE CONTROL

The mechanical properties of steels, particularly the ductility or charpy impact shelf energy values, are profoundly influenced by the amount or volume fraction of non-metallic inclusions, their shape and distribution.[1-5]

The properties which are most greatly influenced by the non-metallic inclusions, are those which involve ductile failure, i.e. the opening up, growth and coalescence of voids within the metal with increasing strain. The nucleation of such voids also probably depends on the nature of the forces causing bonding at the matrix-particle interface and the actual ability of the particle to resist cracking, together with the ability of the steel-particle composite to resist the propagation of such cracks.

It is well known that the major factor which influences the total ductility during, for example, a tensile test, is the volume fraction of second phase particles, the ductility decreasing with increasing volume fraction of particles. To a first approximation, the nature of the particles appears irrelevant, fig 1, although a more careful analysis of the effects indicates this not to be entirely true.[1] Other things being equal, the inclusions, both oxides and sulphides, exert the major influence, the greater the volume fraction of inclusions the lower the ductility.

A similar effect of inclusions is observed for the charpy shelf energy of low alloy steels,[6][7] fig 2, and in fact there is a very close correlation between total ductility

and charpy shelf energy,[1] fig 3.

It is also well known that the total ductility and the charpy shelf energy are very dependent upon the direction of testing,[1][6][8][9][10][11] and that this anisotropy of properties is a consequence of the elongation of the inclusions into elongated stringers or flat plates or ribbons, figs 4 and 5. Elongated (prolate) inclusions tested parallel to their length give much higher ductility and shelf energy than do plate-shaped (oblate) inclusions tested perpendicular to their planar dimensions. This gives rise to the well known decrease in through-thickness ductility in plates of structural steel, and is also related to the phenomenon of lamellar tearing in welds.[12] In fact, in the field of lamellar tearing, it has been shown that very large planar inclusions give the worst effects followed by large ribbons, elongated groups or clusters, elongated single inclusions and small non-elongated single inclusions giving the best results.[12] This really emphasises the importance of both shape and local volume fraction, i.e. the distribution of the inclusions.

It should not be supposed that it is only the planar inclusions which cause problems. Elongated sulphides have been well established to give more anisotropy in the impact properties compared with rounded sulphide inclusions, and recent work has shown that there is a linear relationship between log Crack Opening Displacement and log inclusion length,[13][14] fig 6, and there is a hyperbolic decrease in % R of A with increasing inclusion length.[12] Very recently it has been shown that there is a linear relationship between the Crack Opening Displacement and the inclusion separation,[7] fig 7.

In addition, in hot rolled strip materials which are formed into sections by longitudinal bending, elongated sulphide inclusions can result in longitudinal cracking along the inclusions, whilst bending normal to the rolling direction

gives excellent bends.[6] In many applications such as chassis sections for lorries, longitudinal bending is essential, and thus elongated sulphides are most detrimental.

It is clear therefore that the presence of heavily deformed elongated or plate-like inclusions, be they either sulphides or oxides, are very detrimental and should be avoided. Also elongated stringers of, for example, Al_2O_3 or calcium aluminate or spinel, are also detrimental and if they can be replaced by more isolated spherical oxides, the properties will be greatly improved. The same situation applies for silicate stringers, which are also detrimental.

Because steels contain a much larger volume fraction of sulphides than of oxides, it is generally agreed that the sulphides provide the main problem, and there is thus a need to alter the shape of sulphides away from planar or elongated types. A less urgent requirement, at present, is to alter the oxide inclusion shape, but as either complete control over the shape of sulphides is achieved, or as the economic reduction in the sulphur content becomes realisable, then there is little doubt that oxide shape control will become more important. The need for a full understanding of the mechanism of sulphide and oxide shape control, and the need to develop suitable inclusion shape control methods which can be applied to a wide range of steels is therefore clearly apparent.

THE DEFORMATION OF INCLUSIONS TO FORM PLANAR ARRAYS

The deformability of inclusions depends on their plasticity relative to the steel during hot working. The subject therefore impinges on that discussed in previous chapters, and must be discussed separately for sulphides and oxides because their behaviour is so different. Schematically the resistance to deformation relative to the steel can be depicted as in fig 8.

(a) Sulphides

The main form of sulphide in steel is MnS, which is much more

deformable relative to the steel at low temperatures than at high temperatures.[16] This is a result of the different rate of change of the plasticity of MnS and steel with increasing temperature, as indicated schematically in fig 8. MnS occurs in steel as three distinct forms depending upon the degree of deoxidation of the steel, namely types I, II and III. These have been described in detail in earlier chapters.

There is some controversy concerning the relative plasticity of these three forms of MnS. Some work has shown them to deform to the same extent, especially when the different initial particle sizes are taken into account.[17] The more widely held opinion however, is that the type I inclusions are much less plastic than either types II and III, which form extremely thin, elongated stringers.[16][18] This has been suggested to be due to the oxygen content of type I-MnS, which hardens the MnS and causes it to be less plastic than the purer forms of MnS, types II and III. However, some of the data concerning plasticity, particularly of type II-MnS, may be open to doubt due to the fact that the initial particle size is not equiaxed, but rather vermiform.

In general however, it is observed that the type I-MnS form much less elongated stringers than type II-MnS, and in thin strip or plate materials, in which the rolling temperature can become rather low, very thin MnS stringers are formed due to the greatly increased plasticity relative to the steel, Fig 9. These obviously are detrimental to transverse ductilities and impact shelf energies, particularly in the case of initially type II-MnS because, occurring initially as co-operative monotectics, they form arrays of co-planar or almost co-planar ribbons or plates which are extremely detrimental.

It is clear therefore that any move to reduce the plasticity will be beneficial, and how this can be done will be discussed later.

(b) Oxides

In silicon killed steels, the major oxides are silicates of iron, manganese, aluminium and calcium, depending on their origin. Silicates behave very differently from sulphides in that they are much more plastic than steel at high temperatures, and thus form long, and sometimes very thin stringers, especially if they are glassy silicates, i.e. non-crystalline. However, with decreasing temperature, they lose plasticity over a very narrow temperature range, at some temperature characteristic of their chemical composition, or physical nature, fig 10. Below this temperature, they are virtually non-plastic and tend to fracture if the deformation is sufficiently rigorous. Kiessling[15] has presented a relatively simple picture of the factors controlling this temperature at which plasticity is lost - CaO and Al_2O_3 increase it whilst FeO and MnO decrease it. Waudby[19] has shown that this is incorrect, and that the plasticity transition temperature may be related to the melting point, fig 11. On the other hand, Ekerot[20] has shown that the temperature dependence of viscosity is very important, and that the change in plasticity occurs at a temperature related to the glass transition temperature. It might be anticipated however, that each of these factors may play a role, and that viscosity is important in glassy silicates, but that this might not be so for crystalline silicates or for glassy silicates which are devitrifying due to the temperature, or the strain activation, during hot working. Some interesting possibilities for controlling the inclusion shape of silicates therefore are open to investigation.

In heavily aluminium killed steels, the inclusions may be:

(i) Globular Al_2O_3 clusters formed at low degrees of super-saturation during deoxidation,[21] or due to the breaking away of nozzle blocking agglomerates during teeming.[22]

(ii) Dendritic Al_2O_3 masses formed at high degrees of super-saturation during deoxidation.[21][23]

(iii) Various calcium aluminates, which will have melting points dependent on the CaO/Al_2O_3 ratio, and formed by direct deoxidation by Ca-Al-Si alloys or by reaction of Aluminium with calcareous slags entrapped in the molten steel.[24] These can range from a similar melting point to Al_2O_3, i.e. $CaO.6Al_2O_3$, to a much lower melting point, and therefore probably a more plastic, $3CaO.Al_2O_3$.

(iv) Various spinels formed from a variety of deoxidation or other inclusion reactions, but which will tend to behave similarly to Al_2O_3.

We can consider briefly the Al_2O_3, because it is virtually non-deformable at all temperatures, but tends to fracture and form elongated discontinuous stringers during hot working. When present in quantity, these are very prone to cause poor transverse properties and great anisotropy of ductility and charpy shelf energy. In addition, if low rolling temperatures have been employed, the metal may not have filled in between the fractured fragments, and the discontinuous stringer may be riddled with voids - a very undesirable state of affairs. It can therefore be appreciated that replacement of Al_2O_3 aggregates in the as-cast metal, by more widely disseminated separate particles, even if they have rather more plasticity than the Al_2O_3, would probably be very beneficial. How this can be achieved will be discussed later.

Finally, to return to a further consideration of the differences between sulphides and silicates. Sulphides tend to be most heavily elongated at low working temperatures, if they are MnS. Consequently, controlled rolling procedures to produce optimum strength and ductility or fracture toughness may be just the processing which will cause the most deleterious MnS shape and distribution. Hence the need to alter the plasticity of the sulphides or to eliminate them more successfully from the steel. On the other hand,

once the sulphide problem is overcome, the silicates, or alumina, will tend to become more important. Low rolling temperatures would be beneficial from the point of view of low plasticity, but fracture may occur and lead to detrimental effects, especially with alumina. It is clear that different forms of oxide are required which give more widely dispersed inclusions which will have low plasticity and yet will not fracture.

METHODS OF EFFECTING INCLUSION SHAPE CONTROL

The object of inclusion shape control is the realisation of one of the features for which metallurgists have been striving for many years, namely to "tailor" the composite metal-ceramic which is steel so as to achieve the best from both the non-metallic and the metallic portions. As the objectives are somewhat different with respect to sulphides and to oxides, it will be convenient to consider each separately.

(a) Sulphides

The aim is to cause the sulphides to have a lower plasticity and to prevent the type II arrays from forming. By considering how MnS itself may be modified, it is possible to suggest some simple alternatives:-

(i) the MnS may be made more pure, and so have a higher melting point, i.e. produce type III rather than type I or II. The pure MnS is very plastic and hence very elongated inclusions will form, although groups in co-planar arrays may be prevented.

(ii) the MnS may be physically stiffened, as in type I inclusions by either oxygen in solution or by the formation of fine precipitates of oxide within the MnS. Such a procedure can only be used with virtually undeoxidised steels, or very lightly deoxidised steels, and so is not compatible with the requirements of fine grain, precipitation

strengthening, etc which are required in many low alloy high strength steels.

(iii) the MnS may be solid solution hardened by using elements which dissolve in MnS and strengthen it very considerably. Kiessling[15] has shown which elements are capable of this effect, fig 12.

It is interesting that chromium is very effective in increasing the hardness of MnS, and in high chromium stainless steels which are low in manganese, elongated MnS is seldom seen in quantity. It is one of the features of inclusion shape control by Zirconium, that (ZrMn)S is formed, which is much less plastic than MnS and presumably much harder.

In order to alter the type of sulphide to one which has a lower inherent plasticity, often with an increased melting point, the following are the requirements. The addition element must form a sulphide of lower free energy of formation than MnS. There are many such elements, fig 13,[9] but factors such as the physical properties of the sulphide, cost, availability, ease of handling, solubility in steel etc, must be assessed before their practicability can be determined. The addition must also have a much less affinity for oxygen, nitrogen, carbon etc, than it does for sulphur. Thus ΔG_f (Sulphide-oxide), ΔG_f (Sulphide-nitride) and ΔG_f (Sulphide-carbide) should be as large a negative value as possible. This obviously restricts the possible additions, which should dissolve readily in steel at steelmaking temperatures and should not boil off at such temperatures, i.e. it should have a low vapour pressure. The sulphide formed must not form a sulphide eutectic with steel, or with any other phase in the steel. Also the sulphide should not be volatile, although this could be useful in producing desulphurisation effects - e.g. Na_2S. Finally the sulphide formed should have a high melting point and consequently a low plasticity, and the addition must be capable of a controlled, non-violent reaction with

the molten steel and have a predictable recovery.

These considerations limit the choice of inclusion shape control additions very considerably, fig 13. Alkali sulphides such as Na_2S can be discounted because of the volatility and reactivity of the elements, or because of scarcity and cost. Alkali-earth sulphides are possibilities, but the elements have low solubility in steel, whilst sulphides such as BeS and MgS are too volatile. Of these only CaS is a real candidate. Rare earth sulphides, particularly CeS, produced by Misch metal additions containing rare earth metals, or by rare earth silicide additions, are very real possibilities. Group IV(a) sulphides such as titanium and zirconium are also very real possibilities, and whilst the Group V(a) element niobium is reported to be a weak sulphide former, its possible use cannot be dismissed. In fact, in stainless steels, both titanium and niobium in types 321 and 347, have for long been known to prevent or minimise the occurrence of MnS. In fact titanium forms a very non-plastic carbo-sulphide, Y phase,[25] and there is reason to believe that niobium may form an analogous phase. Clearly this opens up another possibility, namely that instead of forming a stable non-plastic sulphide, the shape control addition may be capable of combining with sulphur in a ternary or more complex compound containing such elements as carbon, nitrogen, oxygen and sulphur.

Finally, it may be that the addition agent forms a sulphide which precipitates on a non-plastic oxidic phase and thus is supported and prevented from exhibiting plasticity. This can be achieved when MnS encapsulates Al_2O_3, but this mechanism is difficult to control. A better example is CaS, which frequently forms a peripheral rim around calcium aluminate inclusions, or encapsulates alumina.[24][26] In addition, calcium lowers the solubility of sulphur in steel and thus forms primary CaS precipitates.

There is, of course, the possibility that the simplest remedy is to lower the sulphur content of the steel, and so decrease the volume fraction of sulphides. There are many methods of doing this, either initially in the iron or later in the steel, but it is reported that attempts to produce sulphur contents lower than 0.01% in tonnage steels are uneconomical.[6]

Of all the possible sulphide modifying agents, rare earths, zirconium, titanium and calcium are currently being used for inclusion shape control, and the effects of these will be considered later.

(b) Oxides

The problem in the case of oxide inclusions may be somewhat different for silicates than for alumina.

In the case of silicates, it is necessary to decrease the plasticity. This can be achieved by increasing the melting point of the silicates,[19] or by increasing the glass transition temperature of a glassy inclusion.[20] Obviously it should be possible so to tailor the deoxidant composition that the correct silicate composition of higher melting point is achieved. But there are problems, in that being less fluid, it is likely that coalescence and growth may occur less readily. Thus the steel may show inclusion shape control but may contain rather more inclusions. Any benefit may therefore be vitiated, because lowering the volume fraction can make as much difference as changing from transverse to longitudinal testing on ductility or shelf energy. The modifying agent must also have a greater affinity for oxygen than the deoxidants giving rise to the original inclusions.

The question of whether the silicate should be glassy or crystalline is also worth consideration. It seems that a crystalline silicate would tend to remain less plastic than a glassy one to higher temperatures, although the possibility

of fracture might be greater. The crystalline silicates might be expected to be near to stoichiometric silicate compositions, and particularly should not be too rich in SiO_2, but richer in CaO and Al_2O_3.

Finally, it may be possible physically to support a silicate by a hard, non-plastic phase, and thus reduce the plasticity. This in fact has been observed where the silicate contains a second phase within it; the second phase being Al_2O_3, spinel or calcium aluminates of the more refractory types.[27][28] The question of fracture of the particles however needs to be considered.

In the case of alumina inclusions, which form clusters and thus alumina stringers in rolled material, the requirement is to alter the inclusion type and therefore the morphology. By using a combination of calcium and aluminium deoxidation, it is possible to form mixed oxides of the calcium aluminate types, which are much less prone to form clusters and which also are relatively non-plastic. The plasticity varies with the composition of the calcium aluminates. There are problems however with the use of calcium deoxidants, as will be discussed later.

SULPHIDE INCLUSION SHAPE CONTROL

The methods currently employed are either to strengthen the MnS by introducing into it elements which decrease its plasticity, or to replace MnS by a more refractory non-plastic alloy sulphide. Schematically it can be shown that as the degree of deoxidation increases, the plasticity of the MnS increases,[6] fig 14. The plasticity is lower for low Mn:S ratios than for higher ratios, and this might be a deoxidation effect or an effect of iron dissolved in the MnS. Possibly FeS precipitates within MnS, may be as very small particles, and lowers the plasticity. As alloying elements, particularly titanium, zirconium, rare earths or calcium replace manganese in MnS, the plasticity decreasing virtually to zero when the MnS is completely replaced by the alloy sulphide.

(a) Zirconium

Zirconium is usually added to a deoxidised steel as zirconium silicide, ferro-silicon-zirconium or even zirconium metal scrap.[6][8][9][29] Because zirconium has a high affinity for nitrogen (ΔG_f = -230 KJ/mol @ 1600°C) it will react with nitrogen even in Al-killed steels. Consequently it cannot be used with steels which depend for their properties on the precipitation of fine nitrides, i.e. vanadium containing low alloy high strength steels. It is however widely used in the currently popular niobium steels. With increasing zirconium in the melt, zirconium dissolves in the MnS, forming (ZrMn)S which have very much decreased plasticity and the plasticity decreases as the substitution of zirconium in the MnS increases. It seems that a maximum amount of ∿12% Zr can dissolve in the MnS. On reaching this saturation limit, it is reported that ZrC and $Zr_4C_2S_2$ are formed, the latter as films at the grain boundaries.[8][30]

With maximum zirconium in the MnS, the sulphides are completely undeformed, but there is no actual data on the quantitative effects of zirconium in MnS on the plasticity of the sulphide. There is also a suggestion that, at high zirconium contents, a zirconium sulphide can be produced, but more work is required to confirm this. The interesting feature seems to be however, that the type II sulphides are not formed, and it appears that zirconium so increases the melting point that isolated sulphides are formed, possibly directly from the melt during solidification.

The effect of zirconium on the longitudinal and transverse charpy shelf energy values is shown in fig 15. It can be seen that the transverse shelf energy increases with increasing Zr content more than does the longitudinal shelf energy, i.e. the anisotropy decreases. However, there is an optimum zirconium content, above which the shelf energy values decrease. This optimum is stated to be associated with the start of formation of ZrC and $Zr_4C_2S_2$ which are reported to cause embrittlement, possibly due to the large grain boundary particles cracking.[8]

The anisotropy of shelf energy is never entirely removed by zirconium, in contrast to rare earth additions, and the ratio of longitudinal : transverse shelf energy is decreased from ∿ 2.6 to 1.6 at the optimum zirconium content, fig 16, which increases with increasing sulphur content. This dependence of the optimum zirconium content on the sulphur content is to be expected, but because of the high affinity of zirconium for nitrogen sufficient must be added to combine with the nitrogen and leave enough over for optimum sulphide modification.

(b) Titanium

Although titanium has been well known to modify sulphides, a typical example being in 321 stainless steel, there have been few studies recently, and little systematic work such as has been done on zirconium additions, although recently titanium bearing high strength low alloy steels have been developed.[31][32][33] Because of its greater affinity for nitrogen than for sulphur, enough titanium must always be added to combine with the nitrogen, as well as leaving sufficient for sulphide modification. Also, in order to achieve a good and reasonably predictable recovery, the steel must be fully killed prior to the titanium addition. There is an even more pronounced tendency for TiN to segregate into bands and stringers than for ZrN, and this can undo all the good provided by sulphide modification. The mechanism of modification brought about by titanium is at present uncertain, and direct substitution of manganese in MnS is not yet proved. Titanium will also form TiC or more commonly Ti(CN), which also tends to segregate, and the complex carbo-sulphides of the form $(Ti\ Fe\ Mn)_4C_2S_2$, may well produce similar embrittlement to the analogous zirconium phase. In general, therefore, the reactivity of titanium may render its control as a sulphide shape control addition somewhat difficult.

(c) Rare Earth Additions

The rare earths, lanthanides, can be added to steel either as:

(i) Misch metal - 50% Ce, 25% La, 10% Nd, 5% Pr + others

(ii) Rare earth silicides - 35% Fe, 30% Si, 18% Ce, 9% La, 4% Nd, 2% Pr etc.

The rare earths have very high affinities for oxygen, hydrogen, carbon, nitrogen and sulphur, particularly for sulphur and oxygen, where CeS and Ce_2O_3 have very negative ΔG_f values. All the oxides, sulphides and oxysulphides of the rare earths have very high melting points, fig 17, and are therefore ideal for producing sulphide shape control,[6][6][9][30][34] being very resistant to plastic deformation even at the highest temperatures.

Due to the high reactivity of rare earths, especially with oxygen, steels must be deoxidised prior to their addition, and even so the best recoveries are only of the order of 70-80%.[34] Oxidation of liquid metal streams in air can also result in large agglomerates of oxides, nitrides, sulphides, which can form massive laminations.[30] In fact, much care is required in the addition of rare earth, because although the sulphide might be adequately modified, the laminates mentioned previously will be as bad or worse than any alumina stringers.

The mechanism of shape control is one of replacing the MnS by a rare earth sulphide. As far as is known, the rare earths do not appreciably replace Mn in MnS.[35] Being of high melting point, and very sparingly soluble in steel, the rare earth sulphides form idiomorphic particles, which being of low density, tend to float and so produce some desulphurisation.

Recent evidence has shown that there is an optimum rare earth : sulphur ratio for sulphide shape control.[9] fig 18. A ratio of $\sim$2.0 gives the highest transverse charpy shelf energy values, and in fact the anisotropy is very nearly completely eliminated, a longitudinal : transverse charpy shelf energy ratio of $\sim$1.1 being achieved at the optimum ratio. In general therefore rare earth additions are more beneficial

than zirconium in eliminating anisotropy in the shelf energy values, fig 16.

Above the optimum rare earth : sulphur ratio, the decrease in transverse charpy shelf energy values may well be due to deleterious carbide or even intermetallic compounds (Fe_5Ce or Fe_2Ce) being formed in the interdendritic interstices of the as cast structure, which persist as segregates in the rolled plates etc. Because of the not too great affinity of rare earth for nitrogen, the $-\Delta G_f$ value being similar to that for AlN, rare earths can be used as sulphide shape control additions in low alloy high strength steels which owe their properties to vanadium nitride precipitation.

(d) Calcium

The free energy of formation of CaS at 1600°C is ∿-343 KJ /mol but for CaO it is about -502 KJ /mol. Thus for effective sulphide modification, the steel must be very effectively deoxidised by aluminium. There are many difficulties in the use of calcium because of its low solubility in steel, and the fact that it boils off rapidly at 1600°C. Thus, the effect of calcium modification by alloys such as calcium silicide is most erratic, although more predictable when the more recently developed barium-containing hypercal or calsibar are used.[10][36] The reasons for this will be discussed later in the section on oxide modification.

Contrary to the view expressed by Hilty and Popp,[10] CaS does not form a series of solid solutions with MnS although both have the NaCl structure. Due to the large ionic diameter of Ca^{++}, there is a marked solubility gap, and MnS can only dissolve about 13% Ca replacing manganese.[15][24] Thus the highly stable CaS is formed whenever calcium is effectively added to the steel, and occurs as isolated particles in some cases. It is very resistant to plastic deformation. In general however, the CaS is frequently observed to form a peripheral rim to calcium aluminate inclusions,[24] when of course it is supported by the calcium aluminate and cannot deform. No quantitative data is known

on the plasticity of CaS.

No data seems to be available on the anisotropy of ductility or charpy shelf energy properties in steels which have been sulphide shape controlled by calcium.

OXIDE INCLUSION SHAPE CONTROL

Very many investigations have been reported on the action of calcium in modifying oxide inclusions, mainly from Russian, German and Japanese sources. The results show often wide discrepancies, but in all cases the object has been to replace Al_2O_3 clusters and stringers by less injurious, widely disseminated calcium rich oxide inclusions. The present discussion attempts to summarise only some of the more well substantiated findings and to present some views on calcium deoxidation and oxide inclusion modification.

Calcium is a difficult element to introduce into liquid steel in a controlled manner. It is generally agreed that its effects in carbon and low alloy steel are erratic. The reasons for this are that:-

(a) Calcium has a very limited solubility in steel,[37] of the order of $\sim$0.03% at 1600°C, fig 19.

(b) Calcium has a high vapour pressure,[38] of 1.6 atmospheres at 1600°C, fig 20.

(c) Many calcium alloys are light and rapidly float to the top of ladles, react with air and thus never really get into the steel.

Thus in view of its low solubility and high vapour pressure, the calcium is often lost by vapourisation before it has time to dissolve and act as a deoxidiser.

It has been observed that calcium is more predictable as a deoxidant in stainless steels because nickel increases markedly

the solubility in molten steel. So do aluminium and silicon, and to an even greater extent than nickel. Consequently it is advisable either to pre-deoxidise the melt or to add aluminium and silicon with the calcium, as often is the case in many calcium bearing deoxidation alloys. These alloys should also be as dense as possible to prevent them floating, and should be kept as low down in the ladle as possible until they melt and react, i.e. allow the ferrostatic head to counteract the high vapour pressure.

More recently it has been discovered that barium added to the calcium bearing deoxidant will very effectively lower the activity of calcium and also decrease its vapour pressure.[10] Various commercial alloys have been developed using both barium and silicon to lower the activity of the calcium, a typical composition being 10% Ca, 10% Ba, 22% Si, 40% Al, 18% Fe. These alloys are reported to give better control of the deoxidation in that the calcium is more uniformly distributed throughout the melt. It is also suggested that the large amounts of aluminium and silicon dissolved locally when the alloy additions are made, raises the solubility of calcium appreciably. A rather improbable explanation also is that when aluminium and calcium are added together, there are films of calcium aluminates formed around the aluminium-calcium rich areas local to the deoxidant, but these collapse because they have fairly low melting points, and thus do not prevent the deoxidants diffusing into the steel. On the other hand, if calcium and aluminium are added separately, solid Al_2O_3 or CaO films form around the regions where the respective metals dissolve, retard diffusion, and inhibit the beneficial combination of the aluminium and calcium.

Experience tends to show that when calcium silicide alone is added, or Ca-Al-Si alloys, the calcium rapidly boils off before it can take part in the reactions. Consequently only Al_2O_3 or aluminium silicates are formed depending on the aluminium content in the deoxidant.[39] It requires very large amounts of calcium-silicide before calcium-

aluminium-silicates are formed, and calcium aluminates are apparently rarely if ever observed. Using the barium containing deoxidants, small additions may give only alumina, as the calcium is rapidly used up, but larger additions give calcium aluminates which can contain up to 30% CaO, and are CA_6, CA_2 or CA. Consequently, although CaO has a lower free energy of formation than does Al_2O_3, (-480 KJ/mol for CaO and -420 KJ/mol for Al_2O_3) a joint deoxidation can take place which causes calcium aluminates to form instead of the alumina clusters. These are of course primary inclusions. It must be remembered that highly aluminous CA_6 can form clusters and may be equally as detrimental as Al_2O_3 itself.

Frequently however, in order to get better recovery of the calcium, and to modify pre-existing Al_2O_3 inclusions formed as primary deoxidation products or as products of air oxidation of liquid metal streams, the calcium alloys are added after aluminium deoxidation. In fact this is often found to be the best method, as the calcium seems protected by the prior deoxidation, and rather surprisingly, modification of the primary Al_2O_3 inclusions clusters is often observed. The solubility product for CaO will be lower than that for Al_2O_3 so that some CaO can precipitate. It probably precipitates on the surface of the pre-existing Al_2O_3. CaO melts at $\sim 2570^{\circ}C$ and Al_2O_3 melts at $\sim 2020^{\circ}C$, so both are solid, and any reaction might be expected to be slow. But at the CaO-Al_2O_3 interface, fluxing to form very low melting point compounds such as $C_{12}A_7$ ($\sim 1400^{\circ}C$) will occur and this liquid layer will act as a sink which dissolves both CaO and Al_2O_3, with the result that liquid calcium aluminates will form and thus modification will be, and is, achieved.

Not only does the calcium, when correctly applied, produce modification of the oxides and inclusion shape control, it also produces cleaner steel, with obvious benefits. In addition it tends to produce CaS instead of MnS, and the CaS associates with the calcium aluminates in the manner previously

discussed. Wahlster has shown that calcium modification increases the toughness of steel plates,[40] but the results do not indicate how much of this benefit is due to oxide modification, sulphide shape control or simply a general increase in cleanness. They do show, however, that the anisotropy of tensile ductility and charpy shelf energy decreases with the improved steel cleanness resulting from the correct use of calcium treatment.

At present, there do not seem to be any very clear indications of the plasticity during rolling of either calcium aluminates or the more complex calcareous silicates.

THE EFFECT OF INCLUSION SHAPE CONTROL ON THE IMPACT PROPERTIES OF STEELS

Whilst it is well known that inclusions markedly decrease the charpy shelf energy, and that inclusion shape control is very beneficial in minimising the anisotropy of this property, the effects of inclusions on the impact transition temperature are by no means so clear cut. Various effects have been reported, the majority indicating that there is little or no effect of inclusion volume fraction on the impact transition temperature, but occasionally some reports are found of an increase in inclusion volume fraction raising the transition temperature. This might be expected because cracked carbides can produce this effect,[1][11][41] and cracked oxides might be expected to behave similarly. The effects might be expected to be small as the overall volume fraction of oxide is small. The nature of the inclusion/matrix bonding forces will also have an effect, as yet unknown.

Recent experimental evidence has shown that for sulphides, increasing the volume fraction of MnS first increases the impact transition temperature and then decreases it, in either longitudinal or transverse testing, fig 21. This may account for the uncertain effect of inclusions on the impact transition temperature, and a tentative reason for

the observed effect has been suggested.[1] Evidence[1] has also shown that by eliminating these MnS fibres by zirconium inclusion shape control, the impact transition temperature can increase by as much as $\sim 50^{o}C$ and recently a similar effect has been observed for rare-earth modification.[42] This may well be because the crack arresting or dividing characteristics are removed. Also there is evidence, as already suggested earlier, that excessive shape control of sulphides by zirconium can give embrittling ZrC and $Zr_4C_2S_2$ films, which as for carbide films, may also increase the impact transition temperature.[1][11][41] ZrN may also cause crack initiation effects.

Thus, whilst certainly being beneficial in terms of charpy impact shelf energy, and particularly its anisotropy, some care should be exercised in using inclusion shape control where the arrest of a running crack is essential, i.e. where a low impact transition temperature is required.

REFERENCES

1. F B Pickering, "Towards Improved Ductility and Toughness" Climax Molybdenum Company Symposium, Kyoto, 1971, 9.

2. B.J. Edelson and W. M. Baldwin, Trans. A.S.M. 1961, 55, 230.

3. J Gurland and J Plateau, Trans. ASM, 1963, 56, 442.

4. F A McClintock, "Ductility", ASM Seminar Volume, 1968, 225, Metals Park, Ohio.

5. T Gladman et al, JISI, 1970, 108, 173.

6. M. Korchynsky and H Stuart, "Low Alloy High Strength Steels", London Scandinavian Conference, Nuremberg, 1970, 17.

7. T J Baker, "Inclusions and their effects on Steel Properties", BSC Conference, 1974, Leeds - Paper 11.

8. J H Little and W L M Henderson, "Effect of Second Phase Particles on the Mechanical Properties of Steels", ISI, 1971, 182.

9. L Luyckx et al. Met Trans 1970, 1 3341.

10. D C Hilty and V T Popp, AIME Elect. Furn. Conf. Proc., 1969, 27, 52.

11. T Gladman et al. "Effect of Second Phase Particles on the Mechanical Properties of Steels", ISI, 1971, 68.

12. J C M Farrar et al, Ibid, 171.

13. T J Baker and J A Charles, Ibid, 79.

14. J A Charles, "Inclusions and their effects on Steel Properties", BSC Conference, Leeds, Paper 6.

15. R Kiessling, ISI Publications 100, 1966; and 115, 1968.

16. T J Baker and J A Charles, JISI, 1972, 210, 680.

17. J R Blank and F B Pickering - unpublished work.

18. W Dahl et al. Stahl v. Eisen. 1966, 86, 796.

19. P E Waudby, Steel Times Annual Review 1972, October, 147.

20. S Ekerot, Scand. J. of Met. 1974, 3, 151.

21. D A Melford. Private Communication.

22. A Kohn, "Production and Application of Clean Steels", ISI Publ. 1972, 92.

23. P E Waudby, PhD Thesis, Sheffield Polytechnic 1974.

24. W J M Salter and F B Pickering, JISI 1969, 207, 992.

25. M G Gemmill et al. JISI 1956, 184, 122.

26. C P Church et al. J.Met. 1966, 18, 62.

27. F B Pickering, JISI 1958, 189, 148.

28. F B Pickering. Jernkon. Ann. 1964, 148, 845.

29. J L Mihelich et al. JISI, 1971, 209, 469.

30. M J Arrowsmith, "Inclusions and their Effects on Steel Properties", BSC Conference 1974, Leeds, Paper 7.

31. F Heisterkamp and L Meyer, Thyssen Forschung 1971, 1-2, 44.

32. L Meyer et al. "Processing and Properties of Low Carbon Steels". AIME. 1973, 297.

33. T Gladman and D Dulieu. To be published in Proceedings of Conference "Microalloying 75", Washington 1975.

34. W G Wilson, "Inclusions and their Effects on Steel Properties", BSC Conference 1974, Leeds, Paper 5.

35. G Rowntree et al, JISI, 1973, 211, 811.

36. D C Hilty and J W Farrell, "Inclusions and their Effects on Steel Properties", BSC Conference, 1974, Leeds, Paper 4.

37. D L Sponseller and R A Flinn. Trans. AIME 1964, 230, 876.

38. A Schoberl and W Holzgruber, Radex Rundschau 1962, 2, 501.

39. P E Waudby, "Clean Steel", Proc. 75th BISRA Steelmaking Conf. 1970, 71.

40. M Wahlster, "Production and Applications of Clean Steel", ISI Publ, 1972, 205.

41. R C Cochrane, "The Effect of Second Phase Particles on the Mechanical Properties of Steels", ISI, 1972, 101.

42. "Inclusions and their Effects on Steel Properties", BSC Conference, 1974, Leeds.

LECTURE 8

THE FORMATION OF NON-METALLIC INCLUSIONS DURING ELECTRIC ARC STEELMAKING

Introduction

Inclusions in steel frequently have very detrimental effects on the mechanical properties, it being well known that the general ductility is decreased by increasing amounts of either oxides or sulphides[1][2][3]. The very injurious effects of oxide inclusions on the fatigue properties of bearing steels, and on the notch toughness of high-strength steels is also well appreciated[4][5][6]. However, it must not be supposed that inclusions are invariably harmful. Manganese sulphides, for example, can be particularly beneficial with regard to the free-machining properties of steel[7][8] and also with respect to hydrogen cracking[9].

The aim of the steelmaker is therefore to ensure adequate freedom from the most injurious types and distributions of inclusions. In order to do this, it is necessary to understand the origin of the inclusions, particularly those of oxide type. It is the object of this paper to describe some of the effects of process variables during steelmaking, tapping and teeming on the formation of non-metallic inclusions, with particular emphasis on oxides. Details of the techniques used have been published elsewhere.[10][11]

Occurrence of inclusions during the steelmaking process

The steelmaking processes investigated were the double-slag basic electric-arc production of 0.65-0.70%C, 1%C-Cr and low-carbon 2%Ni-Mo steels. The double-slag process can be conveniently divided into two stages, namely the oxidising period in which oxygen lancing was usually used, and the refining period under a reducing high-basicity slag to effect sulphur removal and achieve specification.

(a) The oxidising period

The inclusions present at melt-out, a cold charge being used

in all cases, were mainly manganese-aluminium silicates resulting from the oxidation of the charge. As the boil progressed, the Al_2O_3 and MnO content of the silicates decreased, Figs 1 and 2, as the aluminium and manganese were oxidized out of the charge. The most interesting feature of the composition of the silicates was the progressive increase in their CaO content during the boil, Fig 3. Silicon was also oxidized out of the bath, but the SiO_2 content of the silicates did not change appreciably throughout the oxidation period, because inclusions formed by oxidation nucleated on existing inclusions in the bath and were eliminated to the slag by the turbulence during the boil, but this same turbulence caused slag particles also to be mixed into the bath. Thus, the turbulence created by the boil can account for the increased CaO content of the silicates being produced by the entrainment of slag in the bath. Further confirmation of the role of the slag in forming the inclusions present during the oxidation period is given by the observation that, when considerable turbulence was created by charging material, a sample taken immediately afterwards always showed large numbers of the highly calcareous slag inclusions. Also, as occasionally happened, when slag had to be removed during the boil, the bath was partially deprived of its slag cover and the metal surface oxidized to produce iron-manganese silicates, and these were entrapped in the bath by the turbulence. Consequently, a specimen taken immediately after such an intermediate slagging-off contained simple iron-manganese silicates which were free from CaO.

While it is clear that slag entrapment accounted for an ever-increasing proportion of the inclusions throughout the boil, there was not a 1:1 correspondence between the composition of the slag and that of the calcareous silicates at the end of the boil. In fact the inclusions were richer in MnO and SiO_2 and less rich in CaO, and this can be explained on the basis that oxidation products tended to nucleate on entrapped slag particles.

The size of the silicate inclusions tended to vary systematically throughout the boil, being largest at the start of the boil when the reaction was most vigorous, and decreasing in size towards the end of the boil when the turbulence was subsiding.[10] Superimposed on this general trend, there was also a marked effect produced by the vigour of the boil, as indicated by the average rate of carbon removal, Fig 4. As the rate of carbon removal increased, so the size of the slag-based silicates increased. This effect cannot increase indefinitely because eventually with very great turbulence, the particles of slag will be so large that they will separate almost immediately and never be detected. Also, with very turbulent boiling the energy will be sufficient to create the surface area associated with small particles, and hence the slag will be more effectively 'emulsified'. Consequently at very rapid rates of carbon removal, smaller particle sizes may again be detected. There was evidence for this in some work done on the oxygen-injected basic open-hearth (AJAX) process, as shown in Fig 4. At the most rapid rate of carbon removal, smaller silicates were in fact observed, but as the rate of carbon removal decreased towards the end of the boil, the particle size increased and was in agreement with the trend observed for the boil during electric-arc steelmaking.

When the initial charge to the furnace contained some chromium, in a low-alloy steel, it was observed that individual small particles of spinels were formed during the oxidation period. At melt-out the spinels were mainly galaxite, $MnO.Al_2O_3$, formed by oxidation of any aluminium in the charge, but also containing some Cr_2O_3 replacing Al_2O_3. With increasing time during the oxidation period, the aluminium and also the manganese in the charge were removed by oxidation, and the composition of the spinels moved rapidly towards that of chromite, $FeO.Cr_2O_3$. At the same time, chromite inclusions were also seen to be associated with silicate inclusions. Two forms were observed, one being a fairly large angular chromite within a silicate containing only a trace of chromium. It is suggested that

the silicates coalesced or nucleated around these fairly large spinel particles. The other form showed chromite dendrites precipitated from a complex silicate containing 12-15% Cr_2O_3. It seems clear that in this case considerable Cr_2O_3 had been dissolved in the silica, yet the solubility of Cr_2O_3 in SiO_2 is very limited.[12] This solubility can be increased by the presence of other oxides in the silicate,[13] but only at a temperature of about 1800°C. It is suggested, therefore, that oxygen lancing had caused a very high temperature locally, and in these conditions the silicates had been able to dissolve sufficient Cr_2O_3 to result in the precipitation of chromite dendrites on subsequent cooling.

Finally, the compositions of the sulphides also showed changes during the oxidation period as the manganese was oxidized out of the bath. This caused a progressive change from (FeMn)S to virtually pure FeS, Fig 5.

The evidence that slag-based inclusions were picked up during the oxidation period, while being mainly obtained during experiments on electric-arc furnaces, was also confirmed during some limited investigations on the oxygen-lanced basic open-hearth process. There was a progressive increase in the CaO content during the oxidation period, Fig 6. Whilst it is not suggested that the inclusions present in the bath during the boil will persist and appear in the final product, there is ample evidence to show that the type of inclusions can be closely related to the actual processes occurring during this period of steelmaking.

(b) The refining period

At the start of the refining period in double-slag basic electric-arc steelmaking, the oxidising slag is removed and the bath is deoxidized. This causes a pronounced change in the inclusions, and the deoxidation processes can be conveniently classified under the following three categories.

(i) Silicon deoxidation:

At the start of refining, before deoxidation, the inclusions present were calcium-manganese silicates persisting from the oxidation period. Silicon deoxidation was effected either by the use of calcium silicide or ferrosilicon. The addition of calcium silicide led to a pronounced change in the silicate inclusions; those being produced by deoxidation contained up to 40% Al_2O_3, owing to the presence of about 1½% Al in the calcium silicide, Fig 7. The added ferro-manganese also increased the MnO content of the silicates, and dilution effects greatly lowered the CaO and SiO_2 contents of the silicates even though calcium silicide had been used. The inclusions still contained ∿ 15% CaO, however, owing either to the calcium deoxidation or to the nucleation of deoxidation products on small, pre-existing slag globules. Providing no further deoxidation alloys were added, the silicate composition gradually reverted to a lower Al_2O_3 and MnO content and a higher CaO and SiO_2 content, as the first formed silicates were removed to the slag and were replaced by further silicates picked up from the hearth, banks, and possibly the slag. Any pick-up of oxygen would also give rise to deoxidation products, i.e. silicates. The effect of aluminium in the predominantly silicon deoxidation alloy in causing the formation of highly aluminous silicates was clearly established by the similar results obtained in a number of investigations. That slag contributed to the silicates is shown by the fact that when ferrosilicon alone was used for deoxidation, the silicates still contained CaO. They also contained appreciable Al_2O_3 owing to the ferrosilicon containing more than 1% Al. However, the CaO content at the end of refining, when ferrosilicon had been used, was 20-25% compared with almost 50% when calcium silicide was used. It seems therefore that some CaO is being introduced into the silicates from the calcium-bearing deoxidant.

Another feature observed was the gradual increase in the Al_2O_3 content of the silicates if additions of the aluminium

bearing silicon deoxidation alloy were made progressively throughout the refining period in order to bring the steel to specification, Fig 8. If such an addition was made immediately before tapping, the alumina content of the silicates increased sharply, even though immediately before the addition the Al_2O_3 content of the silicates was less than 2%.

The aluminous silicates which also contained CaO, particularly if formed in quantity by a late addition of ferrosilicon or calcium silicide, could be retained in the bath long enough to be tapped into the ladle, and also have been found in the final product where they can give rise to problems with respect to quality. These inclusions were often quite large, and they appeared to increase in size with increasing Al_2O_3 content.[10] If selected ferrosilicon was used for deoxidation, which contained very little aluminium, the Al_2O_3 content of the silicates was greatly reduced, as also was their size, and fewer quality problems were encountered. Consequently it was found beneficial to use silicon deoxidants containing a minimum of aluminium, and to ensure that no such deoxidant was added late in the refining period.

(ii) Simultaneous silicon and aluminium deoxidation:
When ferrosilicon and aluminium were added simultaneously at the start of refining, a number of effects were observed. A joint deoxidation by aluminium and silicon gave rise to manganese-aluminium silicates, the composition of which depended upon the local environment in terms of the aluminium and silicon concentrations. On the other hand, the aluminium and silicon each could accomplish its own deoxidation to produce alumina or silicates respectively in regions rich in aluminium or silicon. These two types of inclusion have been observed simultaneously in the bath immediately after the joint deoxidation, but such coexistence is very temporary because circulation within the bath usually takes these primary inclusions into regions of different deoxidation environment. If the alumina particles

enter an environment of predominant silicon deoxidation, manganese aluminium silicates can precipitate around them. Alternatively the silicates can move into an aluminium deoxidation environment, and reaction can occur to give a silicate rich in Al_2O_3 so that mullite or alumina can precipitate from the silicate. If such a reaction goes to completion, almost all the silicate can be converted to an alumina aggregate. In some circumstances coalescence can occur between a shower of alumina and silicates, giving rise to very irregular silicates enveloping one or more alumina particles.

The complexity of these reactions leads to the resulting inclusions having a wide range of composition and morphology, but the most important observation is that large amounts of alumina were not formed. Consequently, the rapidity of deoxidation was decreased because the aluminous silicates were less readily eliminated to the slag than alumina. In fact, it is suggested that the elimination of existing inclusions, and the formation of new ones from slag entrapment, oxygen pick-up, etc, is a continuous and dynamic process.

As the aluminium is consumed, the Al_2O_3 content of the silicates should decrease throughout refining, and such was the observed effect, Fig 9. The CaO content increased however, indicating the role of slag in providing nuclei for deoxidation products, and in this case no calcium-bearing deoxidant was used. The band of results shown in Fig 9 is probably due to variability in the initial state of oxidation of the bath, and also to variable rates of oxygen pick-up and reaction of aluminium. Because of the dynamic effect of continual removal of inclusions to the slag and the formation of new inclusions from oxygen pick-up, the Al_2O_3 content of the slag increased throughout refining and was at a higher level with increasing aluminium used in the deoxidation process, Fig 10.

(iii) Aluminium deoxidation before silicon addition:
If aluminium deoxidation was used before the ferrosilicon or calcium silicide, alumina showers were produced, and the average Al_2O_3 content of the inclusions increased sharply, Fig 11, to ∿ 80%. The inclusions formed, apart from alumina produced by direct deoxidation, comprised spinels and calcium aluminates, the latter originating from the pre-existing inclusions of slag origin which reacted with the aluminium addition. Providing an adequate aluminium addition was made, the subsequent addition of silicon-bearing ferro-alloys did not produce any silicate inclusions. A similar series of changes was also observed when ferroaluminium was used instead of aluminium. Because the alumina thus produced was fairly rapidly eliminated to the slag, and no silicates were formed, a very clean bath was produced. If, however, the initial deoxidation reactions had to a large extent used up the aluminium added, any oxygen pick-up will result in silicates being formed, and calcium-bearing silicates from the slag were also observed. On the other hand, if the aluminium addition had been sufficient to leave an adequate aluminium content in the bath, further oxygen pick-up resulted in the formation of more alumina particles, and the slag inclusions reacted to form calcium aluminates and spinels ($MgO.Al_2O_3$). The aluminium content in the bath can persist for various lengths of time, depending on the amount of aluminium added, the original oxygen content before deoxidation, the amount of oxygen pick-up during refining, and the extent of reaction between the aluminium in the bath and the refining slag. A high oxygen content at the end of the boil, i.e. a very low carbon content, can cause a very much decreased aluminium content and necessitate the formation and elimination of a larger volume fraction of alumina, which takes time, and thus the primary deoxidation may be neither uniform nor complete when the ferrosilicon is added.

The presence of an adequate aluminium content preserves a clean bath, but the effective aluminium decreases with time during refining, and eventually silicates are formed unless

steps were taken to add further aluminium. As the aluminium decreased in effectiveness, so the Al_2O_3 content of the inclusions decreased. The greater the aluminium content, the higher was the Al_2O_3; CaO ratio in the calcium aluminates. An addition of aluminium later, during refining, readily restored a fading aluminium content, Fig 12. The presence of aluminium to the end of refining therefore preserves a clean bath containing a minimum of inclusions, which also ensures that a minimum of inclusions are tapped into the ladle. Consequently, it is suggested that aluminium should be added as early as possible during refining, and always before the silicon. Also, more aluminium should often be added if the refining period is inadvertently extended.

The role of slag inclusions even in the relatively quiescent refining period has already been mentioned, and a possible cause for their entrapment has been suggested. The fact that any disturbance or turbulence created in the bath can cause admixture of slag into the bath has been observed on many occasions. Immedidately after such disturbance of the bath, an increase in the CaO content of the silicates, in a process not primarily deoxidised by aluminium, was frequently observed. Two particular causes of such entrapment were identified with additions of slag-forming materials and ferroalloys, and with mechanical stirring of the bath, Fig 13.

In general, the inclusion size decreased progressively throughout the reducing period,[10] Fig 14. The silicates in a silicon-deoxidation practice were always much larger (45 μm) than the alumina, spinel, and calcium aluminates (5 - 15 μm) in an aluminium-killed practice. The reason for the decreasing inclusion size is that at the start of refining the super-saturation was relatively great, so that each inclusion had ample opportunity to grow more than later in refining, when the supersaturation was small and due only to oxygen pick-up.

The sulphide inclusions also readily reflected the steel-making process, particularly the ferromanganese additions. The sulphides at the start of refining were mainly FeS, but their manganese showed a parallel increase with the ferro-manganese addition until mainly MnS was observed.

Effect of tapping on the inclusions in the ladle

(a) Launder erosion products

Several effects have been observed during tapping. The first was the pick-up of launder erosion products during tapping down a siliceous (gannister) launder. The result was large, highly siliceous globules which invariably contained particles of silica rich glass and these occurred in the metal stream issuing from the end of the launder, in a silicon-killed steel. These inclusions can contain a little CaO from slag glaze on the launder. It might be argued that they were due to oxidation of the launder stream, but this is not believed to be so because replacing the siliceous launder by a magnesite launder completely removed this type of inclusion. In an aluminium-treated steel, however, launder erosion products are much less prevalent owing to reaction with the dissolved aluminium.

(b) Effect of slag-metal mixing

During tapping, the major effect was produced by tapping through the refining slag in order to promote more effective desulphurization. This has always been observed to result in the occurrence of large inclusions, which undoubtedly originate from the admixture of the slag with the steel during tapping. Two distinct types of inclusions were observed in the ladle immediately after tapping, depending upon whether the steel was silicon killed or aluminium treated.

In a silicon-killed steel, not treated with aluminium, the inclusions in the ladle invariably comprised large calcium-rich silicates originating from the slag, as shown by the close correspondence of the analysis of the inclusions and

the slag, Fig 15. Also, the inclusions in the ladle were always considerably larger than those in the furnace immediately before tapping, Fig 16, and always occurred in much greater amounts.

In an aluminium-treated steel, while slag inclusions were picked up during tapping through the slag, these reacted with the aluminium dissolved in the steel to form quite large calcium aluminates containing $MgO.Al_2O_3$ spinel particles. Again, the size of these calcium aluminates was very much greater than that of the inclusions occurring at the end of the refining period, Fig 17.

Despite the improvements which can be made by varying the deoxidation procedures during the refining period to improve the cleanness of the steel when it is tapped, much of this improvement can be rendered useless if the metal is tapped through the slag in an attempt to produce lower sulphur contents.

(c) Effect of limiting slag-metal mixing

It has been suggested that in order to disperse slag into 30 μm diameter globules, the slag would have to fall some 30ft in order to acquire the energy necessary to generate the new surface area.[14] As the slag seldom falls half this distance, it was suggested that slag entrapment was not likely. However, the evidence of the inclusions present in the ladle all pointed conclusively to large numbers of slag inclusions being present in the steel, and ample energy is available to render this feasible if the total energy of the tapping stream is considered.

On the basis of a very simple calculation it can be shown that the size of the slag-based inclusions should decrease as the amount of slag tapped with the steel decreases. Evidence for this was obtained. In seven experiments using normal slag-metal mixing, the mean maximum inclusion size was $\sim$ 90 μm, whereas in two experiments with very restricted

slag-metal mixing it was ∿ 60 μm. It can also be concluded that the number of larger slag-based inclusions will decrease, while there will also be a larger number of very small slag-based particles. This conclusion was also verified by considering the ratio of slag based to other inclusions, with sizes greater than 25 μm:

	Ratio:- slag:other inclusions
Normal slag-metal mixing	2.28
Very restricted slag-metal mixing	0.87

On the evidence that a restriction of slag-metal mixing produces fewer of the larger inclusions, it would be expected that for a constant amount of oxygen pick-up and precipitation of deoxidation products on the slag inclusions, more dilution of the CaO content of the inclusions should be observed when slag-metal mixing is restricted. This also was observed, as shown by the following results:

	% CaO in inclusions
Normal slag-metal mixing	35
Very restricted slag-metal mixing	21

It can be seen, therefore, that a cleaner steel, containing many fewer of the larger inclusions, can be produced in the ladle if the slag and metal are not mixed during tapping.

Inclusions present in the ladle

During tapping, and also during teeming, oxidation of liquid metal streams occurs. Thus further inclusions are produced either from the deoxidants already present in the steel or from deoxidants deliberately added to the ladle.

In a silicon-killed practice, the aluminium in the silicon-addition alloys entered the deoxidation products and greatly increased the Al_2O_3 content of the silicates, Fig 18. These more highly aluminous silicates were quite large and as they were formed in the ladle had a greater opportunity to enter

the ingot. Wherever possible ferrosilicon additions to the ladle should be avoided in a silicon-killed steel, and the implementation of this suggestion led to a marked improvement in cleanness.[10]

In an aluminium-killed steel, in which an addition of aluminium was also made to the ladle, the mixing of slag and metal during tapping resulted in the formation of calcium aluminates from the reaction between the slag and the aluminium in the steel. The Al_2O_3:CaO ratio of the calcium aluminates increased with increasing amounts of aluminium added to the ladle, Fig 19, changing from $CaO.Al_2O_3$ through $CaO.2Al_2O_3$ to $CaO.6Al_2O_3$. With increasing Al_2O_3:CaO ratio in the calcium aluminates, their particle size decreased, Fig 20. The reason for this is that $CaO.Al_2O_3$ and calcium aluminates less rich in Al_2O_3, melt at temperatures below the ladle temperature, and thus are molten and can coalesce and grow to form larger particles. On the other hand, $CaO.2Al_2O_3$ and $CaO.6Al_2O_3$ are solid and thus form much smaller particles.

During a holding period in the ladle, the larger inclusions can float out into the ladle slag. However there is always the danger that the longer the steel is in contact with the ladle lining, the more tendency there will be for ladle erosion products. Due to cooling in the ladle, further deoxidation products are precipitated, and as the steel is cooled MnO precipitates in larger amounts than SiO_2. Consequently the MnO:SiO_2 ratio of the deoxidation products in a silicon-killed steel increased with increasing time in the ladle.[11]

In an aluminium-killed steel, the calcium aluminates increased in Al_2O_3 content as the time in the ladle increased, Fig 21. The effect is due to the larger size of the less aluminous calcium aluminates which allows them to float out more quickly leaving the smaller, more aluminous, calcium aluminates in the steel. Such a flotation effect was

confirmed by the marked increase in the Al_2O_3 content of the ladle slag with increasing time.

Investigations have been made into the effect of vacuum degassing on the inclusions present in the steel There was no evidence that there was any dissociation of the very stable alumina or calcium aluminates under vacuum, but the size of the inclusions definitely decreased, Fig 22. This was simply due to the holding period of 9-14 min brought about by vacuum degassing, which allowed flotation of the larger inclusions, aided by the evolution of gas and the associated turbulence during degassing. At the same time, the Al_2O_3:CaO ratio of the calcium aluminates increased during degassing, due to the flotation of the larger, more calcareous inclusions during the vacuum-degassing period.

Inclusions present during teeming

(a) Silicon-killed basic electric-arc steels

The inclusions were both deoxidation products of the manganese aluminium silicate type and calcareous slag-based inclusions. During teeming there was a pronounced tendency for the inclusions to increase in Al_2O_3, Fig 23. This was believed to be due to progressive contamination with ladle refractory erosion products. The upper and lower limits of the band shown in Fig 23 probably represent the extremes of ladle-lining condition. Further evidence for the contamination with ladle erosion products is that the TiO_2 content increased with time, TiO_2 being a tracer in these refractories. Ladle refractory erosion can have a major effect on the cleanness assessment of a steel, and can override all attempts in the steelmaking process to produce a clean steel.[15] Ladle linings maintained by a sprayed gannister coating give rise to many more erosion products than either bricked or rammed linings. These ladle erosion products also frequently contained a little CaO, due to the ladle glaze being contaminated by slag.

Using a simple flotation model for inclusions in the ladle,

the maximum size of inclusions of the silicate type can be predicted at any time in the teeming process.[11] This is shown by the full line in Fig 24. The maximum observed particle size should increase with time during teeming, and this is in fact observed. The largest calcium-rich slag-based silicates were never bigger than the predicted maximum, but the largest ladle erosion products were very considerably greater than the predicted maximum size. The probable reason for this is that ladle erosion products were produced continually throughout teeming in a wide spectrum of sizes and at a time dependent upon the local softening of, and scouring action on, the reaction layers. Consequently, flotation models cannot readily be used to predict their sizes, which are often much greater than would be predicted. It was observed that while ladle holding allowed flotation to occur, the extra time for which the steel was in contact with ladle refractories could give rise to more erosion products. The conditions for forming the minimum of erosion products are therefore complex, involving critical interactions between holding time, teeming speed, temperature, and above all the initial condition and type of ladle lining.

(b) Aluminium-treated basic electric-arc steels

In steels which have been heavily killed by aluminium, the occurrence of silicate inclusions which are clearly ladle erosion products is by no means so readily observed, because reaction occurs between the silicates and the aluminium dissolved in the steel, tending to form alumina and spinels and even calcium aluminates from the CaO often present in erosion products. Nevertheless, high Al_2O_3 silicate erosion products were observed in samples taken from the ladle stream, when they had less time to react with aluminium, but not in the ingot itself when the reactions had probably gone more or less to completion to form Al_2O_3 etc. Inclusions of this type have been observed in laboratory investigations into the reaction between silicates and aluminium dissolved in the steel.[16] It is suggested that they probably represent nozzle and stopper erosion products which have not had

sufficient time for complete reaction before the sample was taken, and this is to a large extent confirmed because they contained no CaO, which would have been present had they originated from ladle glazes. This does not imply that ladle refractory erosion does not occur, but rather that such erosion products have time to react with aluminium during their stay in the ladle. Very occasionally highly siliceous particles typical of nozzle drip were also observed.

There was no systematic variation in the Al_2O_3 content of the erosion products during teeming, probably because they varied in Al_2O_3 at the time of their formation, and the analysis would further be randomized by variable reaction with aluminium dissolved in the steel. There was, however, a tendency for the largest erosion products to increase in size as teeming progressed, Fig 25, and this was particularly observed towards the end of teeming, and when teeming was inadvertently prolonged. This shows the detrimental effect of an increasing time of contact between steel and refractory on the formation of erosion products.

In addition to erosion products, there were also calcium aluminates and alumina present during teeming. The alumina particles, and the calcium aluminates of the $CaO.6Al_2O_3$ type were very small in size (less than 5 μm) throughout teeming, and together with $MgO.Al_2O_3$ spinels, were formed by reaction between entrapped slag and the aluminium added in the ladle. The main source of alumina however was direct deoxidation or from the pick-up of oxygen during teeming.

(c) Runner erosion

The runner brick assembly in uphill-teemed ingots has long been recognised as a source of non-metallic inclusions, which originate from the erosion of the aluminosilicates by high-manganese steels. Such erosion products are very readily observed in silicon-killed steels, but for the reasons already discussed with regard to ladle erosion products, they are not so readily observed in heavily aluminium-treated steels. Nevertheless the reaction products between

aluminosilicate runner assembly erosion products and aluminium in the steel will contribute to the total inclusion content of the steel. The surface layers of aluminosilicates which have been in contact with steel can contain appreciable amounts of alumina. It is clear that where such erosion problems are likely to occur, particular attention should be paid to the quality of the runner bricks. In this respect, the use of an aluminium-killed steel may be beneficial in breaking down the large erosion silicates into smaller and possibly less injurious alumina and spinel inclusions, besides possibly decreasing the extent of erosion.

Inclusions which are formed in the ingot

Perhaps the most deleterious place in which inclusions can be formed is in the ingot, because they will then have the least chance of escaping from the steel.

(a) Rimming Steels

The oxygen required in the solidification of rimming steel ingots is more than that available in the liquid steel teemed into the ingot mould, and must be supplied from the atmosphere at the turbulent surface of the ingot. One source of such oxygen is the scum which forms by atmospheric oxidation on the surface of the liquid metal in the ingot mould, and large masses of scum can be engulfed in the solidifying ingot.[17] Some large inclusions comprised (FeMn)O dendrites in a silicate matrix and an examination of the scum from the ingot revealed that it had virtually an identical structure.[11][17]

(b) Ingot head tiles, fluxes, etc

The use of insulating tiles in the ingot head of killed steels has long been practiced, and occasionally a tile may become dislodged and fall into the ingot mould where it disintegrates and forms a large number of siliceous inclusions. In the rolled product these form a large segregate of elongated silicates which obviously produce a quality-control problem. These might be classed as mechanically introduced inclusions, and usually can be readily avoided.

(c) Deoxidants added to ingot moulds

In balanced or semikilled steels, a technique which can be used is to add sufficient deoxidant to the mould so to regulate the gas evolution that a balanced condition results. Such a practice is not perhaps the best because it forms fairly large amounts of deoxidation products in the mould, and ladle balancing is a more effective method to produce clean, balanced steel. Various methods of mould balancing have been investigated. In the first, in which an aluminium-silicon alloy was fed into the mould to regulate the rimming action, a large proportion of defective material was rejected owing to inclusions formed directly by mould balancing. Before the addition of the deoxidants to the mould, the inclusions were primary deoxidation products of manganese silicate or (FeMn)O, but after the aluminium-silicon deoxidant had been added they were very fluid manganese-aluminium silicates, and frequently of large size, Fig 26. The mechanism of their formation is either by a direct deoxidation reaction with dissolved oxygen, which must take place to control the rimming action, or by a reaction between the added aluminium and silicon and the pre-existing inclusions. When the rimming reaction ceased, these manganese-aluminium silicates then segregated into the bottom third of what behaved as a killed ingot, and gave rise to the typical bottom cone segregation of inclusions.[18]

Another practice investigated was in uphill-teemed steel which was poured as a rimming steel and the last metal was treated with aluminium to produce a killed or stabilized steel core within a rimmed periphery. In the rimmed peripheral layers of the ingot, the inclusions were mainly (FeMn)O or silicates, but in the core of the ingot they abruptly changed to aluminous silicates or alumina clusters, depending on the amount of aluminium used, Fig 27. These aluminous inclusions were formed by direct deoxidation, and by reaction with existing inclusions.

(d) Exothermic feeder-head compounds

The use of exothermic feeder-head compounds, which contain

free aluminium in a thermite mixture, can lead to unusual inclusions in the ingot. For example, in a silicon-killed 1½% Mn steel, groups of large alumina inclusions were observed in the upper part of the ingot, although no aluminium had been used at any stage during their manufacture. The alumina inclusions occurred at positions down to 30% from the top of the ingot, and were directly attributable to aluminium deoxidation of the top of the ingot by the free aluminium in the exothermic feeder-head compound. Apparently convection currents within the solidifying ingot were capable of drawing the inclusions down into the body of the ingot.

A second example, which illustrates the rather complex effects which can be observed, concerned the formation of duplex $MgO.Al_2O_3$ spinels with calcium-aluminium silicates, in the tops of ingots of a basic electric medium-carbon steel. At no stage in its manufacture had this steel been treated with aluminium, and the ferrosilicon used for deoxidation had been specially selected to contain a low residual aluminium content. The steel had, however, been tapped through slag in order to achieve a low sulphur content, and a very effective exothermic feeder-head compound had been used. The presence of the calcium-aluminium silicate associated with the spinel indicated that entrained slag was partially responsible for the inclusions, and it was also suspected that the exothermic feeder-head compound played a part in their formation. Experiments in which non-reactive feeder-head compounds such as vermiculite were used, showed a marked decrease in the frequency of occurrence of the detrimental inclusions but did not entirely eliminate them. However, very effective restriction of slag-metal mixing during tapping, coupled with a non-reactive feeder-head compound, virtually eliminated the inclusions, Fig 28. It is suggested that slag inclusions were entrained in the steel during tapping and some also passed into the ingot during teeming. As they floated up to the top of the ingot they reacted with the exothermic feeder-head compound to entrap spinel particles within the calcium-rich silicate

from the slag, which also became enriched in aluminium due to the free aluminium in the exothermic compound. The reason why the use of a vermiculite insulating layer did not entirely eliminate the inclusions is that vermiculite can, at high temperature, break down to form $MgO.Al_2O_3$ spinel, which was entrapped by slag. The lower frequency of occurrence of the inclusions using a non-reactive compound pointed to the added effect played by the exothermic reaction either in promoting the reactions or in helping the entrainment of inclusions into the main body of the ingot.

The use of oxidic materials to help in promoting good surfaces, adequate feeding, etc, in ingots may be expected to lead to some complex inclusions from time to time. For example, a mould flux can react with an exothermic feeder-head compound and impair its performance, and the reaction products could then be entrained in the ingot. Further reactions could also be envisaged with the feeder-head tiles giving very complex oxide inclusions. It therefore seems necessary that in future it will be required for such materials as mould fluxes, feeder-head compounds, tiles, etc, to be mutually compatible so as not to impair each others performance and, moreover, so as not to form exogenous inclusions which might be detrimental to the quality of the steel.

General Conclusions

An attempt has been made to summarize some of the information obtained concerning the effect of variations in the steelmaking, tapping, and teeming processes on the inclusions formed in steel. By using the information such as has been outlined, it has been found possible to bring about significant improvements in the cleanness of steels.[10] In general it is the very large inclusions which provide the greatest quality-control problems, particularly if they occur as segregates. The relative average volumes of the various types of inclusions can be taken as an index of their likely deleterious nature:

Type of inclusion:	Diameter µm	Relative Volume
Alumina, spinel, and $CaO.6Al_2O_3$ (other than clusters)	5	1
Other calcium aluminates	27	160
Secondary deoxidation products (Si-killed steel)	32	260
Primary deoxidation products (Si-killed steel)	49	940
Erosion silicates (Al-killed steel)	64	2100
Erosion silicates (Si-killed steel)	107	9800

These figures clearly show that it is the primary silicate deoxidation products and the erosion products which are likely to cause the most problems. Steps can be taken to eliminate deoxidation silicates by varying the deoxidation practice, but it is clear that a considerable effort requires to be devoted to eliminating refractory erosion products.

References

1 B J Edelson and W M Baldwin, Trans ASM. 1961, 55, 230.

2 J Gurland and J Plateau, Trans ASM. 1963, 56, 442.

3 T Gladman et al. JISI. 1970, 208, 172.

4 J D Murray and R F Johnson, ISI Spec.Rep. 77, 1963, 110.

5 L O Uhrus, Ibid, 104.

6 S Enekes, "Production and Application of Clean Steel". ISI 1972, 215.

7 R Kiessling, ISI. Publication 115, 1968, 58.

8 E M Trent, ISI Spec.Rep. 94, 1967, 11, 77, 179.

9 D Brooksbank and K W Andrews. "Production and Application of Clean Steel" ISI. 1972, 186.

10 E L Morgan et al. JISI 1968, 206, 987.

11 F B Pickering. "Production and Application of Clean Steel". ISI, 1972, 75.

12 M L Kieth, J.Am.Ceram.Soc. 1954, 37, 490.

13 A Muan and E F Osborn, "Phase Equilibria among oxides in Steelmaking" 1965. Addison-Wesley.

14 C E Sims, Trans.AIME, 1959, 215, 367.

15 J R Blank and F B Pickering. Unpublished Work.

16 P E Waudby et al. JISI 1973, 211, 486.

17 F B Pickering. Jernkontorets,Ann. 1964, 148, 845.

18 J R Blank and F B Pickering, "The Solidification of Metals". The Iron and Steel Institute, 1968, 370.

LECTURE 9

THE EFFECT OF INCLUSIONS ON THE MECHANICAL PROPERTIES OF STEEL

1. INTRODUCTION

The dependence of mechanical properties on the microstructure has been known for many years, but the quantitative relationships between microstructure and properties initiated by Gensamer et al[1] in the mid 1940's was stimulated by the development of the Hall-Petch[2,3] relationship in the mid 1950's. Since that time, there have been considerable developments in the effects of microstructure on mechanical properties. Work on strength-structure relationships was broadened to cover impact properties, and in recent years attention has been focussed on the effects of microstructure on ductility, which is an important property in connection with metal forming operations such as bending, and is also related to toughness as expressed by the fully ductile shelf energy.

It is the purpose of the present paper to outline the basic theories of ductile fracture, indicating the important features of the microstructure, and to illustrate the effects of inclusions on important mechanical properties. Ductility properties which are limited by plastic instability rather than by ductile failure account for the insensitivity of certain formability criteria to the inclusion content.

2. THEORY OF DUCTILE FRACTURE

The ductile fracture process involves the formation of cavities in the material, the growth of these cavities during straining, and the coalescence of cavities during the final catastrophic failure.

2.1 Cavity Nucleation

During straining at room temperature, the nucleation of cavities is often observed to occur either by particle

cracking, Figure 1, or by decohesion of the particle-matrix interface. In the case of a carbide such as lamellar cementite in a ferritic matrix, the cavitation process is commonly one of carbide cracking. In the case of inclusions such as sulphides and oxides, cavitation commonly occurs by decohesion of the interface between the inclusion and the matrix, Figure 2, although the inclusion itself may suffer subsequent damage by virtue of secondary (compressive) strains. An interesting experimental observation is that interface decohesion associated with non-metallic inclusions occurs at very small strains, suggesting that the interface has a low mechanical strength. On the other hand, cavitation at cementite particles generally occurs at relatively high strains, whether the cavity is formed by decohesion of the carbide/ferrite interface or by carbide cracking. These observations lead to the concept of a void nucleation strain, ϵ_0, and there is evidence to suggest that the carbide cracking at least is stress dependent.

2.2 Cavity Growth

The strain concentration in the matrix near a void has been assumed to be similar in form to the stress concentrations occurring at discontinuities and has been assumed by Gurland and Plateau[3] to be inversely proportional to the frontal radius of curvature, R, as indicated in Figure 3. The void strain, db, is related to the overall change in strain, d, by -

$$d\epsilon = db/b \left[1 + k(a^2/b^2)\right] \quad \text{---------- (1)}$$

where a and b are principal dimensions of the inclusion as shown in Figure 3, and k is a strain intensification factor basically dependent upon the work hardening characteristics of the matrix. Integrating equation 1 gives -

$$\epsilon = \epsilon_o + \frac{b\left[\ln(b^2 + ka^2)\right]}{L} \quad \text{---------- (2)}$$

where L is the initial length of the void at the void initiation strain ϵ_o. In the case of particle cracking, L = 0, and for decohesion L = b_o. Transposing equation 2 gives -

$$b = \left[(L^2 + ka^2)\, e^{2(\epsilon - \epsilon_o)} - ka^2\right]^{\frac{1}{2}} \quad \text{--------- (3)}$$

If it is assumed that all particles of a given type and shape within a given matrix behave identically i.e. a model system, then the volume fraction of voids, f, can be evaluated from the fact that each void grows at a similar rate, and the appropriate value of L is substituted, then the fraction of voids can be expressed by -

$$f = f_o\left[(1 + k/r^2)\, e^{2(\epsilon - \epsilon_o)} - k/r^2\right]^{\frac{1}{2}} \quad \text{------ (4a)}$$

for particle decohesion, and

$$f = f_o \cdot 3k^{\frac{1}{2}}\left[e^{2(\epsilon - \epsilon_o)} - 1\right]^{\frac{1}{2}} / 2r \quad \text{--------- (4b)}$$

where r is the axial ratio of the inclusions (r = b/a) and f_o is the initial volume fraction of inclusions.

The model given is more appropriate to a system involving uniaxial tension where the void elongates but shows limited tendencies to broadening or narrowing. In different stress systems, the rate of void growth could differ if the void showed dimensional changes perpendicular to the principal strain.

2.3 Cavity Coalescence

There is little direct evidence of the features which control the onset of void coalescence, but theoretical approaches have invoked some concept of a critical ratio of void size to void spacing. As this ratio is directly proportional to the volume fraction, then the criterion is equivalent to

postulating a critical volume fraction of voids, ϕ, for internal necking of the ligaments between voids and the cessation of macroscopic plastic deformation, i.e. rupture. On the basis that there is a critical volume fraction, ϕ, equations 4 become -

$$\epsilon_T = \epsilon_o + \frac{1}{2} \ln \left[\frac{(\phi/f_o)^2 + k/r^2}{(1 + k/r^2)} \right] \qquad (5a)$$

for decohesion, and

$$\epsilon_T = \epsilon_o + \frac{1}{2} \ln \left[\frac{4 r^2 \phi^2}{9 k f_o^2} + 1 \right] \qquad (5b)$$

for particle cracking. It should be noted that when the volume fraction of voids, f, attains the critical level, ϕ, then the strain ϵ becomes the rupture strain ϵ_T. Experimental observations have clearly established that the volume fraction of particles and the shape of particles have important effects on the strain to fracture, the strain to fracture decreasing with increasing f_o and r. Both the theory and the experimental results of Edelson and Baldwin[6] indicate that particle size has no significant effect on ductility.

The shortcomings of the theory become readily apparent when considering the dependence of ductility (reduction of area in tensile testing, and wire drawing) on the stress state. A more comprehensive treatment of the effects of stress state on the ductile rupture process has been published[7] but the present treatment is considered adequate from the standpoint of the significance of the metallurgical structure.

3. EXPERIMENTAL OBSERVATIONS

3.1 Inclusions

An experimental evaluation of void growth and coalescence[8] used ferritic specimens containing sulphides deformed to various

levels of strain at room temperature prior to notching, cooling to - 196°C and fracturing by impact. The voids formed during room temperature straining can be observed in the cleavage facets, Figure 4. The volume fraction was estimated by point counting on the cleavage surfaces. Typical results are shown in Figure 5. The effects of initial volume fraction of inclusions and particle shape were studied and their effects on the evolution of voids can be clearly seen. The development of the voids shows reasonable agreement with equation 4(a) when K = 2 in the initial stages of void growth. At more advanced stages of straining, the volume fraction of voids increases at a greater rate than would be expected from equation 4(a). This may be attributed to premature void coalescence resulting from localised clustering of inclusions, and may in part be due to the fact that some lateral growth of voids takes place when the triaxial stresses increase due to necking of the tensile specimen. The evaluation of the critical volume fraction of voids in equation 5(a) is invalidated by the accelerated void growth, but indicated a critical volume fraction of cavities of about 4% as obtained from extrapolations of equation 4(a) to the fracture strain. Due to the deviations observed, it is certain that the critical volume fraction will be in excess of 4%. Examination of a specimen in which a macroscopic ductile crack had been initiated, however, suggested that the void fraction ahead of the macroscopic crack (assessed from an examination of cleavage induced propagation) was certainly less than 20%, Figure 6. Theoretical studies by McClintock[7] have indicated that a critical cavity fraction of about 10% would be expected in both tensile or shear fractures.

3.2 Interaction with Carbides

Cavities formed by decohesion of the inclusion/matrix interface may interact with cavities formed by other mechanisms such as the cracking of pearlitic cementite, Figure 7. The ductility ultimately attained by reducing the inclusion content would therefore approach the value set by the carbides. Details of the effects of carbides on ductility can be found in reference 8.

3.3 Effects of Inclusion Distribution

Significant variations in the strain to fracture may arise from variations in the distribution of a given volume fraction of particles of a given shape. The inclusions may show a microscopic heterogeneity as shown in Figure 8. The microscopically local high concentration of sulphides, Figures 8(b) and (d), would be expected to give a critical fraction of voids at quite low strains.

Additionally, due to selective freezing of ingots, and macro-segregation, considerable variations in ductility can occur within an ingot due to the variations in inclusion content on a macroscopic scale.

Whilst it is generally true that the inclusion distribution is largely determined by the solidification events, in low sulphur steels, dissolution and reprecipitation of the manganese sulphides can give rise to faceted fractures typical of overheating. The faceted fractures contain many ductile dimples when examined at high magnification, Figure 9. The facets result from precipitation of the sulphides on the coarse austenite grain boundaries.

4. EFFECTS OF INCLUSIONS ON PROPERTIES

It is important to acknowledge that the major effects of inclusions on mechanical properties are observed in connection with fracture processes. Thus, significant effects of inclusions are noted in connection with tensile ductility, ductility in triaxial ductile fracture, and situations where the energy required for rupture is assessed, as for example in the ductile shelf energy of notched impact tests. Inclusions have little effect on yield strength, tensile strength, or tensile elongation; these properties are dependent upon the initiation of plastic deformation or upon plastic instability criteria associated with work hardening characteristics. The situation is illustrated in Figure 10. Only severely reduced fracture ductility would cause fracture to precede the onset of plastic instability in the uniaxial tension tests. In biaxial tension, however, the instability strains are much higher and some effects of inclusions on the extension have been observed[9].

However, the major factors, as mentioned previously, are those associated with ductile rupture such as the Charpy ductile shelf energy (D.S.E.), bendability, and general measures of ductility. Commercially important properties affected by inclusions include:-

(i) transverse bendability - as in chassis members for automotive work.

(ii) transverse shelf energy - required in order to ensure adequate resistance to fracture in, for example, line pipe material.

(iii) short transverse (through thickness) ductility to ensure adequate resistance to lamellar tearing, which is largely a phenomenon of

ductile tears in the plane of a sheet or plate resulting from the stresses produced in constrained weldments.

4.1 Transverse Bendability

The presence of elongated inclusions in steel strip and the effects of inclusion shape on cavity growth, outlined earlier, give rise to anisotropy of ductility. The effects of elongated manganese sulphide inclusions on the longitudinal and transverse ductility are illustrated in Figure 11. Whilst the qualitative aspects of ductile fracture theory can be invoked to explain these results, a direct quantitative evaluation is not possible due to the shape of the particles. The particles can properly be treated as prolate spheroids when tested in the longitudinal direction, but are not oblate spheroids when the tensile axis is normal to the major axis of the prolate spheroid.

The importance of transverse ductility is seen in applications where transverse bending is carried out, as in automotive chassis members. Commercial test procedures involve the use of a sample of steel cut across the width of strip. This is bent around formers of various radii; the transverse formability is given as a ratio of the minimum bend radius to the thickness of the strip. The test can be made extremely critical by using samples with sheared edges, the burr of the sheared edge facing the outside of the bend. Cracks form from the burr of the sheared edge and propagate across the bend surface as shown in Figure 12(a). In practice, the chassis member may be rejected or may undergo expensive reclamation treatment if cracking occurs during transverse bending.

In order to produce steels with good transverse properties, it is clear from the theoretical considerations

that either the inclusion content must be reduced or the inclusion shape must be changed so that the cavity growth is reduced during transverse bending. Considerable attention has been given to the use of sulphide modifying additives such as zirconium or titanium, or rare earths (cerium etc)[10,11], which harden the sulphides either by substitution of the modifier for manganese in the manganese sulphide e.g. titanium, or by the formation of a different sulphide or oxy-sulphide e.g. rare earth sulphires or oxy-sulphides. The stiffening of the sulphides prevents their deformation during hot rolling and consequently the wrought material contains roughly spheroidal sulphides rather than the highly elongated ones. The modification of the sulphides in this way gives rise to very marked improvements in transverse bendability with little or no effect on the longitudinal property. Remarkable transverse bend properties have been attained by sulphide modification and it has proved possible to develop higher yield strength formable steels that can be bent almost flat without any edge cracking occurring, Figure 12(b).

4.2 Transverse Shelf Energy in Notched Impact Testing

The ability of a steel to arrest a propagating ductile fracture in a line pipe is related to the energy absorption per unit increase of fracture length. This is measured by the energy absorption in a fully ductile fracture in the notched bar impact test. The effect of sulphide volume fraction on the ductile shelf energy (D.S.E.) in the Charpy V-notch impact test is shown in Figure 13. The effects of sulphides on the D.S.E. are similar to those observed in the case of ductile fracture strain. The similarity is due to the fact that the energy absorption largely reflects the plastic deformation involved in tearing the notched specimen. The

effects of test orientation in relation to the orientation of the inclusions are clearly seen and again the ductility is reduced by testing with the longitudinal axis of the inclusions lying in the plane of the fracture and normal to the principal stress axis.

It can be seen from Figure 13 that there is some effect of the sulphide content on the impact transition temperature, the impact transition temperature being reduced at high sulphide contents in the case of the longitudinally oriented specimens. The effect of sulphides may be to reduce the intensity of the secondary principal stress by causing delamination. This is a similar effect to that observed by Embury and Petch in the case of composite impact specimens, particularly in the crack dividing composite. Separations are formed normal to the main fracture surface. This reduces the stresses developed parallel with the notch root and thereby lowers the major principal flow stress thus making plastic deformation more preferable to cleavage and lowering the impact transition temperature. This mechanism is not confined to effects of inclusions, but applies in many circumstances when the short transverse strength of a plate material is reduced in relation to the matrix strength.

The effect of inclusion modifiers on the D.S.E. is well documented, and a typical effect of modification is shown in Figure 14. Increasing the cerium content increases the transverse shelf energy until at a cerium to sulphur ratio of approximately 2.0 the material becomes isotropic, with the longitudinal and transverse shelf energies being almost equal. The effect of sulphide modification on the longitudinal shelf energy is relatively slight, whilst optimum additions of modifier can typically double the transverse D.S.E. Excessive

additions of rare earth alloying elements can produce a decrease in the transverse D.S.E., which has been attributed to the reoxidation of elements such as cerium, due to their exceedingly high affinity for oxygen. This leads to a high inclusion content, the refractory oxides forming clusters in the plane of the strip or plate. Excesses of titanium or zirconium have similar effects, although whether the effect is a result of reoxidation, of alloy strengthening, or of embrittlement by intermetallics, is not clear.

Interesting work has been carried out by Baker and Charles[13], on the effects of inclusions on toughness using pre-cracked C.O.D. tests. This test measures the local strain at the tip of the crack either for the crack to propagate into the specimen or for the crack to develop into an unstable condition. It is a very similar test to the Charpy test in that it can involve very high strains to rupture although the strained region is constrained by the sharpness of the notch and the specimen geometry. Baker and Charles related the C.O.D. to the projected length of the inclusions. The correlation was very good Figure 15, although the projected length variations were introduced by changing the volume fraction of inclusions and the shape of the inclusions. These have been shown to influence the strain to fracture, and it would appear that the projected length measurement provides a rational measure of both of these parameters. However, the use of projected length measurements implies a significant effect of inclusion size, which has not yet been conclusively demonstrated. Evidence on this point is conflicting, and suggests that any effect would be small.

The concept of projected length as a rationalisation of both volume fraction and shape factors is useful in indicating the effects of directionality. As shown in Figure 16, the projected length varies according to the direction of projection (irrespective of the plane of section), and the tensile ductility in anisotropic material, such as plate, is obviously a function of the test orientation and explains the general inferiority of the transverse ductility in anisotropic wrought materials.

Basically, the transverse bendability and transverse ductile shelf energy are both reflections of the strain to fracture in the transverse direction.

4.3 Through Thickness Ductility and Lamellar Tearing

It is clear from the preceding section that the projected length measured in the through-thickness direction in plate materials will be higher than in other directions if the inclusions are deformed in proportion to the change in lengths of the principle dimensions of steel during hot rolling, see Figure 16. It is also true that, under these circumstances, the through-thickness (or short transverse) ductility will be much lower than the transverse (or long transverse) ductility, which will be lower than the longitudinal ductility. In certain applications, high stresses are applied to the through thickness dimension, as for example in T-joint weldments where cracking occurs in the highly restrained portions when the inclusion projected length is high. A classification of the relative effects of inclusions has been given by Farrar and Dolby.[14] Remedies for lamellar tearing may involve either a reduction in inclusion content, principally through sulphur control, or a modification of inclusion shape, by producing inclusions which

do not deform during hot working using rare-earth additions, titanium, or zirconium. In some cases both remedial actions may be applied simultaneously, but in order to comply with quality control procedures e.g. 20% reduction of area in a through thickness test, the use of a single remedy is more usual. The low-sulphur approach has resulted in an examination of de-sulphurising methods and sulphur contents of 0.006 wt% are not unusual, in fact sulphur contents of 0.002 wt% have been attained in commercial products. With shape control additions, considerably higher sulphur contents can be tolerated e.g. 0.010-0.015 wt%, but care has to be taken to prevent re-oxidation of the highly reactive alloying additions during steelmaking and casting, otherwise the oxide products can be equally as disastrous as unmodified sulphides. One feature which limits the sulphur content of modified steels is that the amount of the modifying agent required for complete modification increases as the sulphur content of the steel is increased. T ere is therefore an optimum sulphur content which will be associated with a minimum cost deriving from the costs of desulphurisation and the cost of the sulphide modifying agent.

Considerable interest has centred on the relative merits of desulphurisation and of inclusion shape control, either method being capable of producing the necessary through-thickness ductility. In the long term, the dominance of either approach may depend on the relative costs of the two treatments, but also, as further research is carried out, there may be other technical advantages attaching to one approach or the other. For example, it has been reported that very low sulphur steels are prone to underbead cracking resulting from hydrogen

embrittlement. In higher sulphur steels the hydrogen is trapped at the inclusions. Modified steels may at some future time be shown to have advantages in this respect, but the outcome is by no means certain.

4.4 Fracture Toughness

The application of fracture mechanics concepts to 'brittle' materials is relevant not only to fractures involving cleavage, but also to those involving ductile fracture where the ductility is highly localised and ductile rupture occurs with little macroscopic plasticity. Such fractures are termed 'brittle' because they do not involve macroscopic plasticity, even though the failure mechanism is basically a ductile failure mechanism. Lamellar tearing is perhaps a classic illustration of this situation. However, the application of fracture mechanics as a criterion of fitness for purpose does require that the fracture toughness, K_{IC}, be controlled.

Dulieu and Gouch[15], have shown that the basic features of inclusion distributions which control ductility also affect K_{IC} values in ultra-high strength steels when fracture occurs by the ductile rupture mechanism. Increasing the volume fraction of inclusions decreases the K_{IC} value, and the K_{IC} value exhibits a degree of anisotropy that is directly commensurate with the effects of inclusion anisotropy on the ductile fracture process i.e. transverse properties are inferior to longitudinal properties when elongated inclusions are present. In similar materials, there was little evidence of any anisotropy of properties when failure occurred by the cleavage mode as a result of higher strength (reduced tempering treatment) or coarser grain size. These effects are illustrated in Figures 17 and 18.

5. SUMMARY

The effects of inclusions on mechanical properties are of major significance when the ductile fracture process is involved. Such properties include tensile ductility (reduction in area), bendability, ductile shelf energy, and, in certain cases, fracture toughness.

The effects of inclusion content, particle shape, and particle distribution, on the ductile fracture process have been considered in some detail. Phenomenologically, the effects of these variables can be described in semi-quantitative terms, but the important effects of stress state have yet to be rationalised in terms of their effects on strain to fracture. Increasing the volume fraction of inclusions or decreasing the frontal radius of curvature (with respect to the principal stress axis) decreases the strain to fracture. Clustering of inclusions can also be detrimental. However, there is little direct evidence of any significant effect of inclusion size 'per se' on the strain to fracture. The effects of inclusion control and of inclusion shape control on the transverse bendability and ductile shelf energy have been illustrated. Effects of inclusions on the impact transition temperature have been considered in terms of the effects of inclusions in relaxing the lateral stresses in a triaxial stress system.

Attention is drawn to the lack of effect of inclusions when failure is controlled by plastic instability (a feature of the matrix characteristics) rather than by rupture.

6. REFERENCES

1. Gensamer, M., et al Trans ASM. 1942. 30, 983.
2. Hall, E.O., Proc. Phys. Soc. 1951, 64B, p747.
3. Petch, N.J., Journ. Iron and Steel Inst. 1953, 174: p25.
4. Barnby, J.T., Acta Metall. 1967, 15: p903.
5. Gurland, J., and Plateau, J., Trans. ASM 1963, 56; p442.
6. Edelson, B.I., and Baldwin, M., Trans ASM 1962, 55; p230.
7. McLintock, F.A., Int. Journ. Fract. Mech. 1968, 4: p101.
8. Gladman, T., Holmes, B., and McIvor, I.D., 'Effects of Second Phase Particles on the Mechanical Properties of Steel', London, Iron Steel Inst., 1971, p68.
9. Boyles, M., and Haberfield, B., PMC Conference, 'Inclusions and their Effects on Mechanical Properties,' Leeds 1974.
10. Mihelich, J., Bell, J.R., and Korchynsky, M., Journ. ISI. 1971, 209: p.469.
11. Wilson, W.G., BSC PMC Conference 'Inclusions and their Effects on Properties' 1974.
12. Embury, J.D., Petch, N.J., Wraith, A.E., and Wright, E.S., Trans AIME 1967, 239: p114.
13. Baker, T.J., and Charles, J.A., ibid Ref. 8, p79.
14. Farrar, J.C.M., and Dolby, R.E., ibid Ref. 8 p
15. Dulieu, D., and Gouch, A., ibid Ref. 11 p

LECTURE 10

THE EFFECT OF INCLUSIONS ON RECRYSTALLISATION AND GRAIN GROWTH

INTRODUCTION

Finely distributed second phase particles are known to influence recrystallisation and grain growth in a wide range of metallic systems. At one time, the effects of aluminium on grain growth in steel were attributed to the presence of alumina particles, but current views are that the affect is due to the finely distributed aluminium nitride particles. It is of interest therefore to consider the properties of particulate distributions that are required to produce significant effects on grain growth and recrystallisation, and to assess the distribution of inclusions in the light of these requirements.

THEORETICAL ASPECTS OF GRAIN GROWTH

The basic concept for the inhibition of grain growth by second phase particles is the reduction in energy resulting from the elimination of grain boundary area, when a particle occupies a position on the grain boundary. When the boundary is moved away from the particle, energy has to be supplied as grain boundary area is created.

(a) The Pinning Force

Attention has been given to the pinning forced exerted by the particle as the boundary is moved[1]. Certain assumptions are made concerning the local equilibrium, Fig.1, in that the boundary will be normal to the particle surface at the point of contact, and the boundary will flex so that the pinning distortion is inversely proportional to the distance from the particle. Using these concepts, the pinning force, i.e. the rate of increase in energy with respect to boundary displacement, was found to be about $4r\gamma$, where γ is the grain boundary energy and r is the radius of the pinning particle. This is a lower value than would be obtained for a rigid boundary, in which case it would be $6r\gamma$, but slightly higher than the value of $\pi r\gamma$ that would be obtained from classical soap froth models, where some flattening

of the boundary is permitted. However, the theories all show a pinning force which is directly proportional to the particle radius, r, so that large particles are associated with large pinning forces. This force is far greater than could be provided by thermal excitation at temperatures where grain growth can occur, and it is clear that the driving force for unpinning derives from a source other than thermal excitation.

(b) Grain Growth as an Energy Source

Grain growth occurs because the energy contained in the form of grain boundary area decreases with increasing grain size. Using the concept of a tetrakaidecahedral grain of 'radius' R, where R is the half distance between opposite hexagonal faces of the tetrakaidecahedron, in a matrix of tetrakaidecahedral grains of 'radius' R_o, two contributions to energy changes have been identified[1]. The surface area of the growing grain increases, thereby increasing the energy of the system, but this is offset by the decrease in grain boundary area, and therefore energy, as the matrix grains are consumed. The energy change per unit area of advancing interface, E, is given by:-

$$E = S\gamma(2/Z - 3/2)R_o \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where Z is the grain heterogeneity and is equal to R/R_o, and S is the grain boundary displacement. This equation indicates that the energy of the system will decrease progressively as the grain grows, only when R/R_o is greater than 4/3. When R/R_o is less than 4/3, a metastable state is indicated. It should be pointed out that the above model assumes that all the grain boundaries have the same surface energy, which is not unreasonable for an aggregate of grains with high angle boundaries.

(c) The Total Energy Change

As there are $2rn_v$ particles per unit area of interface in a system with randomly distributed second phase particles, where r is the particle radius and n_v is the number of particles per unit volume, the energy release per particle, E, due to grain growth is given by:

$$E = 2S\gamma\pi r^2 (2/Z - 3/2)3R_o f \quad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where f is the volume fraction of particles.

The total energy change is obtained by adding the unpinning energy. A computer evaluation of the total energy change showed that the energy barrier to grain growth could still be very large even when the driving force, dE/dS, for grain growth is considered, until the driving force is approximately equal to the pinning force. A critical particle size, r*, for this condition can be obtained by equating the pinning force and the driving force. Mathematically, r* is defined by the equation:-

$$r^* = 6R_o f/\pi (3/2 - 2/Z) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

As the pinning force is proportional to r and the driving force per particle is proportional to r^2, unpinning is favoured by coarse particles at any given volume fraction. Thus, when the particle size, r, exceeds the critical particle size, r*, as a result of Ostwald ripening, grain growth will commence. It should be emphasised that the critical particle size equation (3) defines the condition at which grain growth can proceed, and does not give any indication of grain growth kinetics.

(d) Theory and Experiment

Experimental assessments of the particle sizes associated with the onset of grain coarsening in steels containing AlN and Nb(CN) have been made[2]. The particle sizes were found to agree with the theoretical predictions when Z values were between $\sqrt{2}$ and 2, commonly about 1.5. Particle shape did not appear to have any significant effect within the limits investigated. Although this value of Z is in agreement with the range of grain sizes observed in many polycrystalline materials, experimental work on the advancement of a planar interface into a polycrystalline aggregate, i.e. when Z is infinitely large, has supported the critical particle size equation(3).

(d) Implications of the Grain Coarsening Theory

As pointed out earlier, the criterion established in equation(3) describes a go/no go situation, i.e. grain growth will or will not occur, and fine particles are more effective than coarse particles in inhibiting grain growth at a given volume fraction. The actual critical particle size depends on the volume fraction of particles, f, the matrix grain size, R_o, and the grain size heterogeneity, Z.

The dependence of the critical particle size on the grain size heterogeneity factor, Z, is very pronounced, r* varying from 1.3 $R_o f$ at $Z = \infty$ to 12 $R_o f$ at $Z = 1.5$. The number of particles of a given size required to pin a planar advancing boundary would therefore exceed the number required to pin a grain 50% larger than the matrix grains by a factor of about one thousand. The sensitivity of the coarsening criterion to grain size heterogeneity has important implications on the mode of grain coarsening. The observed temperature and time dependence of grain growth may be attributed to the kinetics of particle coarsening. As the particles coarsen, the grain with the highest Z factor will be the first to commence growing, and as it grows, the increasing Z value will cause the existing particles to become less of an obstacle to growth. Other grains of smaller initial Z value must await further particle coarsening before they are unpinned. For example, a grain with $Z = 2$ starts to grow when $r = 4R_o f$, whereas a grain with $Z = 1.5$ must wait until $r = 12\ R_o f$, i.e. the particles are three times larger. Thus the mode of growth under these circumstances is basically that of secondary recrystallisation, i.e. a few grains growing to abnormally large dimensions in a matrix of fine grains. At higher temperatures, solution of the particles permits normal grain growth. The result of these effects is that the grain size of the coarse grain structure developed just above the grain coarsening temperature can often exceed that observed after coarsening at much higher temperatures, as shown in Fig.2. A further interesting feature of Fig.2 is that the size of the fine grains is not controlled by the particles, and is established as a consequence of the nucleation frequency of austenite grains in the ferrite/carbide matrix on heating through the critical range.

(e) Calculation of the Grain Coarsening Temperature

Grain coarsening temperatures can be calculated for any given volume fraction of particles, matrix grain size, and heterogeneity, provided that the solubility of the particles and the kinetics of particle coarsening are known[2]. An illustration of the calculation is given in Fig.3. The critical particle size decreases with increasing temperature due to solution of the precipitates. The actual particle size increases with increasing temperature and time, due to Ostwald ripening. Grain coarsening will occur when the actual particle size, r, exceeds the critical size r*.

Such a calculation is valid only when the particles are freshly precipitated. In practice however, the most insoluble particles may not be the most effective type of particle because very insoluble particles will be precipitated at very high temperatures and may therefore rapidly grow to a supercritical size, for example during soaking for hot rolling. They may therefore be ineffective during the thermal cycle during which maintenance of a fine grained structure is important. A practical example of this effect is observed in high aluminium steels, as indicated in Fig.4. The high aluminium content confers such a high degree of stability on the aluminium nitride that coarse particles are developed during soaking, and these reduce the fraction of small particles that can be developed at lower temperatures during normalising. Thus increasing the aluminium content above a critical level results in a lowering of the grain coarsening temperature.

EFFECTS OF SECOND PHASE PARTICLES ON RECRYSTALLISATION

The effects of second phase particles on the recrystallisation of cold worked materials are very dependent on particle size and distribution. Qualitatively the effects can be summarised[4] as follows :-

(a) Numerous fine second phase particles retard or inhibit recrystallisation of the cold worked matrix.

(b) The presence of coarse second phase particles can accelerate recrystallisation of the cold worked matrix.

(c) There is evidence for a range of second phase particle distributions which are not fine enough to retard recrystallisation, and yet which are not coarse enough to cause acceleration of recrystallisation.

(a) Quantitative Aspects of Retardation

The fine second phase particles that are observed to cause retardation of recrystallisation have a size and volume fraction that would effectively stabilise the sub-grains in the deformed structure. Cold worked metals frequently show the development of a cellular dislocation substructure which, on recovery, becomes more clearly defined to give the sub-grain structure, the sub-grains being separated by low angle sub-grain boundaries. The

nature of recrystallisation nuclei is still the subject of some speculation, but may occur by sub-grain boundary migration in a manner analogous to grain growth. A size advantage has been postulated for the selective growth of certain sub-grains, which provides the direct equivalent of the grain size heterogeneity.

The matrix sub-grain radius is of the order of 0.5-1.0μm. With a heterogeneity factor of Z = 1.5, the critical particle radius for sub-grain pinning is 6nm(60Å) for a volume fraction of 0.001(0.1%), and 3nm(30Å) for a volume fraction of 0.0005(0.05%). The particles used in normal austenite grain refinement are commonly in excess of 100Å diameter and are ineffective in stabilising the sub-grains. In fact, they are also ineffective in retarding recrystallisation. The particles observed to retard recrystallisation are extremely small. An example of vanadium carbide particles and their effect in pinning the sub-grain boundaries is shown in Fig.5.

Sub-grain coalescence, attributed to rotation of one of a pair of sub-grains to give a single large sub-grain which is then assumed to grow by boundary migration, implies dissociation of a sub-grain boundary into its constituent dislocations. These move away to other sub-grain boundaries, and it is interesting to note that the particle distributions that are capable of sub-grain pinning are also capable of restricting dislocation movement, i.e. are responsible for a significant degree of precipitation hardening . Thus the observed retarding effect of fine particles would be expected iresspective of whether nucleation occurs by sub-grain boundary migration or by sub-grain coalescence.

An example of the inhibition of recrystallisation commonly utilised in commercial steels is observed in the hot rolling of niobium steels, where the austenite recrystallisation is drastically retarded[4]; it should be pointed out that whilst the inhibition of recrystallisation can be explained in terms of an effect of strain induced precipitation of Nb(CN) in the austenite, the effect could in part be due to an effect of niobium in solid solution.

(b) Quantitative Aspects of the Acceleration of Recrystallisation

There are a number of ways in which second phase particles may affect the kinetics of recrystallisation to give an acceleration of the process. Refinement of the grain size prior to cold working is known to give such an acceleration due to the increased nucleation rate resulting from the increased number of prior grain boundaries, which are potent nucleation sites. The introduction of second phase particles may enhance the work hardening rate and thereby increase the stored energy of cold work, which is the driving force for recrystallisation, again causing acceleration of the recrystallisation process. These are indirect effects of second phase particles, and are a consequence of the effects of the particle on other microstructural features which are important to the recrystallisation process.

However, there is evidence of a direct effect of second phase particles in causing accelerated recrystallisation. This results from nucleation of recrystallised grains on the interface between the particle and the matrix. Direct observations of this effect are confined to large second phase particles. It is clear that the particles must be at least as large as the critical nucleus size, and must be larger than the cell or sub-grain size of the coldworked matrix. Thus, the particles directly responsible for accelerated nucleation and recrystallisation are generally coarse particles in excess of 1-2 μm diameter.

(c) Particles of Intermediate Size and Distribution

It is clear from the foregoing discussion that there are particles which are too fine to accelerate recrystallisation and are not fine enough to retard recrystallisation. Such particles may not affect the recrystallisation kinetics, but could affect the normal grain growth which follows the recrystallisation process. The grain growth effects have already been dealt with quantitatively. In materials which rely on ferrite grain coarsening to attain adequate softness for cold forming operations, the presence of such intermediate particles can be troublesome due to the inhibition of grain growth.

EFFECTS OF INCLUSIONS

The general effects of second phase particles on recrystallisation and grain growth are summarised in Fig.6. The diagram is constructe on the basis of the grain boundary pinning equation, with Z = 1.5. The inter-relation between matrix grain size, particle size and volume fraction is shown, and can be used to establish the stability of matrix grains of a given size for a given volume fraction of particles of specified size. If the grain size of the matrix exceeds that shown in Fig.6, then the grain structure will be stable. If, on the other hand, the grain size is less than shown in Fig.6, then grain coarsening will occur. Alternatively, specified particle sizes and matrix grain sizes can be used to predict the volume fraction necessary to ensure grain refinement.

The particle characteristics utilised in commercial grain refined steels, and those observed to retard recrystallisation are indicated. The effects of inclusions on recrystallisation and grain growth can be defined in relation to these effects.

(a) Recrystallisation

Typical inclusion contents and sizes are indicated in Fig.6. The particle sizes are totally incapable of effecting any inhibition of recrystallisation with sub-grain sizes of 1-2 μm.

(b) Grain Growth

In general, the particle characteristics of the inclusion distributions observed in commercial steels are incapable of maintaining fine grain sizes of less than 20 μm. Reference to Fig.6 indicates that inclusions would only be effective in pinning grain boundaries when the matrix grain size is of the order of 100 μm or more, since the inclusion content of steels is generally low, of the order of 0.1% to 0.3% by volume, and the inclusions are large in terms of pinning particle sizes. Thus, inclusions cannot properly be regarded as grain refining particles, as they can only inhibit grain growth in an already coarse grained structure. However inclusions could be responsible for the very wide range of coarse grain sizes seen in steels of varied inclusion content after austenitising at temperatures in excess of 1100^{o}C

With very large volume fractions of inclusions, as occur in high sulphur free cutting steels, however, some degree of grain refinement can be introduced.

(c) Secondary Recrystallisation

As previously pointed out, secondary recrystallisation, or abnormal grain growth, is frequently observed as a consequence of particle coarsening and the selective unpinning of a few of the coarser grains in the microstructure. This effect is associated with one of the few benefits that can derive from the presence of inclusions, i.e. the use of manganese sulphide inclusions to control the texture development in high silicon transformer steels[6]. Although the solubility of manganese sulphide in steel is not established precisely, the use of steel containing 0.02% S with 0.04-0.10% Mn enables substantial sulphide solution to occur during soaking for hot rolling. Sulphide precipitation occurs during subsequent thermal cycles to give fine particles. The Goss texture, (110) [001], is developed during a high temperature anneal at 1100-1200°C, when the sulphide particles coarsen and abnormal grain growth is observed, giving a coarse grained structure with grains up to 10 mm diameter. Although the use of other additives such as aluminium, titanium, etc, have been used to promote the secondary recrystallisation process, the grain oriented silicon steels currently manufactured are predominantly based on the inhibition of primary recrystallisation by manganese sulphide.

SUMMARY

An account has been given of the theory of the effects of second phase particles on grain growth and recrystallisation. The theory of grain growth predicts the circumstances under which secondary recrystallisation will occur. A summary diagram has been presented which indicates the particle sizes and volume fractions required to inhibit grain growth and recrystallisation. The effects of inclusions are described in relation to this diagram. In general, inclusions are too coarse, and are present in insufficient proportions, to inhibit grain growth, except in materials with an already coarse matrix grain size. The case of

grain oriented high silicon transformer steels is given as an almost unique example of the use of sulphide inclusions as a means of promoting secondary recrystallisation and thereby promoting the formation of the desired Goss texture.

REFERENCES

1. T.Gladman, Proc. Roy. Soc., Series A, 1966 294: 298.

2. T.Gladman, and F.B.Pickering, J.Iron and Steel Inst. 1967, 205: 653.

3. T.Heeley, A.F.Brown and M.V.Speight, International Conference on Physical Metallurgy of Reactor Fuel Elements, September 1973.

4. T.Gladman, I.D. McIvor and F.B. Pickering, J.Iron and Steel Inst. 1971, 209: 380.

5. K.J. Irvine, T. Gladman, J. Orr and F.B. Pickering, ibid, 1970, 208 717.

6. A.Coombs, Steel Times 1970, May, 311.

LECTURE 11

THE NEED FOR INCLUSION ASSESSMENT

Introduction

For many years, both steelmakers and steelusers have been aware that non-metallic inclusions can materially influence the performance of steel during service. Whilst much attention has been concentrated upon the deleterious effects, it must also be remembered that several important beneficial effects can be produced by inclusions. The ever increasing demands for higher quality steels has necessitated not only the control of the occurrence of inclusions, but also the need to quantify the size and distribution of the inclusions both for quality control purposes and also to ensure that the effects on mechanical and other properties can be predicted and foreseen.

Consequently, for many years, non-metallic inclusions have been assessed in steel, and a visual comparison with standard charts was the basis for the technique used.[1] The unsatisfactory nature of this method need not be elaborated upon, and whilst it was possible to distinguish very clean steel from very dirty steel, the method of examination was very subjective and the agreement between operators was extremely poor,[2] mainly due to the coarse steps between graded fields, the very subjective nature of the technique itself and also operator fatigue and pre-knowledge.

Nevertheless much work of a quality control nature, and also aimed at developing improved steelmaking practices to produce cleaner steel, has in the past used this type of assessment. Clearly there was a need for more precise methods of assessment and many quantitative and semi-quantitative techniques were developed and used. These were extremely laborious, and the number of samples counted was kept to a minimum with a resulting deterioration in the statistical accuracy. It has only been with

the development of rapid, automatic and non-subjective counting techniques, that it is possible to begin to place reliance on the inclusion assessments which are made. Even with the increased speed and accuracy which is possible, the problem of ensuring that every potentially dangerous inclusion has been detected still remains to be solved. A 100%, non-destructive technique is required, which is applicable to "on line" inspection on the mill. The future in this respect probably depends on whether the work on quantitative ultrasonic assessment techniques can be brought to fruition.

Much attention has been paid to improving the quality of steel by removing the inclusions, and indeed much progress has been made in producing clean steel. Particular attention has been paid to removing the larger and more deleterious types of inclusions, again with some success. However, it is certain that within the foreseeable future, mass produced tonnage steel will still contain appreciable numbers of inclusions. Consequently, inclusions should be regarded as naturally occurring constituents, and rather than engaging in activities designed to decrease the total inclusion content to lower and lower levels, with a consequent decrease in the return on the effort involved, it will be necessary to learn how to adjust their size and distribution, as well as their type, so as to make the most of their beneficial features and ensure that their harmful effects do not lead to potentially dangerous situations.

The number and size of inclusions in steel

Kiessling[3] has pointed out that every metric ton of steel contains 10^{12}-10^{15} oxide inclusions. The same number of sulphide inclusions also are present. The size of these inclusions can vary widely, as also does their distribution in the ingot, and the following table indicates some of the important size distribution effects. Assuming that the steel contains 100 ppm of oxygen as spherical Al_2O_3 particles of specific gravity 4.0 and uniform size, the following relationships have been shown[3].

Inclusion diameter μm	No. of inclusions per metric ton	Volume of steel per inclusion	Mean distance between inclusions
1000	10^5	1.3 cm^3	1.1 cm
100	10^8	1.3 mm^3	1.1 mm
10	10^{11}	1.3 x $10^5 \mu m^3$	110 μm
1	10^{14}	1.3 x $10^3 \mu m$	11 μm
10^{-1}	10^{17}	1.3 μm^3	1.1 μm
10^{-2}	10^{20}	1.3 x $10^{-3} \mu m^3$	0.11 μm
10 Å	10^{23}	1.3 x 10^5 Å^3	110 Å

The magnitude of these figures can be judged by the fact that, every foot of 5cm square bar will contain 150,000 inclusions of 100μm diameter. Such inclusions, i.e. of 100μm diameter, would be typical of the size of silicates formed from erosion of ladle refractories and runner bricks, and each would appear 10cm in diameter on a projection microscope screen at a magnification of 1000 diameters.

It is also instructive to consider the sizes of typical inclusions which originate from various sources.[4] In the as cast condition, these can vary from 5μm diameter to over 100μm diameter, as shown by the following data:-

Type of inclusion	Diameter μm	Relative Volume
Al_2O_3; $CaO.6Al_2O_3$, Spinel	5	1
Other calcium aluminates	27	160
Secondary deoxidation silicates	32	260
Primary deoxidation silicates	49	940
Erosion products in Al-killed steel	64	2100
Erosion products in Si-killed steel	107	9800

Clearly, if as fracture toughness and stress concentration considerations indicate, it is the large particles which may prove disastrous, the assessment method must have a high degree of certainty for detecting them. The effect of the inclusions on properties is not however most clearly indicated by their diameter in the as cast ingot, because in practice they will occur in rolled or other hot worked products, and will appear with different degrees of elongation. According to the shape of the product, the inclusions can occur either as elongated fibres or as flat plates, and the ratio of length to breadth to width will depend upon the mode and extent to which the steel has been deformed, the temperature and the nature and size of the inclusions themselves.[5,6,7]

Many silicate inclusions can deform very readily at high temperatures, but behave in a brittle fashion at low temperatures. Kiessling[8] has indicated that for silicates an increase in SiO_2, CaO or FeO increases the temperature at which the inclusions become highly plastic, whilst the opposite effect is observed with increasing MnO. This is a very simplified picture, and more recent work[9] has shown that there is an approximately linear relationship between the melting point of the inclusions and the temperature at which the inclusions begin to behave very plastically, Fig.1. At high temperatures where high inclusion plasticities are observed, the plasticity index can exceed unity. More recent work[10] has shown that for glassy silicates, the temperature at which the plasticity increases sharply has been shown to depend on the viscosity, and to be clearly related to the SiO_2 content.

Consider therefore an erosion silicate 100μm in diameter in a 62cm square ingot, being rolled at high temperatures to a 5cm square billet. The inclusion would then be 1.5 cms long, and in 1.25cm dia bar it would be about 30 cm long. This of course assumes that the inclusion has not broken up. These lengths begin to assume some significance when fracture toughness properties are considered, and consequently it becomes necessary to ensure not only that such

inclusions are detected, but also that their size can be adequately assessed.

Role of inclusions on critical defect sizes

In recent years, the concepts of critical defect sizes in relation to the catastrophic low ductility fracture of steels have received increasing attention. Whilst not elaborating on the subject of fracture toughness, suffice it to say that if a defect exceeds a critical size, the stress concentration at the tip of the defect is sufficiently great to cause the propagation of a running crack. Kiessling[3] has calculated this critical defect size for stresses equal to the yield stress of a number of materials, and it can be concluded that this critical size is the borderline between inclusions which are harmless and those which are potentially dangerous. This threshold seems to be, Fig.2, in the range 0.2-1.0mm for inclusions intersecting the surface, and 1.0-5.0mm for inclusions which occur internally. These sizes are generally larger than the spherical inclusions observed in the ingot, which are rarely greater than 0.2mm, i.e. 200μm. One might conclude that inclusions are not likely to be deleterious from this point of view, and that there is little need for the development of sophisticated techniques to assess inclusions. However this would not necessarily be a correct conclusion because:

(a) The defect defined by the inclusion may grow under conditions of cyclic stressing, ie fatigue crack growth may occur and so allow a super-critical crack to develop from a sub-critical inclusion defect size. A knowledge of the rate of fatigue crack growth as a function of stress amplitude in materials of different metallurgical condition would then allow the defect size which would not allow a critical crack size to be developed within the service life, to be assessed.

(b) Under corrosive conditions, such as lead to stress corrosion cracking, the defect size could be reduced to about 1/36

of its value in static non-corrosive environments. Consequently a surface inclusion of 6-30μm could prove super-critical, and this is quite within the range of inclusion sizes observed.

(c) There may be a concentration of inclusions ahead of a propagating crack, which will accelerate failure.

In addition, recent work by Brooksbank and Andrews [11] has shown that internal stresses can be generated around inclusions due to differences in the thermal expansion coefficients of the inclusion and the matrix. They categorise the inclusions in terms of whether they have stress raising characteristics or the ability to form voids at the inclusion metal interface, according as to whether their coefficient of expansion is less than or greater than that of steel, Fig 3. The important feature of this work is that the properties of the matrix around the inclusions may be greatly altered, and indeed localised yielding can occur.[3] It can also be shown that the volume of the steel which has yielded is very dependent on both the volume fraction of inclusions and the number per unit volume, and with high O_2 contents and fairly closely spaced particles, over 50% of the matrix may in extreme cases be deformed. More important however is the fact that if the inclusions are deformed and are arranged co-linearly, then planar volumes of the material can be 100% deformed, thus leading to very different properties in that planar region, Fig 4. This can have a major influence on through thickness properties and the tendency to crack during the longitudinal bending of hot rolled strip.

This effect of co-linear inclusions naturally is related to the plasticity of the particles, and thus the design of rolling or other hot forming practice must be performed with the possible effect on the inclusions in mind. It may be, therefore, that controlled rolling

which gives an inherently tough, ductile structure, may introduce the worst possible defects into the steel through the distribution brought about in the inclusions. It seems necessary to employ methods for assessing inclusions not only for their size and distribution, but also in terms of their shape.

The effect of deformation on inclusions

Some of the first observations on the possible introduction of cracks into steel by inclusions during hot rolling were made in relationship to the fatigue properties of bearing steels [12]. Subsequent work has been more specific in describing the effects which can briefly be summarised as follows.

(a) Oxide inclusions

Some oxides, namely TiN, Al_2O_3 and the very alumina rich calcium aluminates or spinels may be considered to be non-deformable. Consequently the development of cracks or voids around the inclusions during hot working largely depends on the temperature, the higher the temperature the less likely are cracks or voids to develop because the steel is sufficiently plastic to flow around the inclusions. Particularly in the case of alumina and spinels the inclusions in the as cast condition occur as skeletal growths. During rolling these fragment and form the typical alumina stringers in the rolled condition, comprising groups of disconnected particles which often occur as co-planar or co-linear groups. As fracture of the inclusions occurs, if rolling is carried out to low temperatures the alumina stringers may be riddled with voids, and these could produce very severe defects. Some very poor through thickness tensile ductilities in aluminium killed steels may be associated with these effects.

Other inclusions such as silicates and the more calcareous calcium aluminates behave in a highly plastic manner at high temperatures, [5], [6], [7] and can have plasticities similar to or greater than that of the steel. Consequently highly elongated silicates are produced, but as the temperature is

lowered the plasticity falls drastically, and the inclusions, instead of deforming, crack. This often occurs by shearing at 45° to the direction of deformation, or by fragments chipping off the silicates and being distributed down the flow lines of the steel. If, as may occur in some controlled thermo-mechanical treatments, the temperature of the steel is progressively lowered it may pass through that at which the inclusions start to lose plasticity. This can result in the silicate stringer being fractured, and if the steel is still sufficiently plastic it may flow into the voids between the segmented particles. Some of the rectilinear blocks may rotate to produce a streamlined profile to the metal flow, and remnant plasticity can cause fishtailing at the ends of the inclusion segments. Alternatively, if the metal temperature is too low, or fracturing occurs at the end of the deformation process, the metal may not flow into the cracks thus formed, and the defects thus created could be very deleterious. If the deformation is wholly carried out at low temperatures, voids open up at the ends of the spherical silicates, which themselves may or may not crack. These voids, which were first observed in bearing steels[12], occur because the inclusion-metal interface can be decohesed. It can be appreciated that an elongated, cracked and decohesed silicate could give extensive planar defects which might exceed the critical defect size.

Apart from cracking and decohesion which can occur during hot working, oxides may also crack during cold deformation, i.e. during fabrication, Not only can this give rise to failure or fracture during fabrication, but even if this should not occur, the defects thus introduced may give rise to premature failure during service, for example by a fatigue crack nucleation effect accelerating the achievement of a critical defect size by fatigue crack growth.

(b) Sulphide inclusions

Sulphides do not show the plastic-brittle transition typical of silicates. Rather they tend to show a decreasing

plasticity relative to the steel as the temperature of rolling increases, ie the steel softens more rapidly than the sulphide with increasing rolling temperature. Thus high rolling temperatures produce less elongated sulphides; a fact which is made us of in the production of what is often believed to be the optimum sulphide shape in free cutting steels.

There is also an effect brought about by the deoxidation employed in the steel, increasing deoxidation changing the MnS particles from the globular type I variety through the type II form to the idiomorphic type III sulphide. The oxygen concentration in the sulphide decreases as the type changes from I to III, and the particle size is smallest with type II sulphides although these occur in aggregates of many individuel sulphide particles. The deformation mechanisms are complicated by changes in inherent plasticity brought about by the varying oxygen content of the sulphide, and also by the effect of varying initial particle size. However recent work has indicated that:

(i) The purer the MnS, ie with respect to oxygen, the more plastic it becomes, ie plasticity increases from Type I to type III[7].

(ii) The type II sulphides tend to form planar, or near planar, arrays of highly elongated sulphides in hot rolled products[13].

and

(iii) The lower the rolling temperature, the more heavily elongated are the sulphides, eg, in hot rolled strip.

Consequently the presence of these heavily elongated planar groups of sulphides give rise to more nearly critical defect sizes, and indeed are very detrimental to toughness and weldability, as will be shown later.

Very little evidence is available on the effect of alloying on the sulphide plasticity, at least with respect to elements dissolved in the MnS. The work of Kiessling on the hardness of MnS containing elements substituting for manganese[14] may be

indicative of effects which can be used to control plasticity. Work on Zr, Ce or Ca additions[15], [16] has shown how it is possible to prevent the highly elongated stringers of MnS from forming, either by lowering the plasticity of MnS by substituting Zr for Mn in (MnZr)S or by forming cerium sulphides. The improvement in toughness and ductility will be referred to again.

Another feature which is of importance in the deformation of sulphides is the fact that at room temperature they invariably have a decohesed interface with the steel[11]. This is important from the point of view of their behaviour during cold deformation and fabrication, as the voids are already present and available for growth prior to strain being applied[17],[18]. However, cold deformation can also cause the elongated sulphides to crack transversely. Again these features may affect both formability during fabrication and also the serviceability of the fabricated part.

It is clear therefore that not only does one need to be able to obtain a quantitative assessment of inclusion size and distribution, but also of shape and preferably with respect to the shape of inclusions of different compositional characteristics. The need for such assessments will be elaborated upon in the next section.

The effect of inclusions on mechanical properties

This subject is so widespread and complex, that only a brief description of a few of the relevant phenomena can be given. However a very large amount of work has been carried out, and is summarised in some recent publications [1], [19], [20].

(a) Ductility

There is a well known relationship between the volume fraction of second phase particles, which includes inclusions and the total ductility as measure by the strain at fracture in a tensile test[21], [22], Fig 5. The ductility is very adversely affected by an increasing volume fraction of

inclusions. In addition the shape of the inclusions markedly affects the ductility, Fig.6, a sulphide plate tested across its thickness giving much lower ductility than a sulphide fibre tested longitudinally. This is the essence of the well-known lack of ductility in the through thickness direction in plates, and the basis of lamellar tearing in welds. The ductilit of material is controlled by the ease with which voids can nucleate and grow. Sulphides are particularly bad because they are decohesed at the sulphide/metal interface prior to straining[11]. On the other hand, carbides are by no means so detrimental as the interface does not apparently decohese and a certain stress, i.e. strain, must be reached before the carbides crack. Thus the ductility is higher, as much strain has occurred prior to the voids being nucleated, Fig.7. It might be inferred that certain oxides would behave in a similar manner, as they crack in preference to the interface decohesing. The role of the interface and its energy is thus important, as also is the shape of the inclusion. The recently developed methods for inclusion shape control have been very effective in improving ductility, and hence formability. The inclusion assessments needed therefore include not only volume fraction measurements, but also inclusion shape measurements. In addition it is very necessary to ensure that the local segregates of inclusions are picked up with great certainty. The position in the ingot, especially in killed steels, plays a major role in determining the volume fraction and size distribution of inclusions[23][24], and consequently the assessment procedure must be capable of rapid operation in order to obtain a representative measurement as a function of position of the section in the ingot.

(b) Toughness

There is considerable evidence that large carbide particles, which crack during straining, can initiate brittle cracks, and increase the impact transition temperature[18] [25]. The effect of inclusions on impact properties is also well documented, it being known that increasing inclusion content of either oxides[26] or sulphides[17] will decrease the charpy shelf energy value, Fig.8.

The effect of inclusions on the impact transition temperature is not so clearly defined, some evidence indicating very little effect[13 (26)] whilst other evidence indicates a clearly defined effect[27]. Recent evidence[17] indicates that the effect of inclusions, particularly sulphides can be complex in terms of their effect on the impact transition temperature, and under some circumstances can lower the transition temperature. This is an area where further evidence is necessary to obtain quantitative relationships, but it might be anticipated that many oxide inclusions will crack, and in the same way as carbides, will increase the impact transition temperature.

Some interesting effects of sulphide inclusions on a fracture toughness parameter have been shown,[7] which indicate a linear relationship between the logarithm of the crack opening displacement and the logarithm of the inclusion length per unit area, Fig.9.

Recent studies have shown how Zr, Ca or rare earth additions can materially improve the charpy shelf energy[16] by changing the sulphide morphology from elongated stringers (often co-planar in plates) to rounded non-deformable particles. Such inclusion shape control is most effective on the through thickness or transverse properties, but there is also some evidence that the replacement of elongated inclusions by spheroidal types can increase the impact transition temperature[17].

In view of the fact that the shape, and particularly the length of the inclusions has a very great influence on the toughness of materials, the plasticity of inclusions is obviously of major importance. Particularly aggregates of planar, heavily elongated inclusions are likely to be most detrimental[13]. Consequently the need will be to assess not only volume fraction, but also the length:width ratio, and to couple this with a discrimination with respect to the composition of the inclusion. The need for rapidly assessing variations in these parameters for the inclusions in different parts of the ingot is also apparent.

(c) Fatigue

There is much evidence to show the detrimental effects of non-deformable oxide inclusions, and TiN on the fatigue life of high strength bearing steels.[28-32] The major effect seems to be produced by the Al_2O_3 and TiN inclusions, as these tend to have major stress raising potential.[11] Indeed this has been illustrated[31] and it is possible that some of the effect attributed to Al_2O_3 may well have been partially resulting from calcium aluminates which also are potent stress raisers. The general effect of oxides on the fatigue life of bearing steel is shown in Fig.10[33], and the detrimental effect of large oxides is indicated in Fig.11[32]. An indication of the major influence of Al_2O_3 in decreasing the fatigue life is shown in Fig.12[31]. However more work is required before the quantitative relationships can be evaluated, although Murray and Johnson[31] have developed regression equations relating fatigue life to a measure of the number of alumina or silicate inclusions present.

The effect of sulphides is most interesting, as they have no detrimental effect[8] [11], and indeed because of their ability to counteract the stress raising potentialities of alumina or other oxides[11], it seems that if the oxide is encapsulated by MnS, then the deleterious effect can be completely removed. A calculation by Brooksbank and Andrews[11] reveals that an oxygen:sulphur ratio of 0.4 would just eliminate the internal stresses around the Al_2O_3, assuming complete encapsulation by MnS, and evidence to support this general idea has been presented by Enekes[33], Fig.13.

It seems clear therefore that sulphides are by no means detrimental in this respect and that, in deciding the inclusion assessment methods required, one feature is the need to measure the degree of encapsulation of oxide by sulphide.

(d) Welding

Perhaps the major effect of inclusions during welding, which apparently applies to both oxides and sulphides, is on the susceptibility to lamellar tearing. This is a manifestation, in the field of welding technology, of the effect of inclusions on ductility, in particular through thickness tensile ductility. An excellent review paper[34] has shown that the tendency to lamellar tearing increases with increasing inclusion size, and as the inclusions tend more towards the large planar morphologies which may occur in plates taken from the bottom of large ingots. This indicates that the composition, particularly with respect to the plasticity of the inclusion and the influence of rolling conditions, is most important. Consequently attention to overall inclusion content and inclusion shape control should help towards a solution of this problem. The problem is largely one of localised high volume fractions of inclusions of planar form.

Sulphur, and the liquation of sulphides seems to be a prime feature leading to the formation of hot tears in the weld metal and heat affected zones in a wide range of steels[35]. Consequently the size of sulphides, which will influence the liquation behaviour, will presumably affect the tendency for this hot tearing phenomenon.

Finally, there is evidence that the incidence of hydrogen cracking in heat affected zones can be reduced by increasing the sulphur content, i.e. the sulphide inclusion content[36]. This is apparently a similar phenomenon to the reduction of hair line cracking in steels brought about by an increased sulphur content[37]. The beneficial effects occur with sulphur contents in the range 0.01/0.04%, but higher sulphur contents increase the tendency for liquation cracking in welding. A possible explanation of this beneficial effect of sulphide inclusions is that, as shown by Brooksbank and Andrews[11], the voids produced at the interface of MnS inclusions results in a high internal void volume which acts as an internal sink for hydrogen. The possible production of voids created around

inclusions by hot rolling in certain temperature ranges may also be a contributory effect.

Again it would appear that in this field, there is a need for quantitative inclusion assessments, not only with respect to size, shape, and volume fraction, but also with respect to inclusion composition.

(e) Machinability

The beneficial effects of manganese sulphide inclusions on the machinability of steel has long been appreciated, and Kiessling[8] and Trent[38] have summarised much of the available information. Sulphides can act as internal lubricants, as chip breakers and can also deposit MnS layers on the surfaces of carbide tools, thus minimising tool wear. It is often believed that the MnS inclusions should be large, and have a small length: width ratio for optimum machinability, Fig.14, and use is made of the plasticity of MnS inclusions relative to the steel to bring this about, by rolling at high temperatures. The effect of deoxidation on the size and shape of the MnS particles should not be overlooked, and the observed correlation of shape with machinability may only be a reflection of the degree of deoxidation, which might have a major effect in its own right. There is however considerable evidence that the machinability increases with increasing volume fraction of sulphid (39), and it seems clear that more work to quantify the inter-relation between sulphide inclusion parameters and machinability is required.

Oxides have often been thought to be detrimental to machinability, and in large measure this is the case. However, certain types of Ca-Al-Silicates can improve machinability[40],[41], but only at the higher cutting speeds when the increased tool tip temperatures cause these silicates to become quite plastic and to form protective layers on carbide tools. More work to investigate whether other oxidic types of inclusions behave similarly would probably be worthwhile.

(f) Other properties

Amongst the many other properties influenced by inclusions, attention may be drawn to polishability and corrosion. Line defects in polished stainless steel[42] have been shown to be the result of hard undeformable inclusions, which also lead to major polishing defects. Such inclusions are frequently of the spinel or alumina type, or even the more refractory calcium aluminates. By so adjusting the deoxidation and other steelmaking parameters to produce smaller, more randomly distributed, softer and more plastic inclusions, improved polishability may be brought about. Similar line defects can be introduced by large stringer inclusions resulting from exogeneous refractory erosion products in high manganese stainless steel.

The presence of sub-surface inclusions, which are tunnelled out during pickling, can also lead to line defects[42], and this is but a special case of the effect of inclusions on corrosion. The presence of inclusions can, by electro-chemical effects, promote the tendency for pitting corrosion in stainless steels[43].

Some concluding observations

It is clear that non-metallic inclusions have a marked effect on many properties which are vitally important to the steel user. Much work has been done in starting to relate the many parameters, which can be used to describe inclusions, to the mechanical properties. Much still requires to be done however, not only to understand the mechanisms by which inclusions affect various properties, but also to establish quantitative relationships which will enable the properties to be predicted. Even more important is the fact that it is not possible to predict the way in which inclusions are distributed and/or segregated in steel ingots, nor the precise way they will react to hot and cold working processes.

The needs for inclusion assessment therefore fall into two categories. The first is the need relating to the quantitative understanding of the effect of inclusions on properties. This is really a research need, and the ability to measure objectively, accurately and rapidly the many parameters associated with the inclusions is a primary requisite. Such parameters include the volume fraction, size distribution, shape distribution, continuity of stringers, etc, and to obtain such measurements for the different types or compositions of inclusions which may occur in steel; these types and composition differences may occur simultaneously in the same series of specimens. Considerable progress has been made towards these objectives with the continued and rapid development of quantitative image analysing microscopy, but the ultimate research tool would probably be the development of a technique using the methods currently being developed but with the signals being provided by the X-rays generated from compositional differences in inclusions, i.e. by a micro-probe analysis technique.

The second need is a result of the fact that it is not sufficient just to know that such a type, or distribution, or volume fraction of inclusions will produce any specific property. Control of the properties is the key to the problem, and how effectively the properties can be controlled by control of the inclusions is of absolute importance.

This is essentially a production control problem, and in this case it is very important that no potentially dangerous inclusion or distribution of inclusions, escapes detection. This requires 100% inspection, which must therefore be non-destructive. It must also be sufficiently rapid to keep up with production from a modern mill, and it goes without saying that the need is for objective, accurate and easy operation. These are stringent requirements, and not yet able to be approached. Perhaps the most promising field is that of automated ultrasonic inclusion assessment.

References

1. J.R.Blank and T.R.Allmand: ISI Publication 112, 1968, p1.
2. G.R.Bolsover: Metallurgia, 1935, p83.
3. R.Kiessling and H.Nordberg: "Production & application of clean steel", ISI 1972, p179.
4. F.B.Pickering: Ibid, p75.
5. T.Malkiewicz and S.Rudnik: JISI 1963, 201, p33.
6. F.B.Pickering: Ibid 1958, 189, p148.
7. T.J.Baker and J.A.Charles: "The effect of second-phase particles on the mechanical properties of steels", ISI 1971, p.79.
8. R.Kiessling: ISI Publication 115, 1968, p58.
9. P.E.Waudby: Steel Times Annual Review 1972, October, 147.
10. B.I.Klevebring. Scand. J. of Met. 1974, 3, 102.
11. D.Brooksbank and K.W.Andrews: "Production and application of cleen steel", ISI 1972, p186.
12. P.H.Frith: "Fatigue tests on rolled alloy steels made in Electric and Open Hearth furnaces", ISI, 1954.
13. W.Dahl et al: Stahl u Eisen 1966, 86, p796.
14. R.Kiessling and N.Lange: ISI Publication 100, 1966.
15. M.Korchynsky and J.Stuart: "High strength low alloy steels", London-Scandinavian Conference, Nurenberg, May 1970.
16. J.H.Little and W.L.M.Henderson: "The effect of second-phase particles on the mechanical properties of steels", ISI 1971, p183.
17. F.B.Pickering: "Towards improved ductility and toughness", Climax Molybdenum Co. 1972, p.9.
18. T.Gladman et al: "The effect of second-phase particles on the mechanical properties of steels", ISI 1971, p68.
19. "The effect of second phase particles on the mechanical properties of steels", ISI 1971.
20. "Production and application of clean steel", ISI 1972.
21. B.J.Edelson and W.H.Baldwin: Trans ASM 1961, 55, p230.
22. J.Gurland and J.Plateau: Trans ASM 1963, 56, p442.
23. J.R.Blank and F.B.Pickering: ISI Publication 110, 1968, p370.
24. A.G.Franklin: "Production and application of clean steels", ISI, 1972, p241.
25. R.C.Cochrane: "The effect of second-phase particles on the mechanical properties of steels", ISI 1971, p101.

References /Cont.

26. L.Roesch et al: Mem Sci Rev Met 1966, 63,p927.
27. H.J.Kouwenhoven: Private communication.
28. M.Atkinson: JISI 1960, 195, p64.
29. W.E.Duckworth and E.Ineson: ISI Spec Report 77, 1963, p87.
30. R.F.Johnson and J.F.Sewell: JISI 1960, p414.
31. J.D.Murray and R.F.Johnson: ISI Spec Rep 77, 1963, p110.
32. L.O.Uhrus: ISI Spec Rep 77, 1963, p104.
33. S.Enekes: "Production and application of clean steels", ISI 1972, p215.
34. J.C.M. Farrar, J.A.Charles and R.E.Dolby: "The effect of second-phase particles on the mechanical properties of steels", ISI 1971 p.171.
35. T.Boniszweski and R.G.Baker: JISI 1964, 202, p921.
36. J.Hewitt and J.D.Murray: Brit. Weld J 1968, 15 (4), p151.
37. J.Hewitt: 13th Junior Steelmaking Conference, BISRA 1959.
38. E.M.Trent: ISI Spec Report 94, 1967, p11, p77, p179.
39. D.M.Keane: Private communication.
40. H.Opitz and W.Konig: ISI Spec Report 94, 1967, p35.
41. A.Wicher: Radex-Rundschau: 1965: p432.
42. J.C.C. Leach: "Production and application of clean steels" ISI 1972, p105.
43. A.M.Edwards: Private communication.

LECTURE 12

METHODS FOR THE ASSESSMENT OF NON-METALLIC INCLUSIONS IN STEEL

SYNOPSIS

An account is given of the current state of the techniques of Inclusion Counting. Evidence is presented to show that the widely used chart counts are of very doubtful validity. The development of quantitative image analysis instrumentation is outlined, and the results of experiments to assess the accuracy and reproducibility of the data from such instruments is presented. It is concluded that modern instruments of the Quantimet 720 and 360 types are capable of giving an accurate assessment of inclusions present in a sample and that they should allow an assessment to be made of the extent of the sampling problem in the application of inclusion counting as a quality control technique.

INTRODUCTION

The occurrence of non-metallic inclusions in steel and their effects on steel properties have been discussed in previous chapters, and the need for inclusion assessment has been clearly illustrated. As long ago as 1929 workers were debating the same topics and were coming to the conclusion that it was necessary to have techniques which were capable of assessing the inclusion content of steel.[1] It was only after a further six years that a technique was developed for inclusion assessment which achieved fairly widespread use.[2] Much development work has been done since that time, but it is a sobering thought that despite technological advances there are still no B.S.I. or I.S.O. standards relating to methods of assessment.

The purpose of this chapter is to review methods of inclusion assessment, to comment on their effectiveness, and to report on the present 'state of the art'.

The Requirements of a Testing Technique

To be effective, any assessment technique has to give accurate and hence repeatable information about the content, distribution and morphology of each type of non-metallic inclusion present within the material under test. Unfortunately, because virtually all techniques are either destructive, expensive or time consuming, they have to rely on sampling procedures. Thus, not only must the actual measurements made be accurate and repeatable, but the sample examined must be representative of the material under test.

Obviously, if the non-metallic inclusions were randomly distributed throughout the bulk then the sampling technique would be relatively unimportant. Unfortunately, such conditions are rarely met due mainly to the presence and non-systematic distribution of exogenous oxide type inclusions within steel, and a good sampling technique is, therefore, a necessary pre-requisite to accurate assessment.

This has resulted in the development of two types of assessment, one based on optical metallography[3][4][5] and the second on other techniques.[6-12] At the present time cleanness is generally assessed by optical metallographic techniques, but such counts can be susceptible to large sampling errors and, in some instances, freedom from large macro-inclusions has to be checked using other techniques.[9][10][11][12] Whilst such non-optical tests, which include step machining, magnetic testing, fracture tests, radiography and ultrasonic techniques, give valuable information they tend to be limited in application and, apart from ultrasonic techniques, can only be considered as back up methods.

In the absence of a universally accepted non-microscopic

method, attention will be concentrated on a discussion of current optical metallographic techniques.

OPTICAL METALLOGRAPHIC TECHNIQUES

Although a large number of different assessment techniques are in current use, these fall into two main groups. Of these, the chart or indirect method in which a microscope field is compared against a standard chart is probably the most widely used, mainly because it is simple and quick to carry out.[2][13-16] On the other hand, direct methods in which specific parameters of the inclusions present are measured are time consuming and are, therefore, unsuitable for most quality control purposes.

For either method to be of practical use it has to be capable of giving accurate results within acceptable known limits. Otherwise the assessor would be unable to decide whether any measured difference was significant or was entirely due to statistical variation. Thus, in discussing methods of assessment, it is essential to consider their effectiveness in terms of accuracy and hence repeatability.

(a) Indirect Techniques

Within the U.K. the most widely used chart counts are the Fox[2] and J.K.[13] type counts. The Fox Count, Fig 1, is the simplest, because the observer has only to make one comparison for each microscope field and does not have to distinguish between the various types of inclusion that might be present. In principle this involves the operator determining the best fit for 60 consecutive fields. Of the 60 fields the number corresponding with each grade is multiplied by the grade number. The sum of the product of all fields is the inclusion content, i.e. the Fox Count. The usefulness of this method is limited, and other chart counts are available in which the inclusions present in any field are classified into type. Such counts incorporate a more comprehensive range of grading for each inclusion type in their standard charts. Typical examples of this type of

count are the SAE, Diergarten, Timken, General Motors, ASTM and the J.K. methods. J.K. count[13] for example distinguishes sulphides from oxides and divides the latter into morphology, type and width, Fig 2.

In 1968 the B.I.S.R.A Inclusion Assessment Group published the results of investigations intended to establish the accuracy of such counts.[3] A number of observers assessed the same specimens under identical conditions. Five observers examined three specimens in a pre-determined but random order. Each repeated his count on each specimen three times during the day but during this time was unaware of any previous counting results. Each test surface had been marked prior to the exercise to ensure that the observers all assessed exactly the same traverse. There were no sampling errors, and all the errors discussed were therefore either inherent in the count or were operator errors.

(i) The Fox Count

A statistical examination of the results obtained using the Fox Count, together with similar results obtained within one Works is shown in the following table:-

Accuracy of Fox Count (95% Confidence Limits)

	National Exercise		Works Exercise	
	No. of Counts/ per operator		No. of Counts/ per operator	
No. of Operators	1	2	1	2
1	±60	±58	±32	±31
2	±46	±43	±23	±22
3	±40	±36	±19	±18

Thus if two operators, selected on a national basis, count a given specimen once, the above table indicates that if the mean of their two counts was 100, then there is a 5% chance that the true values would fall outside the range 54-146. For operators from one works

only the range would be 77-123, thus, although the error was in fact lower, the magnitude was still very large.

It is interesting to compare these predictions with results obtained in an exercise carried out between seven works within one large organisation.[17]

Results from Seven Works

(After Hardy)[17]

Sample	1	9	13	21	25
Mean Count	131	113	132	100	113
Limits	-39 +66	-42 +30	-64 +86	-63 +44	-29 +30

Predicted Accuracy (3 Operators - 1 Count) based on BISRA assessment[3]

National Exercise (5 Works)	±40
Within one Works	±19

Whilst the results obtained tended to be higher than those predicted from the BISRA exercise, this would be expected since there were variables present which were eliminated in the BISRA work, e.g. different microscopes. Different microscopes have been shown to have a major influence on inclusion count results.[18] From such results it can only be concluded that the accuracy of this count is such that it has little practical application.

(ii) The J.K. Count

This count is more sophisticated than the Fox Count because, as stated previously, the operator is required to classify into types and to use a greater number of field classifications. The operator has, therefore, a larger number of judgments to make, each of which will have its own associated error. For example, the

operator decides the type, then decides which width grade and finally decides the best fit according to the chart.

In fact, both the BISRA work, and more recent work carried out in BSC, showed that observers did not agree on the classification into types, and this had a major effect on the results relating to oxide inclusions, Fig 3. The accuracy of the manganese sulphide assessments from these casts were:-

J.K. Count

Accuracy of MnS Assessment

(95% Confidence Limits)

No. of Operators (1 count each)	National Investigation	Within BSC	Within 1 Works
1	±62.5	±60.2	±69.3
2	±47.0	±44.6	±54.1
3	±41.0	±38.0	±48.0

Once again it is interesting to compare these results with results reported by the seven works referred to previously:-

J.K. Count

Results from Seven Works

Specimen No.	1	2	3	4	5
Mean Count	127	97	145	156	133
Range	+58 / -57	+ 3 / - 2	+50 / -42	+52 / -74	+48 / -43

Predicted Error (BISRA) ±41

The good agreement obtained between the various investigations indicated that the errors associated with these counts are large, and as for the Fox Count, it is difficult to justify the use of the J.K. Count.

(b) Direct Techniques

In view of the lack of correlation of results obtained using chart methods with properties and service performance, it is not surprising that investigators have tended to devise other techniques based on classical quantitative metallographic techniques.

These invariably measure one or more parameters, and relate them to some measure of distribution. Most counts measure one or more of the following:-

(a) area fraction
(b) number in a given area
(c) number on a given length of traverse
(d) size distribution of widths
(e) size distribution of lengths
(f) aspect ratio.

Typical examples are the Berg and LT counts, Fig 4.[15][16]

Tests on such techniques have indicated that the errors present are lower than those associated with chart counts, Figs 5 and 6, and that meaningful correlations can be obtained with properties and performance. The accuracy of the LT technique is illustrated in the following table:-

Lineal Traverse Count
No/cm (10 cm Traverse X90)

Operator	1	2	3	4	5	6	7	8	9	10	11
Sample 1	4	5	5	6	5	-	3	4	6	4	5
Sample 2	5	6	11	7	5	-	6	7	6	6	7
Sample 3	8	8	9	8	8	-	8	10	10	7	8

Specimen	Type	Operator 1	2	3	4	5	6	7	8	9	10
4	MnS	1.9	1.5	3.6	5.3	2.2	1.5	3.6	3.1	3.5	3.8
	Silicate	4.4	4.6	5.9	9.6	7.7	9.9	4.8	6.6	6.4	7.5
	Duplex	0.9	0.1	0.4	2.0	1.5	0.7	0.6	1.3	0.4	1.0
	TOTAL	7.2	6.2	9.9	16.9	11.4	12.1	9.0	11.0	10.3	12.3

Obviously such counts are preferable to the more subjective chart counts, but unfortunately they are by nature tedious and time consuming. For example, a Berg count might take 1 hour and an LT count ½ hour. Thus, whilst they have been used to good effect in research projects, they are in most cases unsuitable for works quality control purposes.

USE OF AUTOMATIC IMAGE ANALYSING TECHNIQUES

The direct technique used to assess inclusion content are all essentially methods of image analysis, but using manual techniques. Since the major disadvantage of such techniques was not lack of accuracy, but speed of carrying out the test, it is not surprising that considerable attention has been given to methods of automation and a number of attempts have been made to develop automatic instruments.[4][11][12][19][20] The first commercially available instrument was the Metals Research QTM model A which was developed and marketed in 1963. This used a TV camera to scan the optical image and record certain inclusion parameters. The principle of detection is shown in Fig 7. The experience gained resulted in 2nd and 3rd generation instruments, the Quantimet B and the Quantimet 720.

During this development period, other manufacturers, realising the potential of this type of instrument used the same principle to develop other models. At the present time there are five models available.

Whilst the QTM Model A indicated that the technique had some promise, its limitations were so severe in terms of resolution,

the parameters measured, time taken, and lack of sensitivity, that it was not possible to distinguish oxides from sulphides without resorting to etching techniques and the use of a double count. It had little or no market appeal.

The second generation instrument, the QTM Manual Model B, Fig 8, was a major step forward and was capable of measuring oxides and sulphides separately, and of giving information on the area, number and particle size distribution.

Early trials were promising, and evaluations indicated that instruments were capable of giving repeatable and accurate measurements and, in certain instances, could be programmed to do chart type counts, Figs 9-14.

Work in France confirmed that over a period of three years from 1969-72, using the QTM Model B and a Zeiss Micro Videomat, area measurements obtained were repeatable to ±5%. They also showed that good correlation and repeatability of results were obtained on size measurements of particles above 4μm. Below this size the results were found to be influenced by the resolution of the microscope used.

In the USA, an experiment using 1 operator and 2 samples indicated an accuracy of ±10%. However, despite this promise the instruments were extremely slow and did not lend themselves to quality control work. A major problem was that the instrument only had a line to line memory, thus if the instrument detected a signal in the next line down within a preset distance, it assumed it was the same inclusion, and if any given line failed to detect an inclusion, then multiple counting occurred and was unavoidable when irregular shaped stringers were sized. A similar problem occurred when parts of an inclusion were too thin to be resolved.

As indicated earlier, in order to overcome the slow speed, the instrument was fully automated and recording systems were incorporated to replace the measuring indicator. In

effect this cut down the inter-field time. Unfortunately the introduction of full automation required the detection control to remain set during the count. Since the operator could no longer adjust between fields, the actual setting became very critical and this, together with problems relating to focus and variation in tube sensitivity across a field, created a number of temporary problems.

In addition, at this point the limitations of analogue measuring systems became apparent, in that it was found that instruments which, to the operator, were functioning correctly could in fact be recording erroneous results. It was also found that the warm-up period for instruments was variable and in some cases rather lengthy.

Nevertheless, these problems were minimised and a Model B was, in fact, and still is used for Quality Control work in one Works. This is programmed to measure total lengths and frequency of occurrence of inclusions, within specified length ratings.

Further developments in the form of the Quantimet 720, Fig 15, which had the built in reliability of a digital logic system, removed these problems. The digital logic employs a system which breaks the monitor image down into individual picture points and only counts and detects phases whose anti-coincidence point lies within the line frame. In addition all information is stored during analysis, and is readily retrieved at the end of the analysis. The use of advanced computer units broadens the scope of assessments possible, and the most sophisticated version can:-

1. Detect and measure the parameters for a number of different phases separately, over a large range of grey levels.

2. Measure area and size on area.

3. Measure perimeter, and size on perimeter.

4. Measure and size on width.

5. Measure and size on length of individual inclusions, or can count adjacent inclusions as stringers.

6. Measure oxides within sulphides separately from similar inclusions not associated with sulphides.

7. Overcome problems associated from internal reflections from within a phase.

8. Recognise shapes and patterns.

9. Automatically focus.

10. Compensate for variation in detection across a field.

Provided that the latter device is used, then the results obtained have been shown to be extremely good. For example, one evaluation indicated that three operators obtained results of 0.494, 0.506, 0.480% area on the same sample. The accuracy of the size distribution is shown in the following table:-

0 - 1½	1½ - 3½	3¼ - 6½
543	391	163
565	404	172
519	336	162

The warm-up period was found to be approximately 15 minutes, and over a period of 40 days a standard specimen containing 30% of a phase was measured within the range 29.9 - 30.1%. In a further test, a sample containing 0.325% of Non-Metallic Inclusions was tested on each of 15 consecutive days. The results obtained indicated a variation of ±0.025% and that there was no more than 1% variation in the percentage of the inclusions falling into each of the 5 size ranges measured.

However, some expertise is required to programme and operate the instrument threshold setting and, despite automatic focus and punch tape facilities, it tends to be unsuitable for quality control work due to the time factor. This all important time factor was no doubt the stimulus for the development of the Quantimet 360, Fig 16. To obtain acceptable times, new systems and some compromise had to be made. The makers having no doubt been influenced in their choice by the requirements of the count currently being used for high quality materials.

Apart from high speed logic systems, Metals Research have developed and incorporated automatic focusing, auto-detection, preset thresholds, electronically enhanced resolution, a synthetic internal standard and a red print out facility when parameters exceed a pre-determined specification. The combination of these systems has produced an instrument which has the required speed and accuracy at the expense of flexibility and, for the first time, a fully automatic instrument requiring little or no operator expertise.

Experiments using the Quantimet 360 have shown that:-

1. Measuring static areas, the errors when measuring sulphide is ±3% and ±5% when measuring oxides.

2. It is possible to measure at a rate of 22 fields/sec without impairing the accuracy.

3. It is possible to assess specimens containing stringers >1½µmwidth within an error of 5%.

4. The instrument is stable.

Thus in the Quantimets 720 and 360 the metallurgist has for the first time instruments which are capable of giving accurate assessment of the inclusions present within an

image.

Given this tool, it should now be possible to evaluate the extent of the sampling problem, and hence to determine the future of optical metallographic techniques in assessing inclusion contents.

REFERENCES

1. R H Sherry, "Steel Treating Practice", McGraw-Hill, 1929.

2. G Bolsover, Metallurgia, 1935, 83.

3. J R Blank and T R Allmand, ISI Publication 112, 1968, 1 and 47.

4. J R Blank, "Clean Steel", Proc. 75th BISRA Steelmaking Conference, 1970, 97.

5. J R Blank, "Assessment of Steel Cleanness", Proc. of Joint BSC-BISPA Conference, 1973, 17.

6. L S Thompson, Ibid, 25.

7. K R Whittington et al, Ibid, 82.

8. K W Andrews, Ibid, 96.

9. B R Jackson, Ibid, 104.

10. B R Jackson, "Clean Steel", Proc. 75th BISRA Steelmaking Conference, 1970, 109.

11. D A Melford, ISI Publication 112, 1968, 14.

12. K A Ridal, Ibid, 40.

13. B Kinman, Jernkon. Ann. 1936, 120, 199.

14. ASTM Standards 1955 (1), 1645.

15. BISRA Report SM/B/71/64 and JISI, 1966, 204, 146.

16. S Bergh and O Linberg, Jernkon.Ann. 1962, 146, 862.

17. J V Hardy and R T Allsop, JISI, 1960, 195, 302.

18. W H Hadfield and G W Giles, JISI, 1940, 142, 11.

19. C Fisher, ISI Publication 112, 1968, 24.

20. D A Melford, "Assessment of Steel Cleanness", Proc. of Joint BSC-BISPA Conference, 1973, 36.