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Interfacial phenomena in high temperature processes

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Interfacial phenomena can have a major effect on high temperature processes; these are reviewed and examples given. Interfacial phenomena have been divided into the following categories (i) Marangoni flows, (ii) Wetting, (iii) Emulsions, (iv) Foams, and (v) Jets and surface waves. Examples and case histories are given for each of the above categories.

1. Introduction

Interfacial phenomena occur in many high temperature processes such as steelmaking, welding etc. This paper seeks to review some cases in which the process control or the product quality is affected by interfacial phenomena. There is a wide range of interfacial phenomena involved in high temperature processes; for convenience these have been divided into the following five categories:

- Marangoni flows
- Wettability, contact angle
- Formation of emulsions
- Formation of foams
- Jets and surface waves

Some high temperature processes make use of a slag or flux, their purpose is usually to protect the metal from oxidation and to remove impurities from the metal (e.g., S or non-metallic inclusions). In this paper *surface tension* γ, refers to a liquid (metal or slag) with a gaseous phase and *interfacial tension* γ_{ms} to two liquid phases (e.g., metal and slag). The interfacial tension is given by

$$\gamma_{\mathrm{ms}} = \gamma_{\mathrm{m}} + \gamma_{\mathrm{s}} - \phi(\gamma_{\mathrm{m}}\gamma_{\mathrm{s}})^{0.5} \quad (1)$$

where γ_{m} and γ_{s} are the surface tensions of the metal and slag, respectively and ϕ is the interaction coefficient which is given by the ratio ($W_{\mathrm{A}}^{\mathrm{ms}}/W_{\mathrm{C}}^{\mathrm{m}}W_{\mathrm{C}}^{\mathrm{s}}$) where W_{A} and W_{C} are the work of adhesion and cohesion, respectively.

One factor which distinguishes surface and interfacial properties from bulk properties (e.g., viscosity) is that small concentrations of *surface active* components (e.g. S, O in metals, CaF_2 in slags) can cause a dramatic change in both the surface (or interfacial) tension and its temperature dependency ($d\gamma/dT$). It can be clearly seen from Fig. 1 that 40 ppm S has the effect of reducing the surface tension of Fe by 25% and changing the temperature dependency from negative to positive. This could lead to a change in direction of the flow in a process.

Surface activity in metals can be ranked in the hierarchy:

1. Group VI elements > Group V > Group IV
2. Within any group the heavier elements are more surface active than lighter elements e.g. Te > Se > S ≈ O.

It should also be noted that it is the *soluble* $\underline{\mathrm{O}}$ and not the *combined* O (e.g., oxides) which affects surface tension. Mills and Keene [1] pointed out that certain elements such as Ca, Al and Mg react strongly with O and reduce the *soluble* O (denoted $\underline{\mathrm{O}}$) to very low levels (e.g., a few ppm) and form stable metallic oxides (Fig. 2). The *total* O is not a measure of the *soluble* O in such cases. Thus very low concentrations of these reactive elements (e.g., Ca) can have a marked effect on the process because of their effect on the surface active elements present. Thus for the FeAlO system in Fig. 2a, ca.10^{-1}% Al will lower the soluble O to <5 ppm.

It should be noted that modern metal processes achieve high refining rates (i.e. productivity) by creating emulsions or foams which have a huge (surface area/mass) ratio. It has been noted [2, 3] high mass transfer rates between metal and slag lead to a dramatic decrease in the interfacial tension. Under these conditions any small disturbance would lead to an emulsion of metal in slag and/or slag in the metal. Recently, Ferrari *et al.* [2] noted a similar, sharp decrease in γ_{ms} associated with mass fluxes of surfactants in organic systems but found that the sharp decrease was absent when equal volumes of the two phases were used. Consequently, this poses the question as to whether there is low interfacial tension in the process where slag/metal volumes are ca.1 (cf. >5 in experiments).

2. Marangoni flows

There are many cases where Marangoni flows have a decisive effect on high temperature processes. Marangoni

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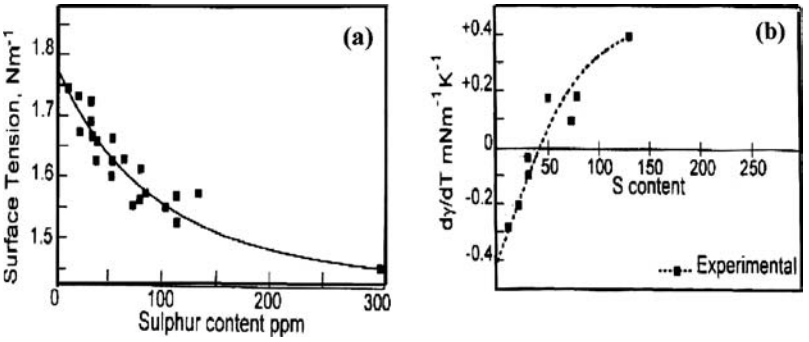

Figure 1 Effect of S content on (a) surface tension (γ) of Fe and (b) temperature dependence of surface tension ($\mathrm{d}\gamma/\mathrm{d}T$) of austenitic stainless steels [1].

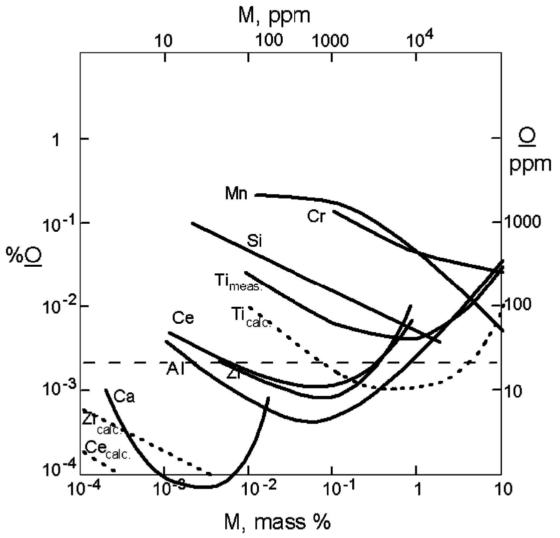

Figure 2 The effect of different alloying additions (M) on the soluble O ($\underline{O}$%) content in the Fe-M-O system at 1873 K [1].

flow always occurs from a region of low surface tension to a region of high surface tension. Surface tension gradients can arise from:

(i) temperature differences along the surface which cause *thermo-capillary* flow;
(ii) composition differences along the surface which cause *diffuso-capillary* flow;
(iii) electrical potential differences along the surface which cause *electro-capillary* flow.

It is generally accepted that no Marangoni flows occur when the liquid with a surface tension gradient is in contact with a solid interface. However Marangoni flow can occur if there is a gas bubble (or liquid drop) present which allows a surface tension gradient to be established at different locations on the free surface. A flow of liquid around the bubble towards the solid surface will result in a pressure increase which causes the bubble to move away from the interface (Fig. 3a). Alternatively, if the flow around the bubble is away from the solid interface the build-up in pressure will be on the far side of the bubble and the bubble will stay close to the interface (Fig. 3b).

Marangoni flow is usually associated with thin layers of liquid (<5 mm) since buoyancy tends to become more dominant in deeper layers of liquid.

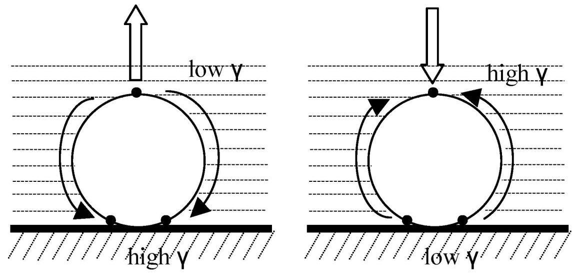

Figure 3 Schematic diagram showing the effect of Marangoni flow on the bubble movement. Bubble (a) moves away from the interface and (b) stays close to the interface.

2.1. Thermocapillary convection

There are many cases of thermo-capillary convection having a decisive influence on product quality.

2.1.1. Variable weld penetration

Gas Tungsten Arc (GTA) welding (sometimes known as TIG welding) is frequently used in applications (e.g., heat exchangers) involving a large number of repetitive welds. Optimum welding parameters are established before the welding programme is initiated. However, it has been found (Fig. 4) that certain batches of steel produced welds with much lower weld penetration than the norm, despite fully meeting the material specifications. Fig. 4b shows a deep penetration weld and Fig. 4a the shallow weld obtained when another cast of steel was used. It was found [1] that deep welds were associated with low values of the surface tension and positive ($\mathrm{d}\gamma/\mathrm{d}T$) values and shallow welds with higher values of surface tension and negative values of ($\mathrm{d}\gamma/\mathrm{d}T$).

The fluid flow in the weld pool contains contributions from (1) buoyancy forces (2) Electro-magnetic (Lorenz) forces (3) aerodynamic drag forces resulting

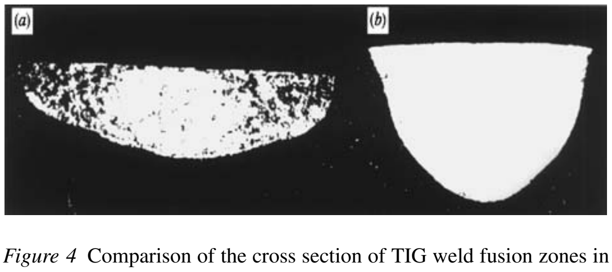

Figure 4 Comparison of the cross section of TIG weld fusion zones in (a) shallow- and (b) deep-welds.

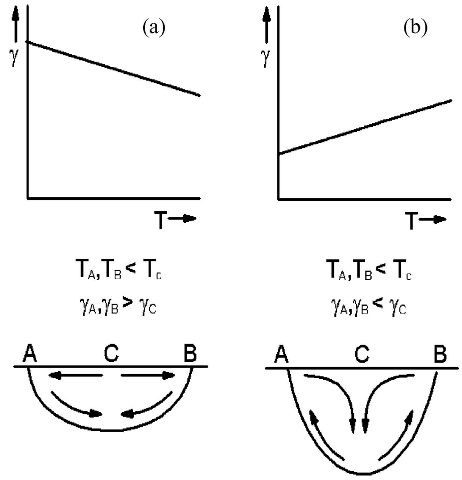

Figure 5 Schematic diagrams illustrating the fluid flow in weld pool for (a) low S and (b) high S steels, respectively [1].

from the flow of Argon gas over the surface of the weld and (4) thermo-capillary forces. It has been shown [1, 4] that under normal welding conditions the fluid flow is dominated by thermo-capillary forces. The S concentration in the steel is the key factor (Fig. 1b) since the temperature dependency $(\mathrm{d}\gamma/\mathrm{d}T)$ changes over from negative to positive around 40 ppm S at 1650°C (and at lower S at lower temperatures.) It can be seen from Fig. 5b that in a high S weld pool, the highest surface tension is in the centre of the weld pool which results in a radially-inward thermo-capillary flow which takes hot liquid down to the bottom of the pool and thus melt-back gives a deep pool. At low S contents the highest surface occurs at the periphery of the pool and this results in a radially-outward flow and melt-back occurs at the edge of the pool giving a shallow weld.

In the electron beam button melting (EBBM) the number and size of inclusions in an alloy can be determined by collecting them as a raft on the metal button formed. Raft formation has been shown to be dependent upon the S and O contents of the metal in a similar way to variable weld penetration [5].

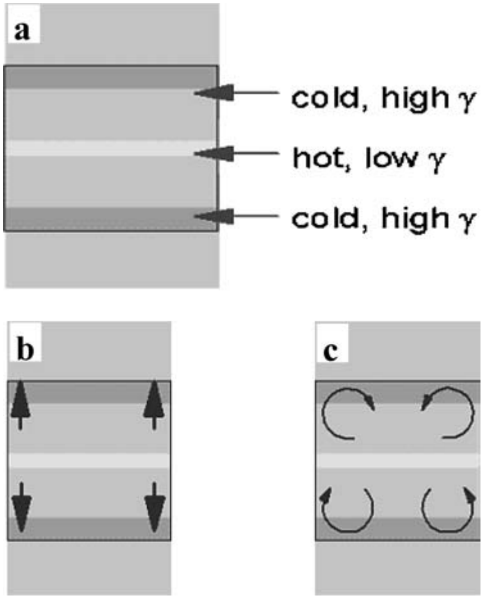

Figure 6 Schematic diagram demonstrating how thermocapillary forces lead to the formation of vortices [6].

2.1.2. Floating zone and Czochralski methods for refining silicon

The floating zone method (Fig. 6) is used to refine impure Si and other semiconductor materials. In this process the impure Si is heated in a furnace and a seed of pure Si is brought in contact with it. Since most impurities decrease the liquidus temperature, the pure material will solidify first leaving the impurities in the liquid. Thus the molten silicon tends to solidify on the pure Si seed leaving the impurities behind in the molten pool; as the impure Si is gradually passed through the furnace the impurity concentrations increase in the liquid. The products are therefore a bar of pure silicon and a region at the end of the bar with a high concentration of impurities. Obviously if there is vigorous fluid flow in the molten metal the impurities will be churned up into the metal. Thus convection has to be minimized. Experiments were carried out in microgravity to minimize the effects of buoyancy-driven-flows but it was discovered that there was little improvement because of the thermo-capillary convection. It can be seen from Fig. 6 that the temperature at the centre of the molten pool is higher than those at the solid/liquid interfaces. The surface tension decreases with temperature so the surface tension is higher at the liquid/solid interface, thus flow will occur, along the surfaces from the centre to the edges (Fig. 6b). This results in the formation of four vortices, as shown, which produces fluid motion in the molten pool. However, the transfer of hot liquid from the centre to the edge reduces the temperature gradient and thereby causes a reduction in thermo-capillary flow [6]. Consequently, this gives rises to oscillating flow and vortex formation. The formation of an oxide skin on the surface of the silicon has been found to “kill-off” the Marangoni flow [6]. The Czochralski method of growing single crystals has also been shown to be affected by thermo-capillary convection [7].

2.1.3. Corrosion of turbine blades

This is an example of how relatively low levels of contamination occurring in service affect performance. Turbine blades are protected by an oxide layer (Al_2O_3 or Cr_2O_3) covering the surface. The fuel contains S and when operating at high temperatures forms a thin layer of molten sulphates (e.g., cobalt and sodium sulphates) on the blade and this dissolves the oxide layer especially in the high temperature regions. Since $(\mathrm{d}\gamma/\mathrm{d}T)$ is negative thermo-capillary convection occurs along the free surface i.e. from the hot to cold region and then returns in a circulatory flow through layers close to the blade. The liquid becomes saturated with Al_2O_3 in the high temperature region. When it reaches the cold region, the Al_2O_3 becomes super-saturated and precipitates. The cold liquid returns by the circulatory flow to the hot region and dissolves more Al_2O_3 and the process is repeated. Thus there is a gradual and eventually catastrophic, dissolution of the protective oxide in the hotter region of the blade and precipitation of the oxide in the cooler regions [8].

2.2. Diffuso-capillary convection

2.2.1. Refractory erosion

The global cost of replacement of refractories is about 2 billion US $ per annum. Frequently, erosion of refractories occurs around the interface (metal/slag or gas/slag interface) which is known as "slag line" attack. Marangoni convection [9] is responsible especially when the flow velocities are low. Mukai [9] has shown that dissolution of refractory causes a local change in composition (and surface tension) compared with the bulk and the resulting diffuso-capillary flow sets up a vortex flow in the slag at the interface which results in the gradual erosion of the refractory at the interface.

2.2.2. Hot cracking

At later stages of the solidification of metal, dendrites hinder the movement of the liquid and *hot tearing* can occur when the rate of feeding of liquid metal is lower than the rate of shrinkage. *Hot cracking* of welds occurs during solidification when low-melting liquid allows boundaries to separate when subjected to shrinkage stresses. Holt *et al.* [10] proposed that the direction of Marangoni flow affected the rate of feeding and hence hot cracking occurred by:

(i) diffuso-capillary flow when the S content of the liquid metal was higher than that at the dendrite tip.

(ii) thermo-capillary flow in high S melts with a positive ($d\gamma/dT$).

As mentioned above a solid surface would tend to kill off the Marangoni flows and the presence of a bubble is needed for this explanation to be valid. However, the solubility of gases is much lower in solids than in the liquid and bubble formation is to be expected especially towards the end of solidification.

2.2.3. Immersion of drops in a pool

In Gas-metal arc (GMA) welding, filler metal drops are added to the weld pool. In some cases the metal drop flows over the pool surface and in other cases the drop is immersed in the pool. It has been shown [11] that there are four forces affecting the fluid motion after the impact of the drop (i) a stirring force due to the momentum of the drop; (ii) a buoyancy force related to the density difference between the drop and the pool; (iii) a 'curvature' force related to the surface tension normal to the surface; and (iv) the Marangoni force related to the difference in surface tension of the drop and pool. Takasu and Toguri [11] showed that when (a) $\gamma_{drop} > \gamma_{pool}$ the drop penetrated into the pool and (b) $\gamma_{drop} < \gamma_{pool}$ the drop will spread out over the surface. Thus immersion will occur when the S content of the pool is greater than that of the drop.

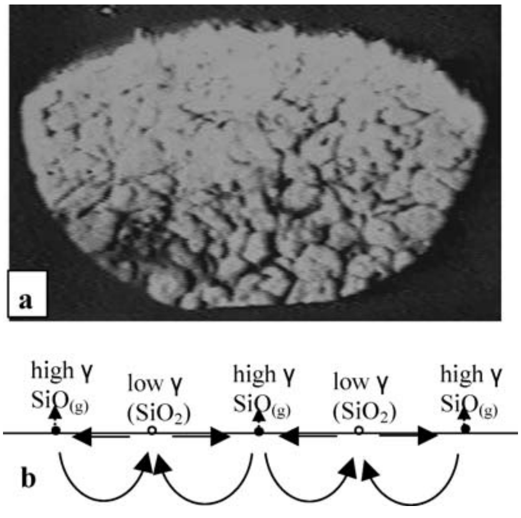

Figure 7 (a) Photograph showing Benard cells formed during vacuum degassing and (b) schematic diagram outlining the proposed mechanism for the formation of Benard cells [12].

2.2.4. Benard cells in vacuum degassing

Vacuum degassing is used to decrease the oxygen content of metals. In this process a foam is formed by the slag covering the steel. Bain *et al.* [12] photographed the process and as can be seen from Fig. 7 Benard cells are formed. The probable explanation is that when a vacuum is applied SiO(g) is formed by the SiO_2 in the slag. Since SiO_2 reduces the surface tension, there will be a local increase in surface tension at the surface site where vaporisation occurred and this results in the formation of Benard cells (Fig. 7).

2.3. Electro-capillary effects

Aluminium is produced by an electrolytic (Hall-Heroult) process using graphite electrodes and a molten cryolite ($3NaF{\cdot}AlF_3$) electrolyte and 3–8% Al_2O_3 (the source of the aluminium). The cathodic reaction is

$$\text{Cathode} : Al^{3+} + 3e^{-} \rightleftharpoons Al \qquad (2)$$

However, the efficiency of the process is reduced by the back reaction in regions where the current density is small. This results in the formation of Al^{3+} (i.e. AlF_3). Takasu and Toguri [11] showed regions of low current density aided this back reaction. When a positive potential was applied to the crucible walls the interfacial tension was seen to increase and TiB_2 marker particles were seen to move from the centre to the walls. It should be noted that (i) the high current density region lies in the centre of the crucible and (ii) $\gamma_{AlF3} > \gamma_{NaF}$ and increasing AlF_3 increases the interfacial tension and (iii) the back-reaction occurred in those regions of low current density. Thus when a positive potential (central electrode = anode and crucible = cathode) was applied the back reaction occurred preferentially in the outer region of the crucible and AlF_3 concentration was lower at centre than in the outer region and thus $\gamma_{wall} > \gamma_{centre}$ and the particle moved towards the crucible wall. In contrast, when a negative potential was applied to the crucible (central electrode is cathode)

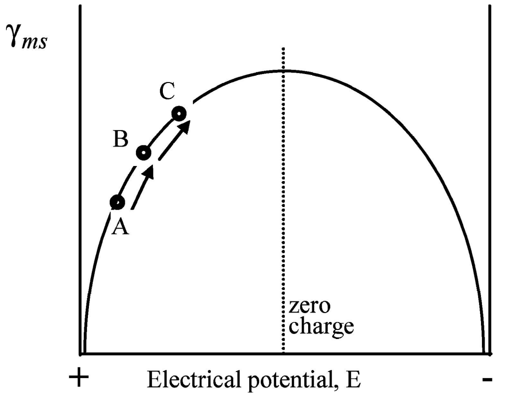

Figure 8 Electro-capillary curve, where B = overall potential and A and C are local potentials.

there was an increased concentration of AlF_3 in the high-current-density region (centre) and so the movement of the particles was radially inwards.

2.4. Interfacial turbulence

Interfacial turbulence has been observed to occur in metal/aqueous salt, metal/molten salt and metal/slag systems. It leads to enhanced mass transfer rates even in stirred melts. Slag/metal reactions are ionic and often involve combined reactions such as that shown in Equation 3. Interfacial turbulence has been reported to increase the rates of reactions in metal/slag systems (13, 14). It has been proposed [15] that interfacial turbulence is caused by *local* differences in interfacial tension along the interface caused by local differences in charge transfer rates or local concentration gradients at the interface resulting from convection. It can be seen from the electro-capillary curve shown in Fig. 8 that if the local potential (at A) for the overall reaction is more positive than the overall potential (at B) for the process, the flow will flow from A to B and if the local potential (at C) is more negative than the overall potential (at B) the flow will be from B to C. Recent support for the electro-capillary nature of interfacial turbulence can be derived from the observations of the transfer of surfactants in organic/water systems which showed that interfacial turbulence occurred when using ionic surfactants but did not occur with organic surfactants [16].

$$S_{\text{metal}} + O^{2-}_{\text{slag}} = O_{\text{metal}} + S^{2-}_{\text{slag}} \qquad (3)$$

3. Wettability, contact angle (θ)

Wetting phenomena are important in the following applications:

1. where good adhesion is needed between two phases, e.g., Metal/matrix composite,
2. in the removal of non-metallic inclusions, e.g., Al_2O_3 from steel.

Reactive wetting is very common in high temperature situations and so when good wetting is a requirement, the common way of accomplishing wetting is to add a reactive component to phase 1 which reacts with phase 2 and brings about reactive wetting.

3.1. Ceramic-metal joining

The brazing of a metal to a ceramic (say Si_3N_4) is achieved using a braze based on Sn or Cu/Ag alloy. However, the contact angle between Si_3N_4 and the braze is $> 140°$ i.e. nonwetting. In order to provide strong wetting conditions ($\theta = 20°$) it is common practice to add 1.5% Ti to the braze since this will react with the Si_3N_4 to produce silicides. This causes a decrease in contact angle and is accompanied by increases in both the work of adhesion (W_A) and metal-ceramic bond strength.

In some application it is necessary to obtain high heat transfer rates (e.g., strip casting steels, cooling electronic devices). The heat transfer coefficient can be an important factor and this parameter increases as the adhesion between the device and cooling system improves. In some cases the adhesion can be influenced by thermocapillary forces. Monti *et al.* [17] found that when a liquid drop touched a substrate it wetted and the heat transfer coefficient was high but when the drop was heated the heat transfer coefficient was much lower. The temperature of the gas surrounding the drop is lowest at the substrate (hence high γ value) and this induces a thermocapillary flow of gas around the drop thereby lowering both the adhesion of the drop to the substrate and the heat transfer coefficient (similar to the movement shown in Fig. 3a).

In some cases there is a requirement for poor adhesion between the two phases. During the continuous casting of steel inclusions adhere to the Al_2O_3/C internal wall of the tube (SEN) delivering steel into the mould. These inclusions build-up (SEN clogging) and can cause asymmetric metal flows with disastrous consequences. Several studies have tried to make the wall surface non-wetting, and thereby reduce adhesion. The removal of carbon from the surface layer has been found beneficial in reducing clogging as it results in an increase in the contact angle. Furthermore, Mukai *et al.* [18] have found that it is possible to create a gas curtain along a refractory wall for non-wetting conditions (of metal/refractory), this could be beneficial in reducing SEN clogging.

3.2. Removal of inclusions

Inclusions such as Al_2O_3 cause a marked decrease in the mechanical strength and hence the performance of high temperature alloys. Considerable effort is focused on the removal of inclusions. Two of the common methods of inclusion removal rely on (i) density difference (flotation) and (ii) attachment to bubbles. Both of these rely heavily on wetting phenomena.

In flotation it is necessary to move the inclusion through the metal to the interface and then move to gas or slag phase. This involves separation of metal (M) from inclusion (I) and creating two new surfaces: metal/gas or inclusion/gas for a gas/metal interface (and metal/slag and inclusion/slag for a metal/slag

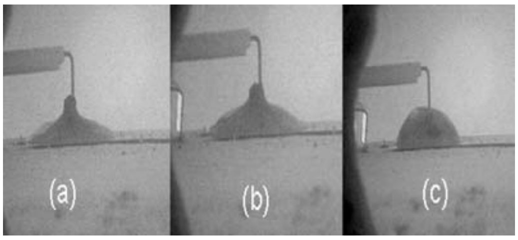

Figure 9 Variation in slag droplet geometry as a function of Electric Potential after 2 minutes at (a) 0 v, (b) –1 v, (c) –2 v [20].

interface). Thus the work of adhesion (W_A) must be satisfactory for good inclusion removal where θ is contact angle.

$$\text{Gas/metalinterface} \quad W_A = \gamma_{MG} + \gamma_{IG} - \gamma_{IM} = \gamma_{MG}(1 + \cos\theta) \quad (4)$$

In the flotation of inclusions on gas bubbles, it has been shown [19] that the flotation coefficient (Δ) should have both a positive and high value.

$$\text{Gas/metalinterface} \quad \Delta = \gamma_{IM} + \gamma_{MG} - \gamma_{IG} = \gamma_{MG}(1 - \cos\theta) \quad (5)$$

3.3. Electro-wetting

When an electrical potential is applied between a drop of slag and a metal plaque (Fig. 15), the contact angle was found to be at a maximum at -2 volt [20]. Young's equation can be written as

$$\gamma_{LG} \cos\theta = (\gamma_{SG} - \gamma_{SL}) \quad (6)$$

where G = gas, L = liquid (i.e. slag) and S = solid (i.e. metal). A double layer of ions exists at the solid/liquid interface and this is affected by the applied potential. Thus when an electrical potential of -1 volt is applied it increases γ_{SL} but has little effect on γ_{LG} and γ_{SG}. Thus the term ($\gamma_{SG} - \gamma_{SL}$) decreases and consequently, $\cos\theta$ decreases and causes an increase in θ.

Electrowetting has been used as the working principle underlying the design of integrated micro-fluidic systems for miniaturised components e.g. fuel injectors, heat sinks in electronic devices [22].

3.4. Slag penetration into refractory

The height (h) of vertical penetration of slag up a capillary is derived from the Hagen-Poisseulle relationship and is given by:

$$h = 2\gamma \cos\theta/(R\rho g) \quad (7)$$

where R = the inner diameter of pore, ρ = density of slag, and g = gravitational constant.

Kazakov *et al.* [21] measured the vertical penetration of slag into the pores of a refractory when applying an electrical potential between the refractory and the melt, and found that the minimum penetration of slag into the refractory occurred when -1 volt was applied. Recent experiments [20] have confirmed these findings. It can be seen from Equation 7 that an increase in θ would lead to decrease in $\cos\theta$ and hence a decrease in the height of penetration, h. Subsequently, Kazakov *et al.* [23] carried out plant trials using the same principle and found that by applying a 2V electrical potential across the refractory and the molten slag, the refractory life could be increased by a factor of 10.

4. Emulsions

Production rates in metal-producing processes can be improved significantly by enhancing rates of refining reactions through large increases of the (surface area/mass) ratio of the slag and metal phases. In practice, this can be achieved through (i) the creation of an emulsion of metal in slag (or vice versa) and (ii) the formation of a slag foam containing metal droplets. It has been proposed [24] that the rate-controlling step in emulsification is associated with the mass transfer of oxides (SiO_2, FeO, MnO) in the slag. Furthermore, it was also suggested that spontaneous emulsification may occur if the relative velocities of the metal and slag phases (Kelvin-Helmholtz instability) are systematically different. This could arise from fluid flow originating from:

(i) natural convection, due to local temperature differences caused by exothermic reactions.

(ii) Marangoni flow resulting from local differences in either concentration or temperature (diffuso- and thermocapillary flows, respectively).

Chung [24] concluded that Marangoni flow was involved and that emulsification occurred by (a) the upward movement of 'pin-shaped regions' of metal and downward movements of cup-shaped regions of slag and (ii) 'necking' and emulsification by eddy currents created by Marangoni flow.

5. Formation of foams

Foams are widely used in iron- and steelmaking process since they provide rapid refining of the metal droplets held in the foam as a result of the enormous (surface area/mass) ratio. Foaming slags are also used on Electric Furnaces (EAF) to stabilise the arc and improve energy efficiency.

There is general agreement [25–28] that the principal factors promoting foaming are:

(i) a low surface tension of slag (γ_s) (P_2O_5, Na_2O, iron oxide additions cause a decrease in γ_s);

(ii) high bulk and surface viscosities which retard draining of the slag film (P_2O_5 and SiO_2 are both surface active and will congregate preferentially at the surface and will tend to increase the surface viscosity);

(iii) the presence of solids in the slag (since this will increase viscosity and tend to lock the bubbles and prevent their escape);

(iv) decreasing temperature since this would increase slag viscosity and encourage the formation of solids (a high solidification temperature of the slag would also be beneficial);

(v) high surface elasticity.

Although there is a general agreement on the factors affecting foam stability there is still some disagreement about the relative importance of the various factors [28].

6. Surface waves, break up of jets

Wave motion at a surface or interface can result from both gravitational and capillary forces. Lord Rayleigh [29] studied the break-up of a jet of liquid into a gas. Capillary forces make liquid jets unstable when their length, L, exceeds their circumference. Axisymmetric disturbances of the surface grow in amplitude until the jet is pinched off. Rayleigh's theory correctly predicted the drop size and the dependence of L on surface tension. Subsequent work [30] for liquid/gas and liquid/liquid jets has shown that the breakup is dependent upon:

(i) mass transfer through the interface e.g. the transfer of a surfactant from jet to the fluid causes the length, L, to increase substantially whereas transfer from the fluid to the jet causes a reduction in L.

(ii) the presence of a surface film (with high viscosity) tends to damp out surface instabilities.

(iii) the presence of surfactants on the jet surface tends to reduce the mass transfer effects, e.g. a high S cast of steel would tend to reduce the effects of oxygen transfer on jet stability .

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