# THE INTERFACE IN SLAG REACTIONS; A MOVING TARGET

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## ABSTRACT

*A knowledge of surface area is key to modeling the kinetics of many high temperature processes. In the case of reactions with slags the surface area may change during the course of the reaction in ways that we are currently not able to predict. In the current paper the authors discuss three examples from their own work and highlight the progress made and challenges still to be addressed.*

*In the case of reaction of single metal droplets with slags, it is shown that the free energy provided by the reaction can be correlated directly with surface area. No explanation is offered for this phenomenon because the free energy involved is several orders of magnitude greater than that required to create a new surface.*

*In the case of droplet generation in the BOF and carbon injection into slag the active surface is a balance between that created and the time for it to be annihilated or become inactive. In the case of the BOF we now have a good understanding of droplet generation and on-going work to predict droplet residence time is described. The interface in slag reactions is certainly a moving target but there is good reason to expect progress in this area.*

# INTRODUCTION

For many years researchers in the field of slag-metal-gas reactions have recognized the uncertainty surrounding the interface [1, 2, 3, 4, 5, 6]. There is uncertainty in the reactivity of the interface, the area of the interface and way in which both can change over the course of a reaction. Together, these phenomena conspire to frustrate the practitioner of slag-metal kinetics. Many workers have studied the reaction between slags and gases and shown that reactivity changes as the chemistry changes with reaction [7, 8, 9, 10, 11, 12, 13]. Because of the extensive work in this area, we are reasonably well equipped to accommodate this changing reactivity within kinetic models. We can also accommodate changes in the physical area of the interface [6], provided we have quantitative knowledge of the change. The most significant challenge lies in predicting the way in which the area of the interface will change as the reaction progresses. The current paper will discuss three examples from the authors' laboratories, highlighting recent progress in this area and identifying barriers still to be overcome.

## Changes in Interfacial Area Induced by Chemical Reaction

Perhaps the most famous example of the changing nature of the interface is that reported by Riboud and Lucas [3]. In their work they show how the interfacial area of an iron-aluminum alloy droplet reacting with an oxidizing slag, changes as the reaction progresses. They evaluate the so called "dynamic interfacial tension" and show that at high reaction rates this drops to zero, recovering to an equilibrium value as the reaction reaches completion. Other workers have shown that similar behaviour is observed for iron droplets alloyed with a range of reactive elements.[4, 5] Three of the present authors [14] attempted to identify the source of the "dynamic interfacial tension" by evaluating the magnitude of the various capillarity effects that exist in a reacting system. Figure 1 shows a comparison between the observed "dynamic interfacial tension" of Riboud and Lucas, and the contributions calculated for soluto-capillary, thermo-capillary and electro-capillary effects.

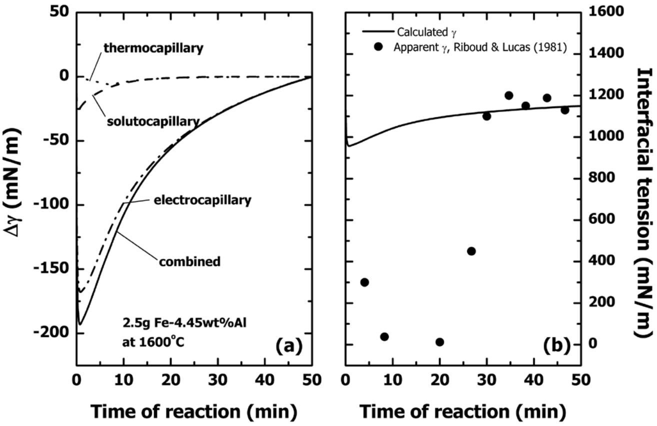

Figure 1: (a) Calculated change in interfacial tension of reactive iron drops due to the thermo-capillary, solute-capillary and electro-capillary effects; (b) comparison between the predicted decrease in interfacial tension with that observed by Riboud and Lucas [3].

It can be seen that the calculated value for interfacial tension decreases as the reaction progresses and then recovers to its original value as the reaction reaches completion. However, the magnitude of the calculated effect, is considerably lower than that observed. The authors suggested that perhaps the observed “dynamic interfacial tension” is not in fact the interfacial tension, but is a balance between the interfacial tension and other forces introduced as a consequence of the reaction. There is indirect support for the concept of dynamic interfacial tension from gas bubble nucleation in liquids. Several workers have shown that gas bubbles nucleate in metals at supersaturation pressures several orders of magnitude less than predicted. This phenomenon is also observed in aqueous and alcohol based systems but only for the nucleation of solute gases. When self-nucleation of vapours is involved, for example in the boiling of water, bubbles nucleate at the predicted supersaturation pressures [16]. Some workers have shown that in the reacting systems, agreement can be achieved by decreasing the value of the interfacial tension used in the calculations. As this only seems to apply in systems where there is a reaction, it would appear to support the concept of dynamic interfacial tension.

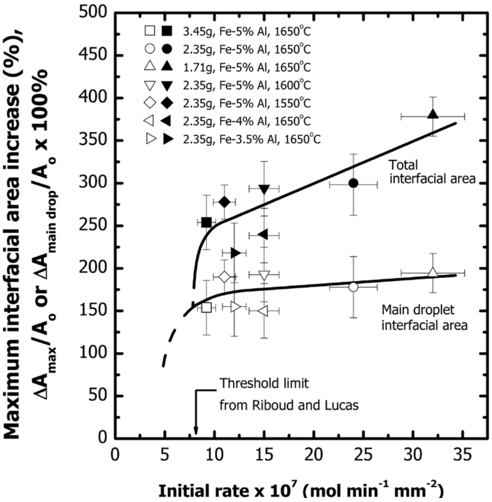

Figure 2: Percent increase in surface area as a function of initial reaction rate, for iron-aluminum droplets reacting with slag

Rhamdhani, Brooks and Coley [15] tried to relate the changes in surface area to the rate of reaction and the free-energy changes during the reaction. It appears from Figure 2 that reaction must exceed a certain threshold value before a significant change in surface area is induced. This result is in keeping with the work of Riboud and Lucas [3]. It is also interesting to note that initial increase in surface area is obtained by roughening of the droplet but after a certain rate is exceeded any further increase is achieved by breaking off, additional droplets. The rate of increase of area due to additional droplets is directly proportional to the rate of reaction, suggesting that the energy released in the reaction is somehow responsible for the increase in surface area. The fact that beyond a certain reaction rate, new droplets form in favour of distortion of the parent droplet, suggests that there is some critical energy required to fracture the parent droplet. This concept is similar to the concepts employed in fracture mechanics of solids.

On the assumption that the energy released by the reaction was responsible for increasing the interfacial area in the system, Rhamdhani *et al.* [15] correlated the increase in interfacial area with the energy released by the reaction. As shown in Figure 3, there is a very strong correlation between the area increase and the energy dissipated by the reaction, in this case the symbol, λ, represents the free energy change up to that point in the reaction. However, if we evaluate the slope in Figure 3 we find that the energy released, is several orders of magnitude greater than that required to create new surface area.

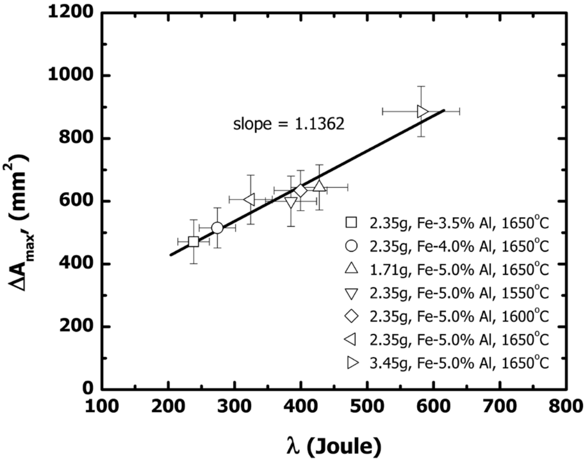

Figure 3: Change in area for reacting droplets as a function of the free energy dissipated during the reaction

## Changes in Interfacial Area Induced by External Stirring

Basic Oxygen Steelmaking can be considered one of the most significant advances in process metallurgy of the twentieth century. One of the keys to the process is the intimate slag-metal mixing created by the supersonic oxygen jet. The impact of the jet generates numerous metal droplets which enter the slag and are refined by reaction with iron oxide. As part of a major effort to develop a kinetic model for the process, Subagyo *et al.* [17] reanalyzed the cold-modeling work of He and Standish [18] and the extension of this work by Deo and Boom [19] in the context of the Kelvin-Helmholtz criterion or interfacial instability. This criterion is stated in Equation 1 [20].

$$\frac{\rho_G u_G^2}{2\sqrt{\sigma g \rho_L}} = 1.0 \tag{1}$$

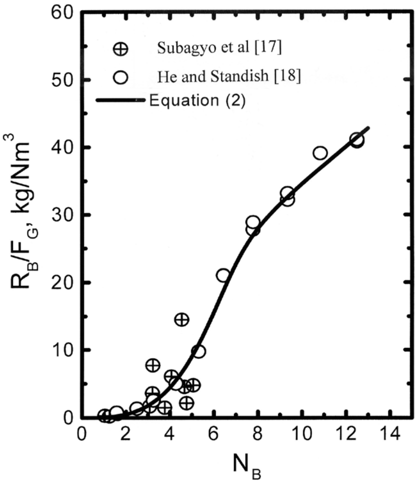

Figure 4: Rate of droplet generation per Nm3 of gas as a function of blowing number

Where $\rho_G$ is the gas density, $\rho L$ is the density of the liquid, $u_G$ is the critical gas velocity, $\sigma$ is the surface tension of the liquid and g is the acceleration due to gravity. Subagyo et al. suggested that the left hand side of Equation 1 should be termed the Blowing Number and given the symbol $N_B$, and that this number would then provide a measure of the extent to which the critical jet velocity for the formation of droplets was exceeded. Figure 4 shows the rate of droplet generation in kg per $Nm^3$ of gas, as a function of blowing number. The correlation given in Equation 2 shows excellent agreement for both cold modeling work of He and Standish and the high temperature data of Subagyo *et al*.

$$\frac{R_B}{F_G} = \frac{(N_B)^{3.2}}{\left[2.6x10^6 + 2.0x10^{-4}(N_B)^{12}\right]^{0.2}} \tag{2}$$

Where $F_G$ is the volumetric flow of blown gas in normal cubic meters per second and $R_B$ is the droplet generation rate in kilograms per second. Subagyo et al. also showed that the droplet size distribution could be described by parameters that are correlated with the blowing number.

Having established the rate of droplet generation and the size distribution of the droplets it should now be possible to determine the slag-metal interfacial area. However, droplet content in the slag is a balance between the rate of generation and the rate of settling back into the bath. Subagyo *et al.* [21] invoked Stokes Law to estimate the residence time of droplets as a function of droplet size, however, these workers found that the predicted residence times were at least an order of magnitude too short to justify refining rates. Following the work of Molloseau and Fruehan [22], Brooks *et al.* [23] recognized that swelling of droplets induced by CO evolution resulted in much lower densities than those of fully dense droplets. These workers used the data of Molloseau and Fruehan to predict the change in density with droplets over their residence time in the slag. The Bloated Droplet Model, developed by Brooks *et al.* showed remarkable agreement with the residence times estimated from refining rates. Droplet residence times predicted from this model are compared in Table 1 with estimates of other workers based on refining rates.

Table 1: Comparisons of bloated droplet motion model predictions with laboratory experiments and plant measurements/ estimations on the residence time of metal droplets in slag in top blown oxygen steelmaking

| **Investigators** | **Methods** | **Residence time (s)** |
|---|---|---|
| Schoop *et al.* [24] | Indirect plant measurement from which the residence time was calculated based on chemical analysis and kinetic model. | ~ 60 |
| Price [25] | Plant measurement with radioactive gold isotope tracer technique. | 120 ± 30 |
| Kozakevitch [26] | Prediction based on the carbon and phosphorus contents in metal droplet from plant measurement. | 60-120 |
| Brooks *et al.* [23] | Bloated droplet motion model predictions on experimental cases of Molloseau and Fruehan [22] and Min and Fruehan [27] | 10 – 200 |
| Brooks *et al.* [23] | Bloated droplet motion model predictions on residence time of metal droplets with 4.0 wt.%[C] in slag containing 15 wt.%FeO | 45 – 75 |

Currently the Bloated Droplet Model is limited by an absence of data to predict the extent of droplet swelling as a function of chemistry. On going work in one the authors labs, reported in part in another paper in this symposium [16] is aimed at developing a model to describe droplet swelling. Initial results have shown that the gas generation within the droplets can be described by classical equations for bubble nucleation, provided a modified surface tension is used.

## Surface Area Development during Coal Injection into Slags

Slag foaming in the electric arc furnace is practiced routinely in order to reduce energy losses from exposed arcs. Foaming of slags has been well studied [28, 29, 30, 31] and effective models have been developed to predict the extent of foaming based on a knowledge of slag composition, temperature and the rate of gas evolution. At present the primary barrier to predicting optimum foaming practice is in knowing how much gas will be evolved and the appropriate balance of carbon and oxygen injected into the furnace. A schematic of the proposed reaction mechanism for the reaction of a single carbon particle with slag is shown in Figure 5. Ji *et al.* [32, 33] have shown that at higher iron oxide contents, typical of electric furnace slags, the reaction is controlled by a combination of $CO_2$ reaction with the carbon particle and CO reaction with the slag. There are good quality data available in the literature for the kinetics of both these reactions [9, 13, 34]. However, one must also know the relative areas of the slag and carbon surfaces, which will change with the progress of the reaction. Also, if the physical picture is different from that presented in Figure 4 and either multiple particles exist inside a single bubble, or multiple bubbles are attached to a single particle, the analysis becomes more complicated. In the latter case, one also has to consider whether all the bubbles remains attached to the particle for the duration of the reaction. In addition, the cumulative contribution of many particles and many bubbles has to be considered.

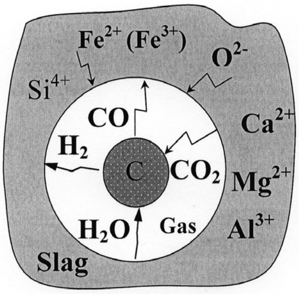

Figure 5: Schematic representation of the reaction between a carbon particle and slag

Ji *et al.* [32, 33] have developed an empirical model that evaluates the balance between the reaction at the slag gas interface and the gas/carbon interface. These authors have successfully employed this model over a range of conditions for pilot scale carbon injections. Ji *et al.* [33] found that the bubble size, $d_b$, in slags foamed by carbon injection was consistent with that predicted using Equation 3 from the work of Jiang and Fruehan [28], where $\mu$ is the viscosity of the slag, $\sigma$ is the surface tension, $\rho$ is the density of the slag, and $\Sigma$ is the foaming index for the slag.

$$d_b = \left( \frac{115\,\mu^{1.2}}{\sigma^{0.2}\rho\Sigma} \right)^{1.11} \tag{3}$$

If the volume -average bubble diameter is known in addition to the volume of the foamy slag, the total surface area of bubbles in the slag, $A_{tot}$, can be determined. By comparing the measured rates of reaction during carbon injection, with literature values of the rate constant, Ji *et al.* were able to calculate the active slag surface area, $A_S$. Figure 6 shows the ratio of active slag surface area to total bubble surface area as a function of carbon injection rate. Clearly from this figure a significant percentage of the bubbles in a foamy slag are not active. This is either because bubbles become detached from the carbon particles or because bubbles survive in the foam beyond the life of the carbon particle in that bubble. The fact that the fraction of active bubbles increases with injection rate suggests the latter explanation is more likely. Work is currently underway in one of the Author's laboratories to develop a fuller understanding of this phenomenon [35].

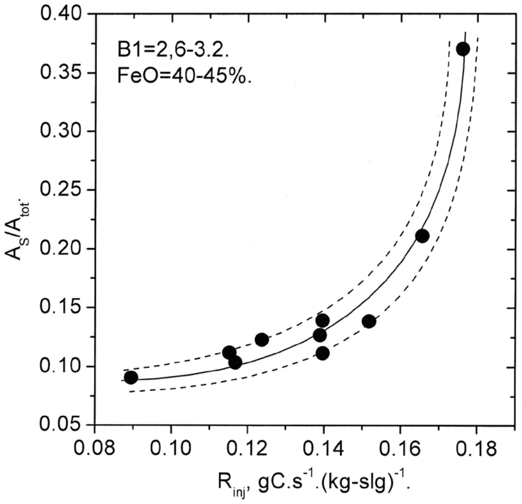

Figure 6: Ratio of active slag surface to total bubble surface in foamy slag

## CONCLUSIONS

Slag surface area is a *moving target* which can change dramatically over the course of a reaction, either because of external influences such as gas jets or because of the reaction itself. In many cases the area of the reaction interface is the greatest unknown in developing kinetic models. Although there is much still to be done, progress is being made and the Authors hope that their work has encouraged others to pursue this important area of research.

## ACKNOWLEDGEMENTS

The authors would like to thank Mr. O. Kelly, Mr. G. Bishop, for their help during the experimental work described in this paper, and NSERC and the members of The McMaster Steel Research Centre, who funded most of the work discussed in this paper.

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