Role of oxygen in interfacial phenomena during high temperature reactions

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ABSTRACT

Interfacial phenomena in high temperature reactions such as between iron alloy and slag is well documented but not fully understood. It is believed that a gradient of oxygen concentration plays an important role to the occurrence of such phenomena. This article describes the results from the continuation of the study of interfacial phenomena between Fe-Al alloy droplets and CaO-SiO$_2$-Al$_2$O$_3$ slag. Materials characterization techniques involving microscopic observations, depth profiling, bulk, point analysis and were carried out. The roles of oxygen as well as other factors that contribute to the interfacial phenomena were evaluated. The results and their implications to steelmaking will be discussed.
INTRODUCTION

Interfacial phenomena have been observed during reactions between liquid iron alloy droplets and liquid slag at high temperature (1-4). The phenomena include droplet flattening or spreading, interfacial turbulence, and spontaneous emulsification. In industry, the phenomena are important in terms of productivity since they significantly affect the reaction kinetics through the creation of high interfacial area. A better understanding of the phenomena is vital due to their importance both from industrial and also from fundamental kinetic science point of view.

Consider a system where a liquid iron-aluminum alloy droplet is reacting with a CaO-SiO₂-Al₂O₃ slag. During the reaction, the droplet flattens or spreads. The droplet may remain flat for some period of time and in some cases where the rate of mass transfer is quite high, the droplet may then undergo a spontaneous emulsification where it breaks up into numerous smaller droplets. As the reaction nears completion and the mass transfer slows down, the droplet re-coalesces and recovers to its equilibrium shape. These phenomena which occur without external forces being applied are schematically shown in Figure 1.

![Figure 1 - Droplet shape changes observed during high temperature reactions](image)

The phenomena described above are usually associated with Marangoni flow/convection; a fluid flow driven by a gradient of interfacial tension. The gradient of interfacial tension itself can be caused by three factors, a gradient of temperature (thermocapillary), a gradient of electrical potential (electrocapillary) and a gradient of surface active solutes (solutocapillary).

Interfacial phenomena have been of interest to many investigators over many decades. Although well documented, they are not fully understood and a lot of questions remain unanswered. For example, the cause of spontaneous emulsification is still a subject of discussion. A procedure in analyzing the kinetics of the reaction in the presence of spontaneous emulsification is also not really defined, although recent work
by the authors has attempted to address this issue (5). The changes in specific interfacial area during the reaction create some difficulty in ascribing a reaction rate constant to a given system under a given set of conditions.

This article describes the results from the continuation of the study of interfacial phenomena in Fe-Al alloy systems reacting with CaO-SiO₂-Al₂O₃ slag. Some scanning electron images of the reacting interface and a procedure of analyzing the kinetic in presence of spontaneous emulsification are presented. The roles of oxygen as well as other factors that contribute to the Marangoni convection are also evaluated.

EXPERIMENTAL PROCEDURE

The experiments involve reactions between liquid Fe-Al alloy droplets of various aluminum contents (3.5wt%, 4.5wt% and 5wt%) with liquid slag of composition CaO-SiO₂-Al₂O₃ (40wt%:40wt%:20wt%). Metal droplets of 2 to 3 grams were made by melting pure iron pieces 99.99%, vacuum remelted with very low oxygen content, and aluminum pieces in a small electric arc furnace in an argon atmosphere. The alloys were then remelted three times to ensure homogenization of the alloying element. A master slag was prepared by mixing measured quantities of the oxides and melting them in a platinum crucible at 1550°C.

A vertical tube furnace equipped with four molybdenum disilicide heating elements was used for the experiments. The slag of about 50 grams was contained in a zirconia crucible and then put inside the furnace under an argon atmosphere and heated to the desired temperatures, i.e. 1550°C, 1600°C and 1650°C. The crucible and the slag were held for some time to allow homogenization. The iron alloy droplet was then introduced into the crucible and allowed to react for certain periods of time, after which the whole crucible containing the slag and the droplet was quenched. The crucibles containing the quenched slag and metal droplets were crushed and the metallic pieces were recovered. Chemical composition of the droplets representing the time sequence of the reaction was determined using an ICP (inductively coupled plasma) spectrometer.

Interfacial area was approximated using two methods. The first method involved direct measurement of the dimensions of each metallic particle using a vernier caliper and a micrometer and also by employing image analysis. An ellipsoid was chosen as the shape that best represented the irregular shaped particles and particles that were near spherical in shape were assumed to be spheres. The interfacial area was then determined. The second method used involved sticking papers sized from 1x1 to 5x5 mm to the surface of the droplets and calculating the total area of the papers. Measurements were repeated several times. The first method was used for droplets with a simple shape while the latter method for more complicated shapes. For a simple shape such as a near spherical droplet, both methods gave the same value within ± 10%.
Reacted samples were cut and prepared for scanning electron microscopy (SEM) observation. A Philips 515 SEM/Link QX2000 EDX was used for investigating the metal droplets. The accelerating voltage was 20 keV. Observations were carried out on the droplets cross section and along the interface of metal and slag. Energy dispersive spectrometry (EDX) analysis was carried out to analyze bulk and local compositions along the interface and from the edge towards the bulk. EDX elemental maps were also acquired.

RESULTS AND DISCUSSION

The shapes of the quenched droplets from each reaction time were examined. Generally, similar phenomena were observed. At the beginning of the reaction, i.e. at 5 minutes, the recovered particle has a flat shape. As the reaction progresses the flattened droplet underwent spontaneous emulsification. The spontaneous emulsification was observed in all three Fe-Al systems studied and occurred as early as 5 minutes of reaction to around 20 minutes of reaction depending on the experimental conditions. In general, during the emulsification, the droplet disintegrated mainly into a droplet of a size less than the original accompanied by numerous much smaller droplets. The increase of interfacial area observed was from 300% to 500% of the original value.

Figure 2 shows the interfacial area changes and the number of particles recovered from the reaction between 2.35 g Fe-4%Al droplet and CaO-SiO₂-Al₂O₃ at 1650°C. In this case, the spontaneous emulsification was observed at about 10 minutes of the reaction and the increase of the interfacial area was up to 375% from the initial value. It disintegrated into one smaller droplet with highly deformed shape (higher interfacial area) accompanied with numerous smaller droplets. More than one hundred of very small droplets, 1 mm and less in average-diameter, were recovered.

Scanning electron microscopy images of the interface of Fe-4%Al system are shown in Figure 3(a)-(d). These images were taken from the sample of the reaction time of 5 minutes. These images suggested that interfacial perturbation at the interface as well as the emulsification at microscopic level was happening from as early as 5 minutes of the reaction. It may be that these microscopic metal droplets then coalesce and form bigger droplets that correspond to the droplets in the millimeter or centimeter scale recovered during the occurrence of “macroscopic” emulsification later at 10 minutes of reaction.

The emulsified metal droplets observed vary in size from less than 1 μm up to 100 μm in diameter along the interface in the slag phase. Figure 3(a) shows both metal and slag emulsification. Both metal and slag emulsification were confirmed by applying EDX elemental mapping analysis. Figure 4 shows the Fe, Al, Ca and Si mapping of the SEM image. It can be seen from these maps that the separated droplets in the slag phase are iron droplets and the isolated areas in the metal phase are slag containing Al, Ca and
Si. The slag emulsification observed is consistent with the results from Chung and Cramb (4) in which they observed slag entrapped in the metal phase in Fe-3.28%Al system at 1600°C. Figure 3(a) and 4 also shows a coalescence of some of the emulsified metal droplets.

Figure 2 – (a) interfacial area changes and, (b) number of particles recovered from the reaction between 2.35 g Fe-4%Al and CaO-SiO2-Al2O3 at 1650°C

Figure 3(b) shows a perturbed interface in another part of the droplet. Also shown in the image, is an array of emulsified slag droplet along the interface the metal phase. The circles highlight some specific areas at the interface. For instance, if an interfacial instability causes a protrusion of slag into the metal phase (left circle), as the tip goes further in to the metal phase it will tend to become spherical to decrease its interfacial area (right circle). Once necking occurs, detachment of the droplet is favorable in order
to decrease its interfacial area. An emulsified slag droplet in the metal phase is then formed. The same mechanism may apply for metal protrusion into the slag leading to metal emulsification in the slag. This mechanism was first suggested by Bainbridge and Sawitowski (6) as discussed in a paper by Chung and Cram (7).

![Figure 3 - SEM images of interface showing metal and slag emulsification, (a) and (b), and metal (c) and slag (d) protrusion, during early stage of reaction between Fe-4%Al and CaO-SiO₂-Al₂O₃ slag at 1650°C.](image)

Figure 3(c) and (d) shows a metal protrusion and a slag protrusion normal to the interface. The diameter of the tips observed were about 1 to 2 μm. This may suggest that the emulsified metal and slag droplet are initially formed in this range of size. Further they may coalesce to form bigger droplets. For example, it may be that the bigger slag droplet of diameter 18 μm in Figure 3(a) is a result of coalescence of smaller droplets 1-2 μm in size in the surroundings.
A perturbed interface as in Figure 3(a)-(d) was not observed at later stage of the reaction, for example at 40-45 minutes. Instead, a smooth interface were observed on both top and bottom part of the droplet. "Microscopic" and "macroscopic" metal emulsification was also not observed. In a very few instances, a slag droplet entrapped in the metal phase was observed in contrast with an array of slag droplets as in Figure 3(a) and (b).

Figure 4 – Elemental maps obtained using EDX analysis confirm the metal and slag emulsification in the Fe-4%Al system at 1650°C.

**Kinetics in the Presence of Spontaneous Emulsification**

Spontaneous emulsification can increase the reaction interface up to 300% – 500% of the original value. The increase of interfacial area is expected to affect the kinetics of the reaction. Complication arises in analyzing the kinetics, such as in ascribing the value of interfacial area in the kinetic equations, due to the fact that interfacial area is changes throughout the reaction. Further, this creates difficulties in ascribing a reaction rate constant to a given system under a given set of conditions. A procedure in analyzing the kinetics of the reaction in the presence of spontaneous emulsification is also not really defined.
Figure 5 - Kinetic data plot for Fe-5%Al droplet reacting in CaO-SiO₂-Al₂O₃ slag at 1650°C; (a) assuming first order reaction with respect to Al and constant interfacial area, (b) first order reaction and time-averaged-interfacial areas are used.

Figure 5(a) shows a kinetic data plot for reaction between Fe-5%Al and CaO-SiO₂-Al₂O₃ slag at 1650°C. The plot is developed by assuming that the kinetics follows a first order reaction with respect to Al in the metal droplet. It can be seen from the graph that there is a change in the slope of the line between 15 and 20 minutes of reaction. This
corresponds to the spontaneous emulsification of the droplet. The rate constant is increased by 2.78.

The authors proposed an approach to accommodate the interfacial area changes in the kinetic equations (5). Time-averaged interfacial areas were used and the kinetic equation of a first order reaction with respect to Al is written as

$$\frac{1}{S'(t)} \ln \frac{Al}{Al_0} = -\frac{k}{V} t$$

where $k$ is the rate constant, $t$ is the time, $Al$ and $Al_0$ are the aluminum content at time $t$ and initial aluminum content, $V$ is the volume of the droplet, and $S'(t)$ is the time-averaged interfacial area calculated using the following equation

$$S'(t) = \frac{1}{t} \int_0^t S(t) \cdot dt$$

The left-hand-side of Equation (1) is then plotted against times of reaction. The approach was adequately describes the kinetics and accommodates the changes of interfacial area. The same approach was applied for analyzing the reaction kinetics between Fe-5%Al and CaO-SiO$_2$-Al$_2$O$_3$ slag at 1650°C. The data from Figure 5(a) are re-plotted by incorporating the time-average interfacial area and shown in Figure 5(b). It can be seen that the data can be re-plotted into a single straight line.

Experimental parameters such as temperature of reaction, initial droplet size and initial Al concentration in the droplet, seem to have an effect to the emulsification, for example they affect the time where the disintegration has the maximum increase of interfacial area and the maximum value of interfacial area itself. Moreover, they affect the overall kinetics of the reaction. However discussions about the effect of these factors and details of the kinetic study are beyond the scope of this article and will be described in a separate article.

MARANGONI FLOW IN INTERFACIAL PHENOMENA

The mechanism described earlier explains the formation of metal and slag emulsion. However, what causes the interfacial instability in the first place is still a subject of discussion. Chung and Cramb (7) proposed a mechanism of interfacial instability through a Kelvin-Helmholtz instability. That is an instability that occurs at an interface between two fluids where there is motion parallel to the interface but with different velocities on each side of the interface. However, their calculation did not agree well with the observed wavelength. The average observed wavelength was three order magnitudes less than calculated. They claimed that the difference may be from an error
in the estimated interfacial tension value used in the calculation or from a much greater driving flow resulting low-wavelength interfacial perturbations.

Regardless of the mechanism of interfacial instability, the Marangoni convection/flow, a fluid flow driven by a gradient of surface and interfacial tension, is believed to play an important role. As has been mentioned earlier in this article, the gradient of interfacial tension can be caused by a gradient of temperature, a gradient of electrical potential, and a gradient of surface active solute. All of these factors can be present and contribute to the creation of Marangoni convection. Nevertheless, one factor may dominate in a given system.

In the system studied, Fe-Al droplet in CaO-SiO₂-Al₂O₃ slag, the effect of temperature and electrical potential gradient is less than the effect of surface active solute gradient, in this case is oxygen (8). The reaction occurs in the system studied is an oxidation reaction of aluminum in the metal by silica in the slag and is highly exothermic. If the droplet is assumed to be thermally isolated, the heat generated can increase the temperature of 2.35g Fe-5%Al droplet by 414°C. However, since the heat released over time during the reaction, the increase of temperature is actually quite small. The authors have developed a simple heat transfer model to analyze the increase of temperature during the reaction (8). The results indicated that the maximum increase of temperature of 2.35g Fe-5%Al droplet is less than 6 degrees which correspond to a change of interfacial tension of 0.7%. This slight decrease is negligible.

There is only limited work on electrocapillary in high temperature systems, especially in liquid iron in the liquid CaO-SiO₂-Al₂O₃ slag (9-11). Electrocapillary behaviour is affected by the chemical composition of both the metal and slag phases. It is thought that in the case of liquid iron in CaO-SiO₂-Al₂O₃ slag, the electrocapillary effect has a less effect on the interfacial tension compared to the solutocapillary effect. It takes some degree of electrical potential gradient, for example sufficient only by an application of external potential, to lower the interfacial tension significantly. A detailed discussion of the evaluation of thermocapillary, electrocapillary, as well as solutocapillary effect on the Fe-Al system, is described by Rhamdhani et.al (8).

Role of Oxygen in Interfacial Phenomena

Certain elements such as oxygen, sulfur, selenium, and tellurium are very surface active. The presence of these solutes has been shown to drastically reduce the interfacial tension of liquid iron and other metals such as Ni and Cu. This also occurs in a reaction between Fe-Al and CaO-SiO₂-Al₂O₃, oxygen preferentially resides along the interface and significantly lowers the interfacial tension. Figure 6 shows the effect of oxygen activity on the interfacial tension between liquid iron and CaO-SiO₂-Al₂O₃ slag at 1600°C (12). It can be seen that the oxygen can decrease the interfacial tension from about 1350 mN/m down to 550mN/m, or about 60%. 


For instance, if there is a non-uniform mass transfer of oxygen from slag to the metal due to either a disturbance at the interface or localized reaction, an oxygen concentration gradient will be formed along the interface. The oxygen concentration gradient will then create an interfacial tension gradient along the interface which induces a Marangoni flow along the interface. The resulting Marangoni flow plays a vital role in the interfacial phenomena and the instability of the interface.

The issue of oxygen in high temperature reactions is complicated and not fully understood. In Fe-Al alloy reacting with CaO-SiO₂-Al₂O₃ slag for example, mass transfer and adsorption of oxygen occurs simultaneously and the fact that oxygen takes part in the reaction makes the matter more complicated. The oxygen is present in several forms. Dissolved oxygen present in the bulk of the droplet and adsorbed along the interface. Oxygen is also present as oxides, for example as an entrapped CaO-SiO₂-Al₂O₃ slag, Al₂O₃ inclusions and as Fe₂O₃.

![Figure 6 - The effect of oxygen activity on the interfacial tension between liquid iron and CaO-SiO₂-Al₂O₃ slag at 1600°C, from Gaye et al (12)](image)

To understand better the effect of oxygen on the Marangoni flow and moreover on the interfacial phenomena in general, knowledge of how oxygen is distributed in the metal is vital. Measurements of oxygen levels in terms of bulk or local composition in specific area are required. Measurement of bulk oxygen contents can be done by employing inert gas fusion analysis. However, oxygen in the form of inclusions and entrapped slag give some complication in determining the actual bulk oxygen content.
There has been a lot of work on oxygen adsorption in high temperature systems, for example in determining the oxygen surface excess (12-14). However, there is only limited work on the actual oxygen concentration distribution along the interface and toward the bulk. The reasons may include the difficulty of the measurements and limited instrument capability. The oxygen content spans from ppb levels to 2800 ppm. An attempt of quantifying oxygen using dynamic secondary ion mass spectrometry (SIMS) has been made by Rhamdhani and Brooks (15). Their results give some idea of the level of oxygen concentration gradient and the length scale in which the gradient is acting.

Figure 7 - Oxygen concentration depth profiles at 5 minutes of reaction; (1) & (2) bottom, (4) & (5) top, and (3) center of the sample; from Rhamdhani and Brooks (15)

Figure 7 shows the variation of oxygen content from Fe-4.45%Al sample at 5 minutes of reaction. The results suggested a presence of pocket of fluids of the scale 1 to 2 μm of different oxygen concentrations moving about in the bulk during the reaction. Differences of oxygen concentration up to 100 ppm and 250 ppm were found near the interface and towards the bulk. Scanning electron microscopy observations of the interface show metal-phase protrusions normal to the interface within the slag-phase with a round tip of 1 to 2 μm in diameter as shown in Figure 3(c) and (d). The similarity of the length scale of the protrusions with the scale of the pockets of fluid from dynamic SIMS results may suggest that some pocket of fluid was once at the interface before it moved to the bulk (surface renewal model) and this same pocket of fluid caused the oxygen
concentration gradient along the interface at the same length scale and may be responsible to the formation of the protrusion which lead to emulsification in micro scale.

The effects of oxygen on the surface or interfacial tension are described by the Gibbs-Langmuir adsorption-isotherm equation. By means of curve fitting of data from Gaye et al. (12), the effect of oxygen on the interfacial tension between liquid iron and CaO-SiO$_2$-Al$_2$O$_3$ slag can be written as

$$\gamma = 1350 - 233 \ln(1 + 328a_o), \text{mN/m}$$  \hspace{1cm} (3)

where $\gamma$ is the interfacial tension and $a_o$ is the activity of oxygen in the metal. It implies that

$$\frac{d\gamma}{da_o} = -\frac{76424}{1 + 328a_o}, \text{mN/m}$$  \hspace{1cm} (4)

or considering discrete changes,

$$\frac{\Delta\gamma}{\Delta a_o} = \frac{233}{\Delta a_o} \ln \left[ \frac{1 + 328(a_o' + \Delta a_o)}{1 + 328(a_o')} \right], \text{mN/m}$$  \hspace{1cm} (5)

where $a_o'$ is the initial oxygen activity and $\Delta a_o$ is the difference in oxygen activity along the interface. Our experiments utilized metal samples with initial oxygen content of as low as 50 ppm in average. By combining this data with results from Rhamdhani & Brooks, the change of local interfacial tension along the interface due to solutocapillary effect can be determined. Assuming Henry's law is valid and taking the value of $a_o' = 50$ ppm and $\Delta a_o = 100$ to 250 ppm, one can get the local decrease of interfacial tension of $\Delta\gamma = 189 - 330$ mN/m. The decrease of interfacial tension of these magnitudes over distance 1 to 2 $\mu$m along the interface is significant and may produce enough driving flow to induce interfacial instability.

It is shown that oxygen as a surface active element plays a significant role in the occurrence of the Marangoni flow and interfacial phenomena. In pyrometallurgical processes, such as steelmaking, gradients of temperature in addition to concentration are present and both have a relatively large magnitude. The generated Marangoni flow and interfacial phenomena have a direct effect to the kinetics of the process. In terms of the kinetics of reactions, they are important because they can enhance mass transport up to several orders and also form a very large reacting interface.
CONCLUSIONS

1) Contribution of oxygen to the formation of Marangoni flow and interfacial phenomena has been analyzed and found to play a dominant role.
2) The use of time-averaged interfacial area adequately describes the kinetics of the reaction in the presence of spontaneous emulsification.
3) Micro and macro emulsification were observed during the reaction. It may be that the microscopic metal droplets re-coalesced during the reaction and formed larger droplets.

REFERENCES


