

SIGNIFICANCE OF REOXIDATION IN STEELMAKING

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In recent years, reoxidation has clearly emerged as a major source of non-metallic inclusions in steel, and the main contributory causes have been clarified. These are direct oxidation of the steel stream as it falls through the air, chemical erosion of siliceous refractories and oxidation by air entrained during casting, the last being the most important. In spite of this the factors governing entrainment are not well understood. Consequently, in this work, falling water jets were used to carry out a thorough investigation of the effects of nozzle diameter, height of fall, discharge rate and turbulence level of the stream, on jet disintegration, the rate at which air is entrained and the volume of air retained in the receiving pool during pouring. Of the variables employed, the turbulence level emerges as the most important. Four mechanisms of entrainment were distinguished and their relative contributions to the overall rates elucidated. The way in which entrained air is distributed as bubbles, their residence times and their effect on flow patterns within the receiving pool are also mentioned, since these factors influence the gas-metal area and time available for oxygen pick-up. Experiments have also been conducted to study gas absorption by molten steel droplets falling through air. The practical implications of the results are discussed with reference to the reactions which occur as steel is transferred from the furnace to the ladle and then to the ingot mould. The influence of reoxidation on alloy loss, slag formation, refractory interactions, sulphide shape control and steel cleanliness are described and the paper concludes with a discussion of the critical importance of controlling stream characteristics and eliminating air entrainment.

LIST OF SYMBOLS

b_r, b_u	Lateral radius of the aerated zone for restricted and unrestricted stream penetration.	d_1, d_2	Diameters of jets at point of impingement with the pool surface
C	Air concentration within the aerated zone	ϵ_1, ϵ_2	Turbulence intensity of the streams
d	Restricted pool depth	H	Fall height of the stream
d_p	Penetration depth of an unrestricted stream	Q_A	Air entrainment rate of the falling stream
		Q_W	Water discharge rate

r	Radial distance on a lateral plane within the aerated zone
U_n	Stream velocity at the nozzle exit
V_1, V_2	Stream velocities at point of impingement with the pool surface
Vol_A , (or V)	Volume of air retained within the receiving pool,
Vol_A , (or V)	Volume of air retained within the receiving pool.
$Vol_{A(R)}$, (or V_r)	Volume of air retained within the receiving pool, when the penetration depth of the stream is restricted.
$Vol_{A(u)}$ (or V_u)	Volume of air retained within the receiving pool, when the penetration depth of the stream is unrestricted.

INTRODUCTION

Reoxidation is the increase of the total oxygen content of deoxidised steel caused either by the pickup of atmospheric oxygen or by the chemical erosion of siliceous refractories. Neither the mechanical erosion of refractories nor the entrapment of protective fluxes during casting should strictly be included since these cause exogenous inclusions, whereas reoxidation results in indigenous inclusions.

The boundary between the two can become rather diffuse, particularly since the resulting inclusions can be very similar in size and composition, and also since entrapped flux or slag can act as oxidising agents, mainly by reaction with aluminium dissolved in the steel, as well as providing exogenous inclusions. However, the distinction will be retained, and reoxidation discussed in terms of the limited definition given above. That due to chemical erosion will only be discussed briefly, the emphasis being placed on that due to atmospheric oxidation, with which our experiments have been concerned.

LITERATURE REVIEW

The existence of the problem has been known for many years. As far back as 1945, Hultgren(1) drew attention to the presence of large inclusions in ladle

samples of electric arc steel deoxidised in the furnace, which contained no large inclusions prior to tapping. In 1950 Brower et al (2) reported that reoxidation during tapping of open hearth heats was the main cause of alloy losses, while oxygen pickup during casting was reported by various authors between 1959 and 1970.

Vingas and Caine(3) have ascribed macro-inclusions found in steel castings to reoxidation, while Van Vlack and Flinn(4-7) have discussed the reoxidation of steel deoxidised by aluminium during the manufacture of castings. Wilson(8) reported on oxygen pickup during teeming, while Hoffmann et al (9), Adilstam et al(10) and Ericsson(11) have all given clear demonstrations of the benefits of protecting the teeming stream with argon. Hoffmann et al reporting a 30-65% decrease in oxide inclusions brought about by complete argon shrouding. A comparison of the results of Adilstam et al(10), where the upper surface of the ingot as well as the stream was shielded from oxidation, with those of Ericsson where the surface was not protected shows that surface oxidation and air entrained at the point of impact of the stream together contribute a significant proportion of the inclusions in the final ingot. Little et al (12) and Kenney (13) were among the first to show the importance of reoxidation during continuous casting.

It is important to note that the studies cited cover teeming into ingots and castings as well as continuous casting i.e., any situation in which a stream of molten steel fell through air, so that a high surface area per unit volume was exposed to contact with the air. However, it is really in the more recent literature, and particularly in that relevant to continuous castings, that reoxidation has become accepted as a major source of inclusions in the final steel. Its importance can be deduced from reports(14-16) of marked increases in oxygen contents between ladle and tundish and from the significant improvements which can be obtained when some practical modification is employed to minimise contact between the metal stream and air(17-20). This can take various forms involving physical shielding, inert gas shrouding and combinations of these.

Evidence for reoxidation is also provided by the size and composition of

inclusions. Farrell et al (21) pointed out that reoxidation products are usually very much larger than deoxidation products and tend to be richer in the weaker oxide forming elements such as silicon and manganese than the indigenous inclusions. More specifically, they concluded that in steels such as most fine grained qualities which contain sufficient aluminium for this to be in control of deoxidation, the presence of silicate inclusions is direct evidence of reoxidation. More recently, Venkatadri(22) has concluded that any spinel-type inclusions are very probably the result of reoxidation leading to localised regions of high oxygen content. This view was adopted after having established, in agreement with the majority of relevant work, that spinel-type inclusions are characteristic of dissolved oxygen contents appreciably above those normally found in low carbon steels prior to tapping, and that those formed earlier in the process will be reduced to alumina during holding in the ladle. However, Pickering(23) has shown that spinels can also result from the reaction between refractory erosion products and aluminium dissolved in the steel.

In the practical casting situation, there seems to be agreement that reoxidation products are generally $>100\mu$ in size. This is consistent with the laboratory studies of Farrell et al(21), but not with those of Brabie et al (24-26) who found that only small inclusions are formed in this way. Part of the discrepancy is due to the fact that most of the practical results relate to continuous casting, where erosion of silica immersion nozzles, either chemically or mechanically, and entrapment of the fluxes used to cover the metal surface in tundish and mould can also be significant sources of large inclusions, and separation of the contributions from the various sources is not a simple matter. However, it also seems clear that under the turbulent conditions of pouring the final size range is a result of a considerable amount of agglomeration of oxide particles within the bulk of the metal, and Brabie's technique of blowing oxygen-containing gases onto the surface of deoxidised steel in a crucible may not provide the correct conditions for this to occur to as great an extent as in practice.

Brabie's results on the protective effect of carbon in the steel have also

been found to apply in practice by Matsunaga et al(19), who found only a few large inclusions in a 0.5%C steel, and by Ohno et al(14), who demonstrated that the extent of reoxidation was inversely related to the carbon content of the steel. This effect is due to the fact that carbon reacts with some of the oxygen and also creates a protective shroud of reducing CO gas which inhibits ingress of oxygen in much the same way as argon. As already mentioned, Farrell et al(21) have shown that silicon and manganese play an important part in the atmospheric oxidation of steels with residual aluminium content of $<0.01\%$, but above this value aluminium takes over as the dominant element, because it has a much greater affinity for oxygen. For the same reason, aluminium also creates inclusions by the chemical erosion of siliceous refractories and converts siliceous inclusions in situ in the steel to alumina or aluminates.

Reoxidation by erosion of ladle, nozzle and stopper refractories has been shown by Pickering(23) to be a very serious source of inclusions, mainly manganese aluminosilicates, in both silicon-killed and aluminium-killed steels. In the latter case, they are more difficult to identify because of their reaction with the dissolved aluminium. The two main factors which make these so unacceptable are their large size (twice as large as primary and three times as large as secondary deoxidation products), and the lateness of their formation in the steel which minimises the chance of escape. The conditions for forming a minimum of these erosion products are complex, involving holding time, teeming speed, temperature and, most importantly, the condition and type of the ladle lining.

It is worth stressing that what makes reoxidation so significant as a source of non-metallics is that the inclusions are created immediately before solidification when the possibilities of escape are at a minimum, even though agglomeration is favoured by the turbulence caused by pouring, and in fact the benefits of excellent furnace and deoxidation practices can be completely lost by allowing reoxidation to occur subsequently. The incidence of reoxidation products can be reduced but not eliminated by changes in deoxidation practice, the only complete remedy being isolation of the metal from air, or other oxidising agents during casting. Since contact with refractories in

runners, ladles, nozzles, stopper rods and the runner brick assembly in uphill teeming systems clearly cannot be eliminated, the solution lies in the selection of refractories with compositions shown to be resistant to erosion. This will generally involve higher alumina and lower silica contents and greater use of basic refractories, the ultimate solution probably being dictated by economic rather than metallurgical aspects. Presumably, reoxidation by erosion occurs when aluminium-killed steels are cast into sand moulds, but since the composition of the moulding sand is determined by other criteria, it is difficult to see what can be done in this case, other than minimising the residual aluminium content by careful deoxidation practice.

MODELLING OF ATMOSPHERIC REOXIDATION

From a simple model in which the metal stream is considered to behave as a moving solid cylinder, Szekely(27) has deduced that the amount of oxygen entrained by a smooth stream is many times larger than that picked up by mass transfer from the air as the stream falls through it. McCarthy et al(28) have since confirmed this by water modelling experiments and indicate a factor of >100 between the two quantities. This was for relatively short streams for which break up was not severe. When it is, the simplified model of Schwerdtfeger and Wepner(29) becomes more relevant. This applies to the oxidation of completely disintegrated streams, assuming mass transfer to the droplets to occur by a combination of convective flow and diffusion. If a droplet radius of 0.25 cm is chosen, this model predicts that the rate of oxygen pickup is approximately sixty times as great as that of a smooth stream. However, the entrainment rate is also greatly increased by increasing jet turbulence and break-up, so it would seem that this remains the major mechanism of oxidation of the relatively rough streams more typical of the practical casting situation. This is certainly the conclusion drawn by Maddever et al (30) from a room temperature chemical model for gas absorption by molten steels for the case of a turbulent system.

In view of this evidence, and the very considerable financial cost of steel reoxidation, it was decided some time ago that a detailed study of air entrainment using water modelling techniques could well yield important and

valuable information. Details of the experimental apparatus, instrumentation and techniques, including the way in which the turbulence intensity can be measured quantitatively, are given elsewhere (31). The variables employed were nozzle diameter, height of fall, discharge rate and turbulence level of the stream, and the effect of each of these on jet disintegration, the rate at which air is entrained and the volume retained in the receiving pool during pouring were determined. The effect of restricting the penetration depth of the plunging jet and the way in which the entrained air is distributed as bubbles, their residence times and their effect on flow patterns within the receiving pool were also examined since these factors influence the gas-metal interfacial area and the time available for oxygen pickup by liquid steel.

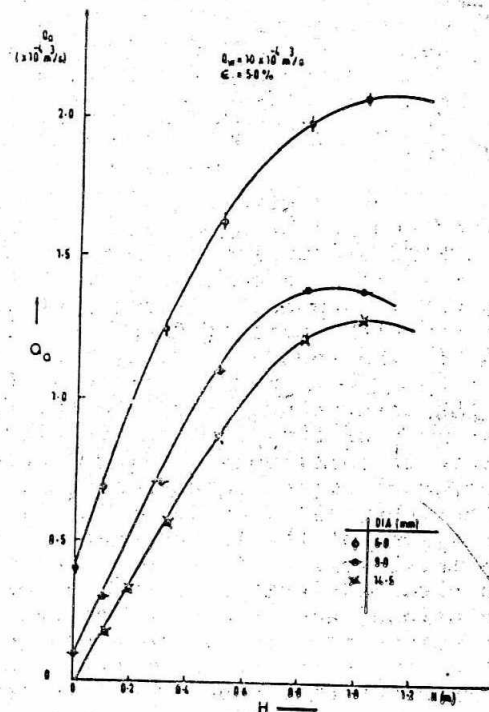


Fig.1 Influence of fall height H , on rate of air entrainment Q_A , for streams with a turbulence intensity of 5 pot, existing from nozzles of different diameters at a constant discharge rate Q_N of $10^{-4} \text{ m}^3/\text{s}$.

Rate of Air Entrainment

As far as nozzle diameter, height of fall and discharge rate are concerned,

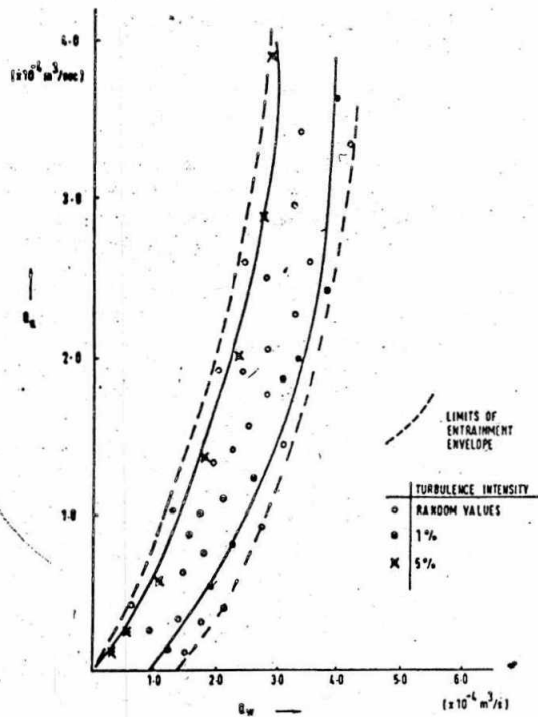


Fig. 2 Influence of discharge rate Q_W on rate of air entrainment Q_A , for streams with different levels of turbulence intensity.

the effects are exactly as expected, namely that the entrainment rate, Q_A , is inversely related to nozzle diameter at constant discharge rate (Fig. 1) and directly related to height of fall (Fig. 1) and to discharge rate (Fig. 2). However, the major point to emerge from this work is that turbulence or surface roughness is the most important parameter governing Q_A . This in turn is due to its decisive effect on the mechanism of entrainment, the disintegration length of the stream and the minimum velocity required for entrainment.

From a detailed study of photographs of the falling jets, it has been proposed (31) that there are four distinct mechanisms of air entrainment into a liquid pool by a falling jet of the same liquid. The main factor governing which of these is operative in any given situation is the turbulence level of the stream, and the mechanisms will be described in the order observed as the turbulence is increased.

When the jet is laminar the annular oscillation mechanism operates. In this case, air in the attached boundary layer strikes the pool surface causing a depression of the meniscus between the

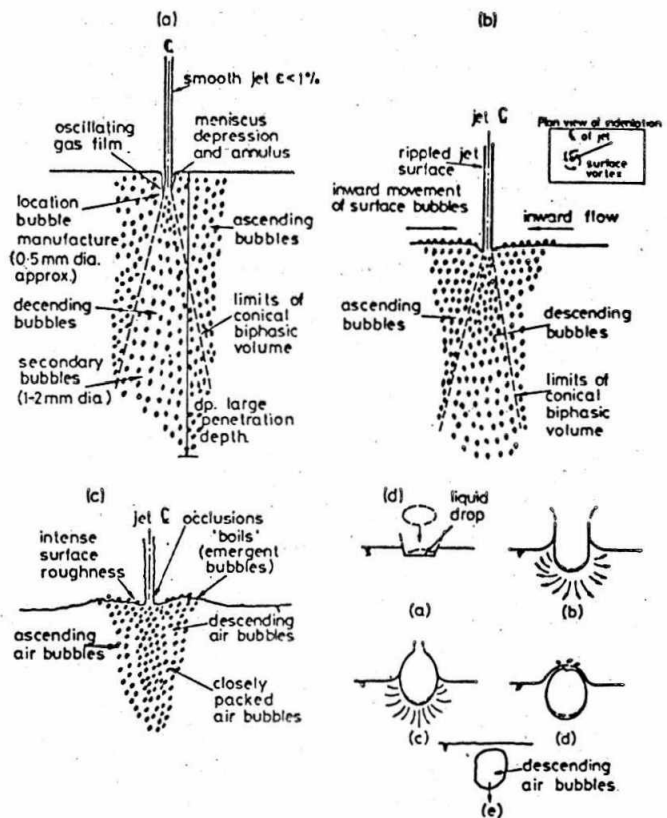


Fig. 3 Mechanisms of air-entrainment: (a) Annular oscillation; (b) Intermittent vortex; (c) Turbulent occlusion. (d) Droplet entrainment.

pool and the jet periphery. The plunging jet thus maintains its identity for a short depth along which it is surrounded by an annulus of air. The lower part of this gas film exhibits oscillations which are roughly symmetrical in the axial direction and which increase in intensity with depth until the annulus collapses to form a large number of very small bubbles, as shown in Figure 3(a).

At slightly higher turbulence levels the jet characteristics become transitional between laminar and turbulent and the intermittent vortex mechanism occurs. In this case an indentation appears around the jet periphery, as in Figure 3(b), caused by a combination of the downward jet flow and the pressure of air within the boundary layer surrounding the jet. A general energy level is produced in the pool as a result of momentum transfer which is seen as a random eddying motion of the biphasic flow. When an eddy interacts with the peripheral indentation the pool liquid surrounding the jet assumes a vortex motion. This happens

intermittently so that vortices are continually reforming the decaying. Associated with these free vortices there is radial inward surface flow so that emerging bubbles can be re-entrained, the overall effect being to increase, quite significantly, the rate of entrainment.

When the jet becomes turbulent, the indentation on the surface at the point of impact becomes highly irregular in form due to the rough jet periphery. Ambient air is entrapped by the surface roughness and is distributed as bubbles of 2-3mm diameter by a diffusion mechanism, as illustrated in Figure 3(c). The volume of air entrained by this turbulent occlusion mechanism is considerably greater than that introduced by the two mechanisms discussed previously.

Once disintegration of the stream into droplets is well advanced the droplet entrainment mechanism becomes the major one, each discrete droplet producing its own quantity of entrained air. The behaviour of a liquid drop impinging on a liquid pool has been studied by Engel(32), to whom the steps shown in Figure 3(d) are due.

As would be expected, both disintegration length and the minimum velocity required to cause entrainment are inversely related to the turbulence level. Consequently, the more turbulent the stream, the greater the height over which entrainment is occurring and the greater the length over which disintegration is either progressing or complete.

The total effect of turbulence on entrainment rate is produced by a combination of its effects on the three factors just discussed. Of these, it seems clear that it is the changeover in mechanism which is the major factor responsible for the five-fold increase in entrainment rate at the same height shown in Figure 2, turbulent occlusion being by far the most effective mechanism. Another point that is clear from Figure 1 is that for any constant linear velocity of the stream, as determined by the nozzle diameter and discharge rate, Q_A eventually reaches a maximum value at a certain height. This is caused by the fact that the droplet entrainment mechanism is considerably less effective than the turbulent occlusion, so that disintegration of the stream past a certain point causes

a flattening of the rate curve followed by a decrease.

Volume of Air Retained in the Pool

The air entrained by the various mechanisms discussed is carried as bubbles by the flow within the pool and distributed throughout the submerged aerated region. Eventually these bubbles escape from the zone of influence of the downward flow and rise to the surface. Thus, at any particular moment, there is a certain volume of air retained within the pool in a state of dynamic equilibrium. In other words, a stage is reached at which air is leaving the biphasic region at the same rate at which it is entering it, so that the dimensions of this zone remain reasonably constant as long as the variables are held constant.

Just as for the rate of entrainment, the volume of air retained within the receiving pool was found to be directly related to the height of fall, discharge rate, emission velocity of the stream (Figures 4(a) and 4(b)), and to its turbulence level. However, comparison of Figures 4(a) and 4(b) reveals a direct dependence of Vol_A on the jet or nozzle diameter at the same stream linear velocity, whereas Q_A showed inverse dependence on the nozzle diameter when the discharge rate was constant. This direct dependence of Vol_A is presumably due to the fact that as the jet diameter is increased, its impact area with the pool and hence the volume of the biphasic zone is increased.

The other interesting difference is one of degree. Whereas, as shown in Figure 2, a five-fold increase in turbulence produced a five-fold increase in the rate of entrainment at the same height, the effect of a similar increase in turbulence is to increase the volume retained by only about 20%. This is because the more turbulent stream is more highly disintegrated and the area of its impact on the pool greater, so that the penetration depth and hence the total volume of the aerated region is decreased although the bubble intensity within the zone is greatly increased. Because of the decreased penetration depth the residence time of bubbles within the pool is also reduced, so it would seem that bubbles escape faster as well as being introduced more rapidly as the turbulence intensity is increased, so that Vol_A is not greatly affected.

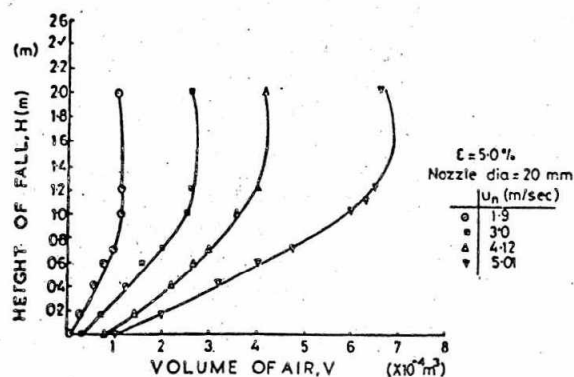


Figure 4a

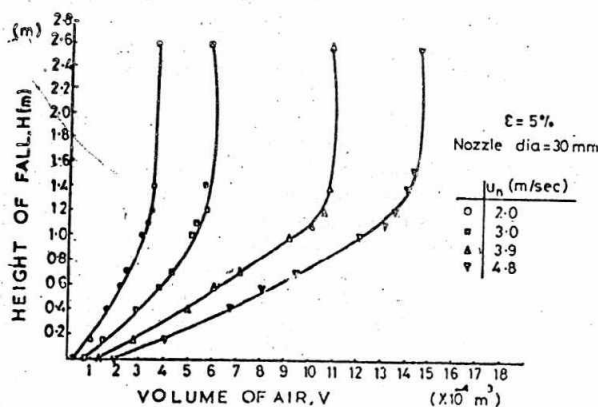


Figure 4b

Fig. 4 Relationship between volume of air retained within the pool and the fall height for different emission velocities U_n of the stream, and different nozzle diameters.

Thus neither Q_A nor Vol_A provides a quantitative measure of the effect of varying stream turbulence on the likelihood of oxidation of liquid metal by entrained air bubbles. In a sense, the variation of Q_A with turbulence over emphasizes its importance while the variation of Vol_A underestimates it, so that the true situation lies somewhere between them. The other factors involved in assessing the importance of turbulence are its effect on bubble size and distribution, since these also influence the gas-liquid interfacial area and the residence time of the bubbles.

Before examining this further, the effects of restricting the penetration depth should be noted. The effect on the air concentration profiles is shown in Figure 5 and the effect on Vol_A in Figure 6. Clearly the lateral extent of the aerated zone is greatly increased, the magnitude of the difference between the two cases increasing

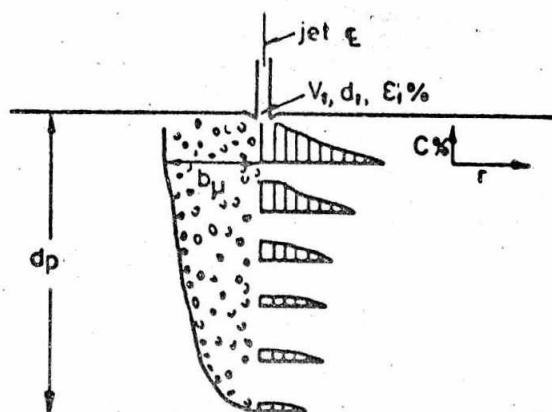


Figure 5a

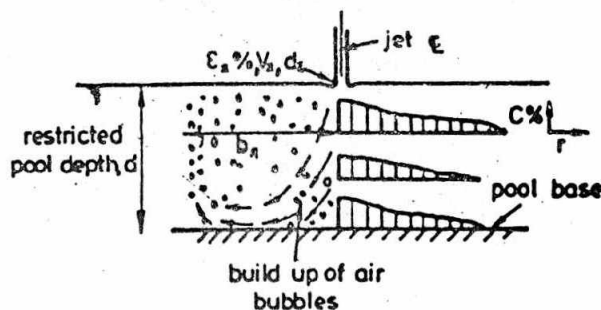


Figure 5b

Fig. 5 Air concentration profiles associated with stream penetration in a pool of unrestricted depth, Fig. 5(a) compared with those in a pool of restricted depth, Fig. 5(b). In each case the stream velocities V_1 and V_2 , diameters d_1 and d_2 , and turbulence factors 1 and 2, are equal. Lateral radius b_r is greater than b_u .

with depth. Also the volume of air retained is raised quite significantly, the maximum occurring at a value of d/d_p of 0.6 when the ratio $Vol_A(R)/Vol_A(u)$ is 1.28. The results in Figure 6 also show that if the pool depth is equal to 0.33 of the free penetration depth, the value of $Vol_A(R)$ is equal to that of the undisturbed case, and any further reduction in pool depth beyond this causes a further decrease in $Vol_A(R)$.

Distribution of Air Bubbles in the Pool

The distribution patterns induced by the different entrainment mechanisms operating at various turbulence levels are clearly shown in Figure 3. By exciting the pool turbulence, the entrained air accelerates the dispersion of energy in the diffusion zone and the

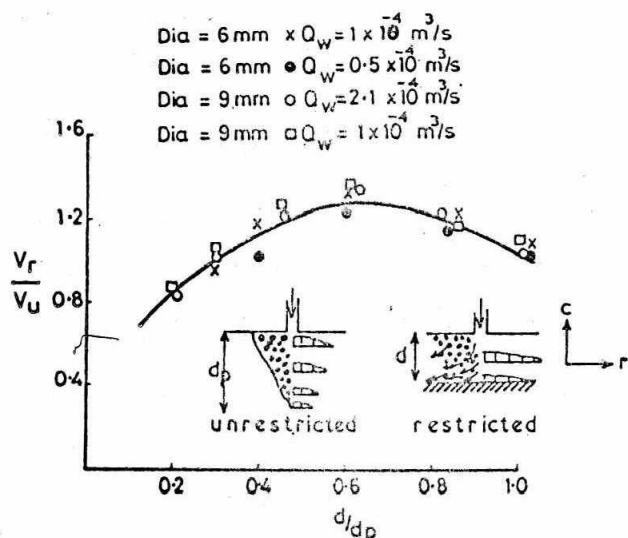


Fig.6 Influence of the ratio of penetrating depths d/d_p on the ratio of volumes of air retained in the pool corresponding to restricted and unrestricted streams.

decrease in velocity of the downward flow in this biphasic region, so reducing the penetration very markedly. Thus, the distribution of air throughout the aerated region is very dependent on the turbulence level of the impacting jet. A smooth jet produces a very deep aerated region in which the bubble density is very low, whereas a rough jet produces a much shallower region of smaller, very densely packed bubbles. It should also be noted that whereas the lateral extent of the downward moving zone increases with depth for the annular oscillation and intermittent vortex mechanisms, it decreases with depth for turbulent occlusion. Thus it would seem on the whole that the effect of turbulence on the amount of oxidation is more nearly measured by its effect on Vol_A rather than its much larger effect on Q_A . It should be borne in mind, however, that the bubbles created by entrainment are very much smaller than those generally produced by injection through a nozzle, so that any given volume represents an appreciably larger interfacial area than would be the case for larger bubbles and hence an enhanced opportunity for mass transfer of oxygen from the bubbles. The smaller bubbles will also have less buoyancy and consequently longer residence times, so on both counts Vol_A clearly underestimates the likelihood of oxidation.

Analogy between Water and Molten Steel

The validity of water as a modelling medium for molten steel has been demonstrated repeatedly over the years. Turkdogan(34) used water to illustrate the effects of height of fall and "ropiness" of the stream. Since then, Maddever et al(35,30) have shown that water modelling can be used most successfully to reproduce the behaviour of steel casting streams. Fraser and Rachmann(36) designed extension tips to reduce the harmful effects of sliding gate nozzles on stream quality using water modelling, and the effectiveness of these has recently been amply demonstrated(20). Water modelling has also been applied to the AOD process(37) with excellent results, and these instances, together with others which could be cited, provide strong justification for the use of water modelling.

The similarity criteria and the role of the very different temperatures involved have been discussed at some length in previous papers(35,31). For the present purpose it is sufficient to note that the most important single property in this context is the kinematic viscosity, and the fortuitous similarity of the two quantities (within 10%) for water at room temperature and liquid steel at 1600°C provides a strong basis for the analogy between the two fluids. Thus there is good reason for considering that the trends and effects produced by the variables discussed will be at least qualitatively similar for steel, and that their role in causing reoxidation of steel will be proportional to their effects on air entrainment.

Some Chemical Aspects of Atmospheric Interactions with Molten Steel

In addition to water model studies, experiments have been conducted with molten steel droplets, to investigate factors affecting the pick-up rate of oxygen, nitrogen and hydrogen from air atmospheres of controlled humidity. The equipment employed for this work is shown in Figure 7. Steel droplets are melted within the levitation chamber and then allowed to fall for various times through the reaction chamber which may contain air or other gas mixtures of controlled composition. The droplets are solidified in a copper mould and the oxygen, nitrogen or hydrogen contents determined by inert gas fusion analysis.

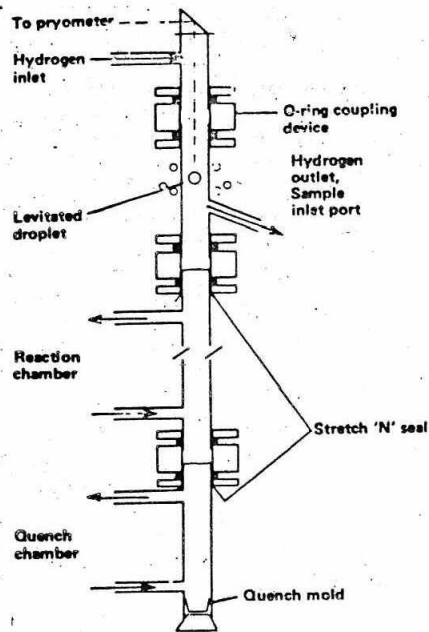


Fig. 7 Levitation facility for studying reactions which occur when molten steel droplets fall through air.

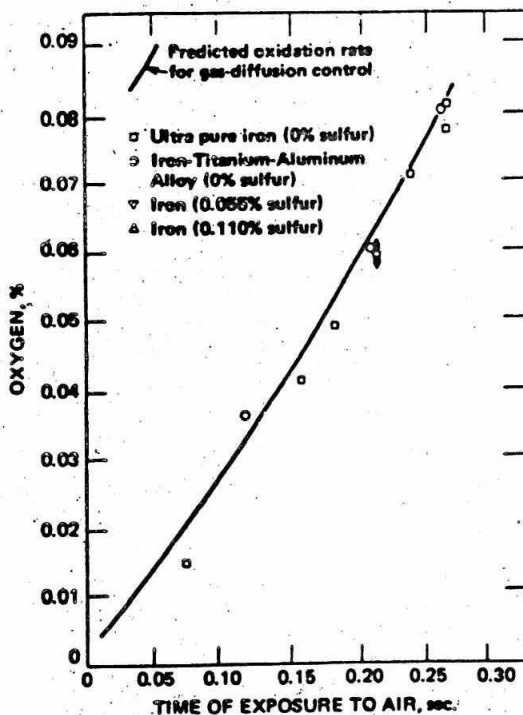


Fig. 8 Oxygen content of different iron alloys after falling for various time through air.

An example of the type of results obtained with respect to oxygen absorption by iron droplets falling for various times through air is shown in Figure

8(38). Results are presented for droplets of pure iron and for iron with different initial sulphur concentrations. Results are also included for iron droplets containing approximately 0.1 pct aluminium and 0.1 pct titanium. The solid line corresponds to the predicted rate of oxidation based on diffusion control within the gas phase. It is evident from this graph that the observed rate of oxidation is in good agreement with the predicted relationship. In addition, the oxidation rate is unaffected by concentration changes in the surface active element sulphur, or by the presence of deoxidizers such as aluminum or titanium. It is worth noting that when the molten steel droplet was in contact with air for only 0.25 sec., the oxygen pick-up was approximately 700 ppm or 0.07 wt pct. It is not at all surprising therefore, that steel, even aluminum-killed steel, which has undergone reoxidation, can exhibit oxygen levels in localized regions well in excess of 100 ppm. These high oxygen levels cause the formation of reoxidation inclusions which are then responsible for a serious deterioration in product quality.

In the case of nitrogen absorption by falling droplets, Figure 9, the rates observed are very much slower than those for the absorption of oxygen. In addition, nitrogen pick-up is strongly influenced by the concentration in the steel of the surface active element sulphur(39). As the steel sulphur content decreases, the nitrogen absorption rate increases. This same behaviour is observed for the effect of oxygen on nitrogen pick-up. This has particular significance with respect to those grades of aluminum-killed steels which are subsequently desulphurized by ladle additions of calcium, rare earth elements or other sulphide shape control agents. In steels which have been strongly deoxidized and strongly desulphurized, final nitrogen concentrations have been reported which are in excess of 150 ppm. Concentrations of this magnitude can adversely influence mechanical properties. This problem can be minimized by either eliminating air entrainment or working at the higher end of the sulphur specification in order to inhibit nitrogen absorption.

In the case of hydrogen absorption, both laboratory and plant data indicate that higher hydrogen levels are observed when steels are treated in the ladle to produce low residual concentrations

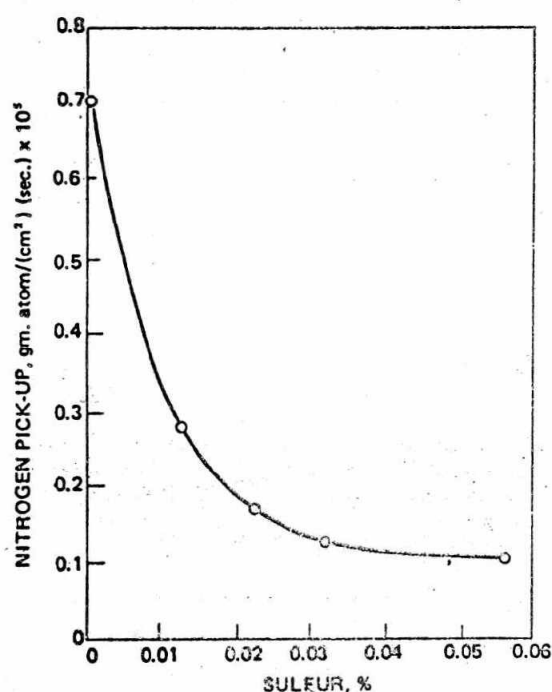
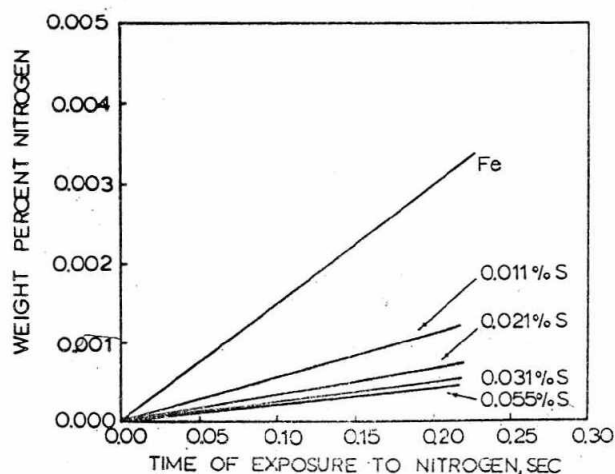


Fig. 9 Influence of sulphur on nitrogen absorption by molten steel droplets falling through pure nitrogen.

of oxygen and sulphur. These very clean steels of low inclusion content, particularly when produced in the form of thick plate, also appear to be more susceptible to hydrogen damage.

SOME PRACTICAL CONSIDERATIONS PERTAINING TO METAL TRANSFER OPERATIONS

Several important changes take place in the characteristics of molten steel as it plunges from the furnace into the ladle. For example, there is generally a large temperature drop which is in-

fluenced by the amount of superheat in the steel and the extent to which the ladle is preheated. An approximate value for the temperature decrease would be about 50°C.

Chemical reactions will occur between the tap stream and the atmosphere, and more importantly, between air entrained by the tap stream and molten steel in the ladle. This will result in absorption of oxygen and nitrogen by the molten steel, and in the case of moist air, of hydrogen.

Deoxidizers and alloy additions are frequently made to the ladle during the tapping operation. The extent of alloy recovery in the metal is strongly affected by the time of the addition to the ladle and the opportunity available for the alloy to dissolve in the steel before it is driven to the metal surface by the turbulence associated with the plunging furnace stream. Unfortunately, considerable alloy loss occurs in many operations due to chemical action of alloys which have floated to the surface and come in direct contact with the atmosphere. This same mechanism of course also accounts for considerable loss when alloy additions are made to the ingot mould.

Stubbles and Aurini(40) have investigated factors which influence the recovery of manganese from ladle additions in both open hearth and B.O.F. shops and concluded that manganese losses are due mainly to reaction with entrained air. Data were examined for both low manganese steels (<0.45%) and high manganese steels (>0.9%). The percentage loss in the former, (25%), was much greater than that in the latter, (11%). However, in the latter case, the ferromanganese addition is much larger and the actual loss due to air oxidation is essentially the same as that with low manganese steels, i.e. about 2.4 lbs/ton. Recoveries will vary from one plant to another and will be influenced by ladle additions of aluminium, which act sacrificially to protect manganese from oxidation loss due to entrained air. The same workers(40) also studied carbon loss between furnace and ladle due to air oxidation and found that it was almost linear with tap carbon in the range 0.03 to 0.2%. Within this range carbon losses varied linearly between zero and 0.06%. There was some indication from results at higher carbon levels, that the carbon loss during tapping reached a maximum of about 0.05 to 0.06%.

Oxidation of molten steel during tapping operations will also contribute to the formation of an iron oxide-rich ladle slag. This will certainly have an adverse influence on ladle refractory life. In addition, as the ladle is emptied during the casting operation, the interaction between the slag and refractory will produce an iron oxide-rich glaze, which is in effect, an oxygen reservoir. When the next heat of steel is tapped into the ladle, and deoxidized, the oxygen potential of the glaze is greater than that of the steel, and consequently oxygen stored from the previous heat is progressively transferred back into the steel again. This hereditary effect of reoxidation occurring during one heat and then exerting an influence on the subsequent heat is often overlooked when investigating the reason why a particular heat failed to meet specification. This type of behaviour is also important with respect to ladle desulphurization treatments. Again slags containing sulphur can react with ladle refractories during the casting operation to form a glaze in which sulphur is stored and then subsequently released when the next ladle of steel is being desulphurized.

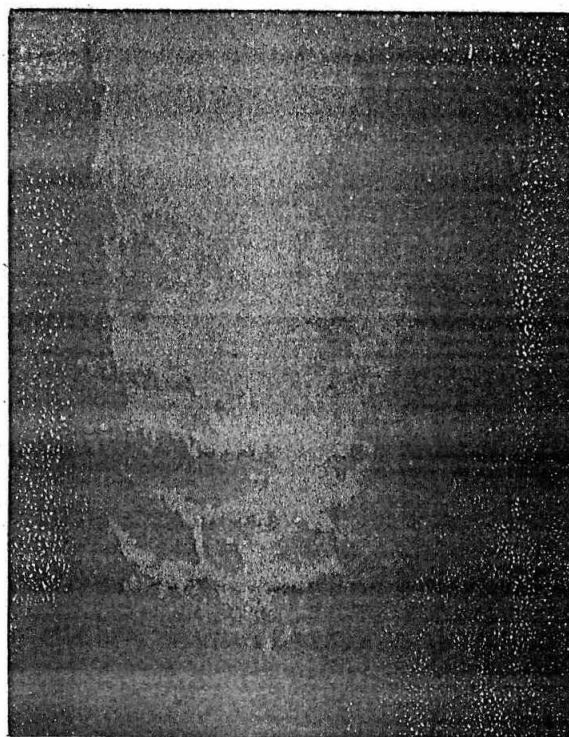


Fig.10 Molten steel plunging from the ladle into an ingot mould.

When elements such as titanium, zirconium, calcium, magnesium or the rare earth elements are added to the ladle in order to obtain shape control of sulphide inclusions, the anticipated benefits in mechanical properties may be lost due to reoxidation reactions and sulphur reversion to the molten steel with subsequent formation of plastic manganese sulphides. The following reactions are typical of this behaviour, where the underlined symbols represent elements dissolved in molten steel:-



The oxygen required for the above reactions may come from the glaze formed in part by atmospheric reoxidation of the previous heat, or it may be supplied from air entrained by the ladle stream during casting, Figure 10. The thermodynamic aspects pertaining to reoxidation and sulphide shape control have been discussed in more detail elsewhere(41).

As mentioned previously in the literature review, Farrell et al (21) have discussed in detail the formation of

inclusions by reoxidation during casting. They have shown very clearly that in the case of aluminum-killed steel containing manganese and silicon, the first reoxidation products formed consist of large alumina galaxies. With continuing reoxidation, the inclusions formed contain decreasing amounts of aluminum and increasing amounts of manganese and silicon. The presence of silicate inclusions in aluminum-killed steel is strong evidence that reoxidation has occurred. An example of a multiphase inclusion formed by reoxidation of aluminum-killed steel is shown in Figure 11. This is taken from the work of Luyckx et al (42) who have described the conditions affecting the formation of spinel inclusions in steel during deoxidation and casting. In Figure 11 the sequential formation of alumina, followed by manganese aluminate or galaxite, and finally manganese aluminosilicate is typical of inclusions formed by a reoxidation mechanism. The thermodynamic criteria which govern the sequential reactions occurring during deoxidation and reoxidation have been investigated by Iyengar and Philbrook(43), and Kim and McLean(44). A multiphase inclusion formed by reoxidation of a levitated droplet of 430 stainless steel is shown in Figure 12(12). It consists

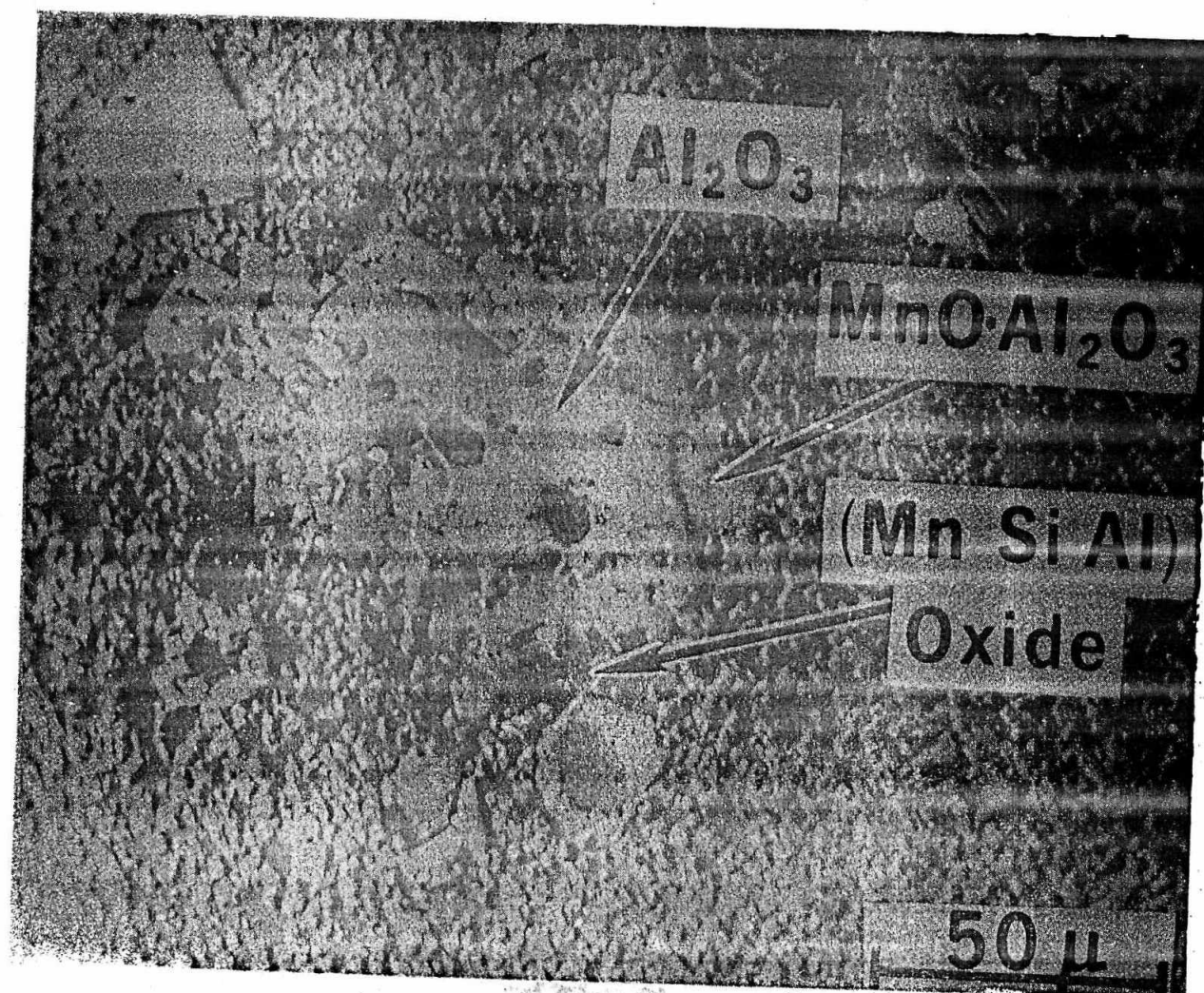


Fig.11 Sequential formation of alumina, galaxite and manganese aluminosilicate by reoxidation of aluminium killed steel. The surface relief effect is due to the variation in hardness of the different oxides.

of manganese chromite spinel with some vanadium in solid solution, imbedded in a matrix of manganese-chromium silicate. Graham et al(45) have reported that the formation of these defects during the continuous casting of stainless steel slabs can be prevented by the use of submerged nozzles and synthetic mould slags. These same defects will also occur during normal ingot casting of stainless grades, unless an appropriate system can be devised to effectively eliminate air entrainment during the transfer of steel from the ladle to the ingot mould. It is easier to achieve this objective when ingots are bottom poured.

The oxidation rate of liquid iron and the formation of oxide films have been measured by Pehlke and Radzilowski (46). These workers concluded that the presence of alloying elements in dilute concentrations typical of those found in killed steel are unlikely to form effective oxide films which might prevent further reoxidation during casting operations. Emphasis was placed on the fact that when oxygen is present in a gas mixture, and diffusion in the gas phase is the rate controlling step, reoxidation effects will be decreased by minimizing stream break-up and air entrainment and incorporating within the casting system an appropriate gas shroud.

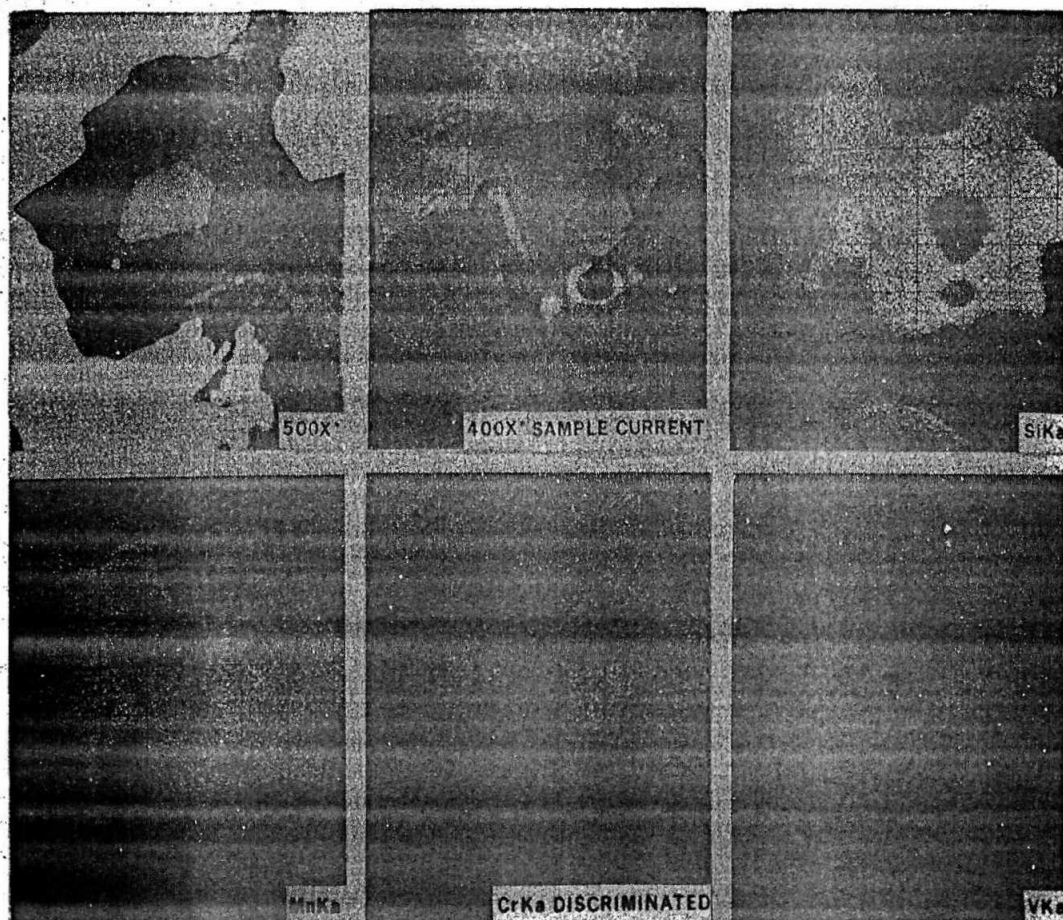


Fig. 12 Manganese chromite spinel formed by reoxidation of molten droplets of 430 stainless steel. Vanadium is present in solid solution within the spinel crystal.

ing facility which would decrease the oxygen concentration in the gas phase and consequently diminish reoxidation effects.

While this discussion has emphasized reoxidation reactions resulting from air entrainment, mention should be made again of some of the factors influencing the absorption of nitrogen. As discussed in the previous section, the rate of nitrogen pick-up is very much less than that of oxygen. However, in aluminum-killed steel which has also been desulphurized, for example, by the addition of sulphide shape control elements, nitrogen absorption can be increased by a factor of about five(39) due to almost complete elimination of the surface active solutes, oxygen and sulphur. A good example of the influence of the oxygen content of steel on the pick-up of nitrogen is given in a paper

by Koros et al(47). Based on results from an extensive plant study, these workers reported that the nitrogen content of steel killed in the ladle with aluminum, increased by 15-20 ppm during the tapping operation and a further 15-20 ppm during ingot casting. On the other hand, in the case of rimmed steel, there was essentially no change in the nitrogen content between the furnace and the mould due to the inhibiting effect of the higher oxygen concentration on the nitrogen absorption process.

It is probably worth stressing again at this point that oxidation of the casting stream is a serious matter in ingot teeming as well as in continuous casting, although it has received less publicity. The average height of fall is in general considerably greater than those used in continuous casting, giving more scope for disintegration,

and the effects of restricted penetration noted earlier will be more applicable to ingot moulds than to tundishes. A major advantage in the case of ingots is the appreciably longer solidification times which allow a greater degree of inclusion removal by flotation in the mould. Even so, Lunner(48,49) found that the frequency of large inclusions in austenitic stainless steel made in electric arc furnaces was highest in the ingot mould, while Köhig et al(50) consider that of the inclusions in an ingot, 30-36%, depending on the type of steel, are caused by reoxidation during teeming, a range which agrees well with the results of Hoffmann et al mentioned earlier. In a very thorough series of studies, Pickering et al(51-53) also concluded that reoxidation was a very significant source of inclusions in ingots. Oxidation of the upper surface producing scum which can be drawn down into the body of the ingot by convection currents within the solidifying mass is also a serious source of large, harmful inclusions, particularly in rimming steels(54). This has also been observed by other workers(55-57), and the use of protective fluxes is not a complete answer either since these also can become entrapped, giving rise to large exogenous inclusions. Protection of both stream and surface seems to be the only real answer. For example, Tamamoto et al(17) have used a completely enclosed casting system for ingot production and obtained markedly reduced nitrogen pick-up, a reduction of the average oxygen content in the mould from 43 to 29 ppm and a decrease in defects found by the ultrasonic test from 3.2% to 0.5%.

There is normally ample time for corrective measures to be taken in the ladle to deal with the products of reoxidation occurring during tapping of steel from the furnace, and in fact in many cases the steel is at its cleanest at the end of the holding period in the ladle. The point which does not appear to have been appreciated sufficiently is that there is very little point in applying expensive vacuum treatment or secondary steelmaking processes to steel if this is later to be allowed to suffer reoxidation during casting, since the benefits in terms of cleanliness can be almost totally lost. Even argon flushing in the ladle may not be worthwhile if the steel is subsequently reoxidised. Thus, improvement and protection of the ingot teeming stream is an absolutely vital part of any serious efforts to

improve steel cleanliness and retain the advantages conferred by recent advances in the field of steel treatment prior to casting.

Control and improvement of stream stability can be achieved in tundishes or pouring boxes by the use of castellated nozzles(30) which greatly narrow the range of turbulence encountered, lower the average turbulence by reducing the incidence of rough streams, and impose a minimum turbulence level. For the case of sliding gate nozzles, extension tips(36) can be used to dissipate the lateral velocity components of the stream caused by throttling, with the same effects as above. Alternatively, some form of rotary nozzle with several nozzles of different diameter can be employed so that by selection of one or more nozzles the volume flow rate of the stream can be maintained approximately constant as the ferrostatic head in the ladle falls, without having to resort to throttling. All these methods of stream compaction reduce the extent of disintegration and hence the surface area of steel exposed to contact with air.

In the manufacture of clean steel, stream protection will almost certainly be required as well as stream compaction. Protection is by the interpolation of some shield between the molten steel and the atmosphere where the shield can be either solid as in physical shielding or gaseous as in inert gas shrouding, or both. Each has advantages and disadvantages, each demands a considerable amount of care in its application to ensure success, and each will be made much easier, more effective and less expensive by efficient stream compaction. In the case of argon shrouding, it would seem that perhaps more attention should be paid to the impact area on the pool and less to the point of emergence from the ladle(30). This is in line with the mechanisms of entrainment outlined in this paper, and also has the advantage of providing greater protection from oxidation of the turbulent upper surface of the receiving pool which can, as has been noted, cause a significant proportion of the total oxidation. The obvious drawback to having the gas manifold immediately above the mould is its susceptibility to damage by flaring streams and here again efficient stream compaction will play an important part. Thus, it seems clear that protection and compaction must be employed, together to complement and supplement one another.

in order to obtain the maximum advantage in terms of cleaner, higher quality steel.

CONCLUDING REMARKS

At this point in the history of steel-making development, it must be stated emphatically that while blast furnace practice, steelmaking process and rolling and finishing operations are becoming increasingly instrumented and brought under control, the changes in composition which occur when steel plunges from the furnace into the ladle, and from the ladle into the ingot mould, are largely out of control, Figure 10. There is an immeasurable and highly variable quantity of air carried into the molten steel. This contributes to both poor and erratic alloy recovery in the ladle and also in individual ingot moulds; oxygen, nitrogen and hydrogen absorption; the formation and entrapment of mould scum in the solidifying ingot; the formation of splash defects and massive non-metallic inclusions; and finally deterioration in physical properties due to increased concentrations of nitrogen and hydrogen.

When molten steel is contaminated by the entrainment of copious quantities of air in continuously varying amounts, good blast furnace practice is nullified, excellent refining operations are ruined, metallurgical benefits from careful deoxidation and desulphurization practices are destroyed, and all of the attributes of controlled rolling and careful heat treatments will not be enough to eradicate the damage.

If steel quality is important, if yield improvement is critical, if energy units associated with each ton of steel shipped is of concern, then it is imperative that the transfer of molten steel between furnace and ladle, and ladle and mould must be brought under control. This could involve the application of known technology or the implementation of novel developments in the following areas:-

Improved furnace tap-hole systems.

Pouring boxes or tundishes to obtain compact streams.

Appropriate nozzle configurations, slide gates and extension tips.

Protective gas shrouding and/or physical shielding of the stream.

Mould powders with optimized physical and chemical characteristics.

There is substantial evidence now available in the literature to establish with certainty the benefits claimed with respect to alloy recoveries, product quality, metal yield and energy efficiency, when appropriate measures are taken to improve pouring stream characteristics and eliminate air entrainment. While the task is not easy, the objectives are well defined, and the benefits are sure.

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