ABSTRACT

Interfacial phenomena, which include interface turbulence, lowering of apparent interfacial tension, and spontaneous emulsification, have been observed in high temperature metal processes involving reactions between liquid metals and liquid slags. The major importance of these phenomena are that they can increase the reacting interface up to five hundred percent of initial value and can also increase mass transfer rate, thus significantly enhances the overall reaction rate. It has been almost six decades since the phenomena was first documented in laboratory by Kozakevitch using x-ray radiography technique and numerous studies have been carried out since then. However, the complexities of the problem, limitations in experimental techniques, difficulties in experimental work resulting in the lack of quantitative experimental data, among many, prevent the holistic understanding of the phenomena. The current paper will review the previous studies, the present understanding and challenges as well as the future research on interfacial phenomena in slag-metal reactions along with their potential application for a new advanced metal processing.

I. INTRODUCTION

Interfacial phenomena have been observed during liquid metal processing. In the case of reactions between droplets of liquid metal and liquid slag, the phenomena observed include interfacial turbulence, lowering of apparent interfacial tension (indicated by droplet flattening or spreading), and spontaneous emulsification. The phenomena are important since they directly affect the rate of the process through spontaneous increase of interfacial area and mass transfer rate across the interface. They are usually associated with a convective fluid flow along the interface driven by gradients of surface/interfacial tension caused by gradients in solute (surface active elements) concentration, temperature and electrical potential. This type of flow is termed the Marangoni flow, named after an Italian scientist, Carlo Marangoni (1871) and are sometimes referred to respectively as the solutocapillary, thermocapillary and electrocapillary effects. These gradients can be the direct result of non-uniform mass and heat transfer between the phases or indirect result of another type of convection, forced flow or any disturbances along the interface. This article reviews the previous studies, the present understanding
and future directions in fundamental understanding of the phenomena, particularly during reaction between liquid iron alloy and liquid slag.

II. PREVIOUS STUDIES ON INTERFACIAL PHENOMENA

Kozakevitch and co-workers in 1955 were among the first who reported the interfacial phenomena during reaction between an iron alloy and slag. They conducted experiments where liquid Fe-C-S droplets (of about 2g) were reacted with a blast furnace slag, CaO-SiO$_2$-Al$_2$O$_3$. During the desulphurization reaction, they observed a drastic lowering of apparent interfacial tension (indicated by droplet flattening) and droplet shape changes. They calculated that the minimum dynamic interfacial tension observed was about 1/160 of the equilibrium value.

Deryabin et al. (1968) and Saburov et al. (1971) confirmed the phenomena in the Fe-S and Fe-C-S metal droplets reacting with CaO-SiO$_2$-Al$_2$O$_3$ (40:40:20 in wt%) slag at 1450°C and 1550°C; Fe-Ti metal droplets reacting with CaO-SiO$_2$-Al$_2$O$_3$ slag at 1540°C and 1580°C; and Fe-Al metal droplets reacting with CaO-Al$_2$O$_3$-TiO$_2$ slag.

Ooi et al. (1974) also observed the phenomena during oxidation reactions of Fe-Al and Fe-Ti alloys with CaO-Al$_2$O$_3$-SiO$_2$ and CaO-SiO$_2$-TiO$_2$ slag. The droplet profile during the reaction was studied by x-ray radiograph. In the case of Fe-Al alloy system, the decrease in dynamic interfacial tension, down to 100mN/m, was observed when the Al concentration was higher than 2wt%. Figure 1 shows the x-ray photographs showing the change in the droplet shape during oxidation reactions of Fe-4wt%Al and Fe-7wt%Ti alloy. The droplet flattens at the beginning of the reaction and recovers to its original shape at the end of the reaction. Ooi et al. suggested that droplet dynamic phenomena were due to the reduction of silica in the slag by aluminum dissolved in the iron, i.e. Reaction (1):

\[
4 \text{Al} + 3 (\text{SiO}_2) = 3 \text{Si} + 2 (\text{Al}_2\text{O}_3) \tag{1}
\]

More extensive experiments in this area were carried out by Riboud and Lucas (1981). They studied the influence of mass transfer upon surface phenomena. The change of the shape of the droplet during reactions was observed by using an x-ray. They...
evaluated the overall flux of oxidizable element leaving the metallic phase by determining the slope of the curve of concentration change of the metal as a function of time. Apparent interfacial tension measurements were conducted by evaluating the shape of sessile metal droplets in the slag from their x-ray images. Figure 2 show successive X-ray images of the profile of a metal droplet. When alloy and slag are brought in contact, Figure 2(a), the droplet flattened progressively (lowering of interfacial tension), followed by disappearance of interfacial forces, Figure 2(b), and after a period of time it recovered to its original shape, Figure 2(c). They observed numerous metallic droplets near the interface in the slag for systems with high rates of mass transfer, i.e. when the reaction was at most intense or when the interfacial tension seemed to have disappeared, Figure 2(d). The dimensions of the droplets varied from smaller than 1 µm up to 100 µm.

Riboud and Lucas observed the phenomena in a number of alloy-slag systems, which include Fe-Al, Fe-P, Fe-B, Fe-Cr, Fe-Si, Fe-Ti alloys reacting with CaO-SiO$_2$, CaO-Al$_2$O$_3$-Fe$_2$O$_3$, CaO-Al$_2$O$_3$-TiO$_2$, CaO-Al$_2$O$_3$-SiO$_2$, CaO-Al$_2$O$_3$-SiO$_2$-Fe$_2$O$_3$, CaO-SiO$_2$-FeO, Cu$_2$O, Cu$_2$O-Al$_2$O$_3$ slags. They reported that interfacial forces seem to disappear when the oxygen flux is larger than about 0.1 mol m$^{-2}$ s$^{-1}$. For values of this flux lower than 0.01, interfacial tension recovers rapidly to high values.

Figure 2. X-ray images of droplet shape profile during reactions, (a) 7 minutes, (b) 18 minutes, (c) 40 minutes of reaction, and (d) polished section of Fe-4.45wt%Al droplet at 18 minutes (Riboud and Lucas, 1981).

Sharan and Cramb (1995) observed a lowering of interfacial tension during reaction between Fe-20wt%Ni-2.39wt%Al and CaO-SiO$_2$-Al$_2$O$_3$ slag at 1550°C. Chung and Cramb (2000) studied the reaction between Fe-Al alloys (with Al content ranging from 0.25 to 3.3 wt%) and CaO-SiO$_2$-Al$_2$O$_3$ slag and observed the phenomena for Al content as low as 0.25wt%. However, spontaneous emulsification was observed only for systems with Al greater than 3wt%. Upon microscopical observation of quenched samples, they found that at 5 minutes of reaction, one side of the droplet was deformed and optical microscopy observation showed entrapped slag in this region which suggests that a reaction may have also occurred locally. Chung and Cramb (2000) also investigated the dynamic interfacial phenomena during a reaction between Fe-Ti alloy and CaO-SiO$_2$-Al$_2$O$_3$.
slag. Significant interfacial disturbance and spontaneous emulsification were only observed in droplet containing high amount of 11wt%Ti.

III. PROPOSED MECHANISM FOR INTERFACIAL PHENOMENA

Richardson (1982) suggested that the explanation for the lowering of dynamic interfacial tension lies in the build up of interfacial charges during rapid reaction which increases the electro-capillary effect. In the Fe-Al system in contact with CaO-Al$_2$O$_3$-SiO$_2$ slag; if Al moves out of the iron more quickly than Si moves in from the slag, the interface of the metal would become negatively charge due to accumulation of Al$^{3+}$ (or AlO$_2^-$) on the slag side. This may lead to the lowering of interfacial tension due to increased London forces or dipole interactions across the interface. This mechanism is similar as postulated by Brimacombe et al. (1970) in explaining the mechanism of interfacial turbulence at the interface of amalgam-electrolyte systems.

Sharan and Cramb (1995) proposed another mechanism for the lowering of the dynamic interfacial tension. The presence of a large amount of Al in the alloy greatly reduced the oxygen potential within the metal. Since the slag surrounding the metal has a higher oxygen chemical potential, this will lead a mass transfer of oxygen form the slag to the metal due to an imbalance of oxygen potential. As a result, there would be a gradient in oxygen content and the oxygen at the surface would be higher than in the bulk of the droplet. The increased oxygen content at the interface is responsible for the lowering of interfacial tension due to dipole interactions as in electrocapillary effect as explained by Richardson (1982) and the fact that oxygen lowers the surface tension of liquid iron.

Spontaneous emulsification is usually associated with an interfacial turbulence and instability. Theoretical descriptions to explain the interfacial instability in aqueous systems have been proposed many investigators (Sternling and Scriven, 1959; Berg, 1972; Defay and Sanfeld, 1973; Sorensen et al., 1980).

Chung and Cramb (2000) proposed a mechanism for spontaneous emulsification through interfacial instability due to the Kelvin-Helmholtz instability. They described two sources of fluid flows that interacted with the interface, i.e. natural convection due to exothermic thermal energy released at the interface due to reaction, and/or Marangoni flow due to concentration or thermal gradients at the interface. The reaction that occurs at the interface is exothermic and can drive natural convection. Since, the reaction appears to initiate locally, the reaction will cause both thermal and chemical variations at the interface. These will lead to variations of surface tension and give rise to Marangoni flow within the system. The resulting Marangoni flow will give rise to what is called Kevin-Helmholtz instability and eventually the interface will become unstable and lead to emulsification. Chung and Cramb (2000) suggested that the interface would become
unstable if the difference of velocity of metal and slag is greater than 25 cm/s. This will create wavy interface with wavelength of 0.82 cm and velocity 18.4 cm/s. However, the observed wavelengths were much shorter than those obtained from the Kelvin-Helmholtz instability model, i.e. less then 1 µm. 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.

IV. CHALLENGES

Although there have been a lot of work on the interfacial phenomena in high temperature systems, the holistic understanding of the phenomena is not achieved yet. This maybe due to various reasons as described below.

The interfacial phenomena are very complex with various elemental reactions and fundamental phenomena occurring simultaneously and affecting each other. There are interrelationships between interfacial phenomena, reaction kinetics and interfacial area changes during high temperature reactions. Reaction kinetics may induce interfacial phenomena, which in turn alter the interfacial area, for example due to a lowering of interfacial tension and spontaneous emulsification. Further, this spontaneous increase of interfacial area will again affect the reaction kinetics. This interrelationship is schematically shown in Figure 3. To fully understand the phenomena, one needs to understand these interrelationships, which require information and knowledge on the following:

1. Information on the reaction kinetics, which include the change of chemical composition in the liquid metal and liquid slag with respect to reaction time.
2. Information on the interfacial area changes with respect to the reaction kinetics or with reaction time. These include information on how much the interfacial area change and knowledge on droplets distribution and the physical pictures.
3. Local information on the chemical compositions (including surface active elements concentration), temperatures, and physicochemical properties at both metal and slag sides of the interface.
4. Knowledge of how interfacial area change affects the reaction kinetics and vice versa. These include using a transient approach in dealing with the kinetics and how to predict the interfacial area change.
5. Knowledge of how the reaction kinetics affects the interfacial phenomena and vice versa. These include knowledge in predicting the apparent interfacial tension change and spontaneous emulsification.

The phenomena are also complex to be modelled as simultaneous phenomena are occurring (i.e. combined heat transfer, fluid flow, kinetic and thermodynamic problems). Fully modelling studies have been carried out mostly in low temperature
systems. Applying the available models in low temperature systems to high temperature systems also present a different challenge as there are only limited quantitative data at high temperature systems as most of them are phenomenological/qualitative data. The lack of quantitative experimental data maybe due to the fact that, in general, high temperature experiments are quite difficult in terms of the actual procedure and in obtaining meaningful quantitative information. There are also factors of high cost and safety issue associated with high temperature experiments. The nature of the high temperature experiments where the changes on the interface and the shape of the droplet cannot be seen directly (unlike in low temperature systems) makes it difficult to carry out online measurements. Most of the quantitative data were obtained from snapshots of the phenomena at particular reaction times by carrying out measurements on the quenched samples. Experiments have to be carried out properly and very carefully to avoid any artefacts due to the quenching process.

![Image of interrelationship between interfacial area changes, reaction kinetics and interfacial phenomena](image)

**Figure 3.** Interrelationship between interfacial area changes, reaction kinetics and interfacial phenomena

**V. CURRENT PROGRESS**

The most recent studies on the interfacial phenomena in metal-slag reactions were carried out by the authors, which were focused to address some of the challenges described in Section IV. Rhamdhani et al. (2005a) studied and tracked the change of interfacial area during the reactions between Fe-Al alloys and CaO-SiO$_2$-Al$_2$O$_3$ slag. They showed that the increase in interfacial area can be up to 500% of the original value. Figure 4(a) shows an example of the instantaneous interfacial area and droplet shape changes during reaction between Fe-Al alloys and CaO-SiO$_2$-Al$_2$O$_3$ slag.

The information on the change of interfacial area is important as it enables the development of an appropriate approach for analysing the kinetics of the reaction. Rhamdhani et al. (2005a) have developed a procedure for treating the transient nature of the interfacial area into the kinetic equations. This was carried out by introducing a time-
averaged interfacial area which can be calculated from the instantaneous interfacial area shown in Figure 4(a). The following paragraph provides an example of the approach.

\[ 4 \text{Al} + 3 (\text{SiO}_2) = 3 \text{Si} + 2 (\text{Al}_2\text{O}_3) \]  \hspace{1cm} (4)

For a first order reaction kinetic with respect to Al in the metal droplet, the kinetic equation is written as:

\[ \frac{1}{A^*(t)} \ln \frac{A(t)}{A_0} = \frac{-k}{V} t \]  \hspace{1cm} (5)

where \( k \) is the rate constant, \( t \) is time of reaction, \( A(t) \) and \( A_0 \) are the aluminum content at time \( t \) and at initial, \( V \) is the volume of the metal droplet, and \( A^*(t) \) is the time-averaged interfacial area calculated using the following equation

\[ A^*(t) = \frac{1}{t} \int_0^t A(t) \cdot dt \]  \hspace{1cm} (6)

where \( A(t) \) is the instantaneous interfacial area, i.e. from Figure 4(a).

In the case of reaction between 2.35g Fe-4wt%Al and CaO-SiO_2-Al_2O_3 slag at 1650°C. The kinetics were evaluated by plotting the left-hand side of Eq. (5) using constant \( (A_0) \), and time-averaged \( (A^*(t)) \) interfacial areas against reaction time, as shown in Figure 5. It can be seen from Figure 4(b) that in the case of constant interfacial area, there is a change in the slope by a factor of approximately 2 at 10 minutes of reaction, which is associated with the increase of interfacial area due to spontaneous emulsification. On the contrary, all the experimental data closely follow a straight line when the time-averaged interfacial area is incorporated. The slope of this line represents the value of \(-k/V_m\). In this case, the rate constant \( k \) is calculated to be \( 1.9 \times 10^{-6} \text{ m.s}^{-1} \). This
also suggests that the “average” rate constant (or mass transfer coefficient) does not change during the reaction. More detailed information on the approach and its applicability in high temperature system has been described elsewhere (Rhamdhani et al., 2005a).

![Graph showing interfacial tension depression](image)

**Figure 5.** Calculated interfacial tension depression due to thermocapillary, solutocapillary and electrocapillary effects during reaction between 2.5g Fe-4.45 wt% Al droplet and CaO-SiO$_2$-Al$_2$O$_3$ slag at 1600°C.

As has been mentioned earlier in the text that information on the local composition such concentration of surface active and other reacting elements along the interface and towards the bulk are important to evaluate the relative importance of the capillary effects. The presence of surface active elements such as oxygen at the interface significantly lowers the interfacial tension and may create interfacial tension gradients along the interface. An attempt has been made in studying the solute oxygen distribution by using dynamic secondary ion mass spectrometry (Rhamdhani and Brooks, 2003). Solute-oxygen depth and lateral profiles of samples generated from reactions between Fe-Al droplets and CaO-SiO$_2$-Al$_2$O$_3$ slag were determined. The results suggest the 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, which correspond to the interfacial tension decrease of 189 to 330 mN/m.

Using these information along with the kinetics and interfacial area data above, Rhamdhani et al. (2005b) evaluated the relative importance of the electrocapillary, solutocapillary and thermocapillary effect on interfacial tension change during reaction between liquid Fe-Al alloy and liquid CaO-SiO$_2$-Al$_2$O$_3$ slag. These capillary effects and the dynamic interfacial tension depression were determined using a local equilibrium model utilizing the kinetic data.
Figure 5 shows the effects of temperature, electrical potential and oxygen on the dynamic interfacial tension during the reaction between 2.5g Fe-4.45wt%Al and CaO-SiO$_2$-Al$_2$O$_3$ slag. It can be seen from the graph that the effect of temperature is very small and can be neglected. The dominant effect in the system comes from the electrocapillary effect especially during the period before emulsification when the rate of mass transfer is the highest, i.e. up to 15 minutes. A mechanism involving the electrocapillary effect as proposed by Richardson (1982) to explain the lowering of interfacial tension appears to be most significant. The contributions of electrocapillary and solutocapillary effects at the maximum interfacial tension depression are about 85% and 15%, respectively. Also shown in Figure 5, is the combined effect on the dynamic interfacial tension depression during the reaction.

VI. FUTURE DIRECTIONS

The previous studies described above have brought tools for further understanding of the dynamic interfacial phenomena. Further works need to be done for the comprehensive understanding of dynamic interfacial phenomena. Systematic experimental study to provide new data (dynamic interfacial tension, interfacial area, chemistry changes) to demonstrate the effects of key process variables such as kinetics and thermodynamic driving forces and physicochemical properties; the development of predictive model for interfacial area changes and computational fluid dynamic modelling on the interfacial instability leading to spontaneous emulsification also plays an integral part in the development of the complete theory.

As has been shown that electrocapillary effect plays the dominant role in the case of high temperature reactions between iron alloys and slags, much emphasis must be put on the understanding of the kinetics of electrochemical reactions and its relations to the interfacial phenomena and interfacial area generation.

VI. SUMMARY

Review on the previous studies, the present understanding, and future directions on the fundamental understanding of dynamic interfacial phenomena occurring in high temperature metal-slag reactions have been presented. Challenges and difficulties faced have also been outlined. The studies up to date have provided a first base for understanding of dynamic interfacial phenomena, however, do not fully explain all of the observations of the phenomena. There are insufficient data available at present to accurately determine the factors resulting in the onset of interfacial phenomena including droplet emulsification. From a scientific point of view, there is a need to develop a general theory that connects and explains all the observed phenomena. Understanding the
phenomena, including the ability to control them, is also important for the improvement of existing technologies toward more energy efficient processes, as well as for the development of new processes.

REFERENCE


