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Interfacial tension effects on slag–metal reactions

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Dynamic X-ray imaging of a metal droplet in a slag phase is an elegant way to monitor the rate of the interfacial reactions. In an attempt to follow the kinetics of dephosphorization, the changes in the shape of the sessile drop of molten iron with 0.1 wt% P immersed in a slag kept in MgO crucibles were recorded as a function of time. The slag had an initial composition 40 wt% CaO, 30 wt% SiO_2 and 30 wt% Fe_2O_3. While in a set of runs, solid iron was added to the molten slag, the sequence was reversed in others, where a pellet of the slag was added to the molten iron. In the former case, it was found that after 10 s, the drop flattened and the contact angle, θ was well below 90°, indicating a significant increase in the contact area. Beyond 250 s, the contact angle showed a gradual increase. In the second series, where the slag was added to the metal, the contact angle remained high throughout the dephosphorization reaction, indicating a rapid mass transfer of phosphorus.

Similar application in the field of copper metallurgy, where the transfer of arsenic and antimony from copper metal to molten Na_2CO_3 was studied, confirm that this technique is very useful in understanding the mechanisms of the slag–metal reactions.

Keywords: Marangoni flow; surface tension; contact angle; sessile drop; slag–metal reactions; metal refining

1. Introduction

In modern processes, such as bath smelting and basic oxygen steelmaking, fast reaction kinetics are obtained by creating an emulsion of metal in the slag phase, leading to a large surface-area/mass ratio. In experiments carried out at the beginning of the century on the formation of emulsions, NaOH was injected onto opposite sides of a drop of gear and rape seed oil. The NaOH saponified the oil and the mass transfer resulted in, sequentially, a low interfacial tension, large surface tension gradients around the drop, Marangoni–Behara flows, turbulance and disintegration of the oil globule into a fine emulsion. Work carried out by Kozakevitch (1957) indicated that the desulphurization of iron was accompanied by a rapid decrease in the slag–metal interfacial tension. Subsequent results obtained by Gaye *et al.* (1984) indicated that for slag–metal reactions, rapid mass transfer was accompanied by a sharp decrease in interfacial tension γ_{MS} to a very low value and when the mass transfer gradually decreased, the interfacial tension increased to its original value. Obviously, a low interfacial tension would encourage emulsification and faster kinetics. It was our

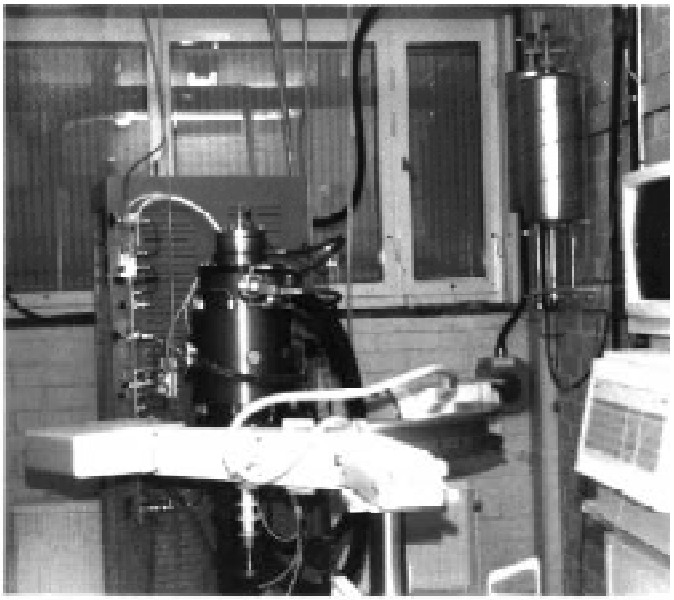

Figure 1. The sessile-drop unit.

aim in this investigation to see what effects the interfacial characteristics had on the kinetics of certain slag–metal reactions:

(i) the dephosphorization of iron to see if P, which is less surface active than S, would have the same effect on γ_{MS}; and

(ii) the removal of As and Sb from liquid copper to see if the dramatic decrease in γ_{MS} also occurred in non-ferrous systems.

2. Experimental aspects

The X-ray image analyser used for the dynamic interfacial tension studies is shown in figure 1. The X-ray unit is a Philips BV-26 imaging system with an X-ray source of 40-105 kV. The X-ray tube has a focal spot size that varies between 0.6 and 1.5 mm. The imaging system consists of a CCD camera, with a digital noise-reduction. The unit is capable of detecting dynamic movements and has a storage capacity of 34 images. The recording system consists of an IBM-PC equipped with a video card to monitor and record the X-ray images at a maximum rate of 12 pictures per second. The graphics have a resolution of 575×900 matrix. The system can store 192 images with a video memory of 32 images.

The furnace used in the equipment was acquired from Thermal Technology Inc. (model 1000-3500-FP20). It is equipped with graphite heating elements (effect = 20 kVA) and is capable of attaining a maximum temperature of 2300 °C. The furnace is controlled by a Raytek single-colour optical pyrometer. The outer jacket of the furnace is provided with quartz windows of 40 mm diameter on either side for the X-rays from the source and the detector. The reaction tube inside the furnace is made of recrystallized Al_2O_3. Appropriate radiation shields are provided to ensure a good even-temperature zone, the length of which is about 100 mm in the middle of the furnace. The assembly is capable of operating under vacuum, inert gas or gas mixtures. Appropriate gas-cleaning trains have been assembled to ensure that

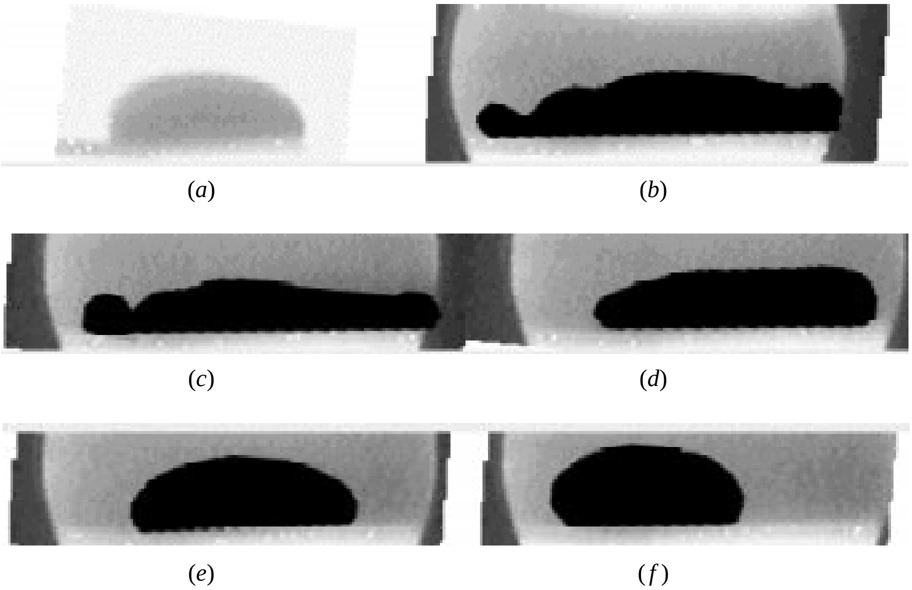

Figure 2. X-ray images of an iron drop with 0.1 wt% P in a slag of initial composition 40 wt% CaO–30 wt% SiO_2–30 wt% Fe_2O_3 in an MgO crucible at various time intervals (solid slag was added to liquid metal).

the impurity levels are very small. A ZrO_2–CaO oxygen probe is mounted at the outlet side of the experimental unit in order to monitor the oxygen partial pressures continuously.

3. Study of dephosphorization reactions (Nasu *et al.* 1997)

(*a*) *Experimental procedure*

The dephosphorization studies were carried out by following the change in shape of a sessile drop of molten iron containing 0.1 wt% P. The slag used had the initial composition of 40 wt.% CaO + 30 wt% SiO_2 + 30 wt% Fe_2O_3. The choice of the crucibles was limited; zirconia, as well as thoria, crucibles could not be used as they were opaque to X-rays. With alumina crucibles, Al_2O_3 pick-up was excessive. Some preliminary experiments were carried out with boron nitride crucibles, but the results had to be discarded due to the low dephosphorization levels, presumably due to the reaction with the crucible forming a silico-borate slag. The only choice of crucible material was MgO and three experiments were performed with MgO crucibles. The experiments were carried out in two different ways:

(a) addition of a slag-compact to the molten metal; and
(b) addition of solid metal to the liquid slag.

(*b*) *Results and discussion*

(i) *Addition of solid slag to the liquid metal*

Figure 2*a* shows the initial molten Fe–P alloy just before the slag was added. It is seen that the contact angle between the molten metal drop and the MgO base of the crucible is greater than 90°. With the gas atmosphere prevailing over the metal, the metal is non-wetting with respect to the crucibles. At 10 s the drop has flattened and θ is quite low ($\theta \ll 90°$), as can be seen in figure 2*b*. As the slag replaces the

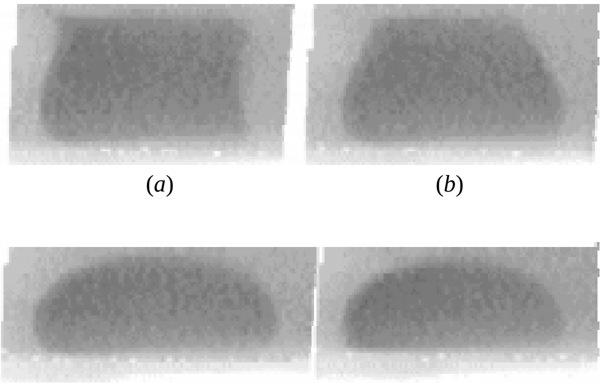
(a) (b) (c) (d)

Figure 3. X-ray images of an iron drop with 0.1 wt% P in a slag of initial composition 40 wt% CaO–30 wt% SiO_2–30 wt% Fe_2O_3 in an MgO crucible at various time intervals (solid metal was added to liquid slag).

gas atmosphere surrounding the metal droplet, there is a significant drop in the interfacial tension (γ_{MS}) between the metal and the slag. As mentioned earlier, this would lead to an increase in the contact area between the two phases with high mass-transfer conditions. These conditions favour emulsification of the metal drop in the slag. This is evident at higher reaction times when the metal drop develops a neck. This situation is illustrated in figures 2*c*, *d*, corresponding to 70 and 231 s, respectively. Even slight disturbances at this stage can lead to the breaking of the drop at the neck thus increasing the interfacial area further. However, beyond 278 s, the shape of the drop changes resulting in an increase in the contact angle and the interfacial tension. It can be expected that the intense mass-transfer step may have slowed down very much and the system is near equilibrium conditions.

The initial rapid decrease in the interfacial tension during a rapid mass-transfer step followed by a gradual increase in the interfacial tension is similar to the interfacial phenomenon changes observed in the case of desulphurization. Kozakevitch (1957) has shown that due to the transfer of sulphur from a drop of iron containing carbon and sulphur to a $CaO–Al_2O_3–SiO_2$ slag at 1550 °C, the interfacial tensions may even decrease to 5 dyne cm^{-1}. The reason for this drop is attributed to the simultaneous transfer of Fe and S to the slag phase as Fe^{2+} and S^{2-} ions, providing probably a good bonding between the metal and slag phases in this process. In order to visualize a similar mechanism in the case of the transfer of P from iron metal to the slag, further experimentation may be necessary.

(ii) *Addition of solid metal to liquid slag*

Figure 3*a* shows the solid metal added to the molten slag. The contours of the unmelted metal pellet are clearly seen in this figure. After 30 s, the metal phase is molten (figure 3*b*). The contact angle between the metal and the slag is high and so consequently is the interfacial tension. This situation remains the same throughout (figures 3*c*–*f*). This could perhaps be indicative of the end of the rapid mass-transfer step within the first 30 s, even as the solid metal melts forming the drop. This would mean that the mass transfer of P in molten iron is rapid and cannot be the rate-determining step.

Looking at the two experiments together, it is interesting to know why the reaction is slow when the solid slag is added to the metal. If the fusion of the slag is a slow

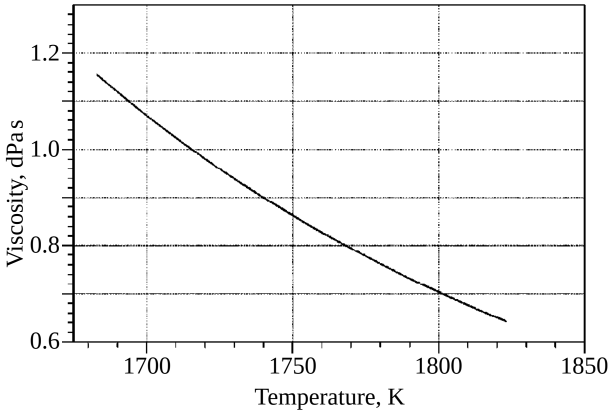

Figure 4. Variation of the viscosity of CaO–FeO–SiO_2 slag as a function of temperature in the range 1420–1550 °C.

process, then the amount of liquid slag available for dephosphorization would be limited, thus a slower dephosphorization rate. However, this possibility seems unlikely as the experimental temperature of 1550 °C is greatly above the liquidus temperature of the initial slag according to the literature (Kowalski *et al.* 1995). Another important factor may be the high viscosity of the slag as the molten slag heats up. The effect of temperature on the viscosity of the present slag in the temperature range 1410–1550 °C, assuming all iron oxide present is in the form of FeO, as calculated by the viscosity model available in the Division of Theoretical Metallurgy (Seetharaman & Du 1997) is shown in figure 4. It is seen that the viscosity decrease is substantial as the temperature rises. If this affects the rate of the reaction, it would lead to the conclusion that the dephosphorization reaction is likely to be controlled by the mass transfer in the slag phase.

4. Study of As and Sb transfer from molten copper to liquid Na_2CO_3

The abatement of As and Sb from copper is followed by changes in the oxygen content of the Cu melt. Oxygen is a strong surface-active element in liquid copper, as shown by Monma & Suto (1961). Thus, de-arsenification and de-antimonization can be expected to be accompanied by changes in the interfacial tension.

(*a*) *Experimental procedure*

Copper metal containing As or Sb was premelted in the sessile drop unit in Al_2O_3 crucibles at 1200 °C. The atmosphere was purified argon. Solid Na_2CO_3 was added from the top and the changes in the drop shape were observed. Some experiments were performed in CO_2 atmosphere instead of Ar.

(*b*) *Results and discussion*

Figure 5*a* shows the initial shape of the copper drop containing 0.2 wt% $\underline{O}$ and 0.56 wt% As in Ar atmosphere before the addition of the slag. After 23 s of Na_2CO_3 addition, a momentary decrease in the interfacial tension was observed, as seen in figure 5*b*. However, this momentary decrease was not reproducible and needs further experimentation. The shape of the drop was restored to its original shape very quickly at 72 s and remained so even after 372 s (figure 5*c*–*f*). In a parallel chemical kinetics experiment carried out at Imperial College (Mangwiru & Jeffes, personal

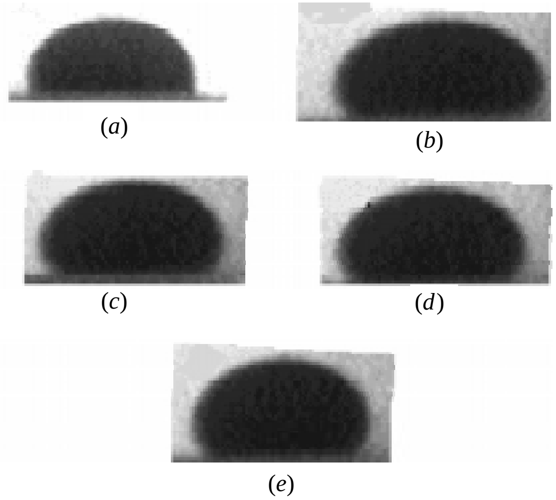
(*a*) (*b*) (*c*) (*d*) (*e*)

Figure 5. X-ray images of an coppar drop with 0.2 wt% O and 0.56 wt% As in an Na_2CO_3 melt kept in an Al_2O_3 crucible at 1200 °C at various time intervals in an Ar atmosphere (solid Na_2CO_3 was added to liquid metal).

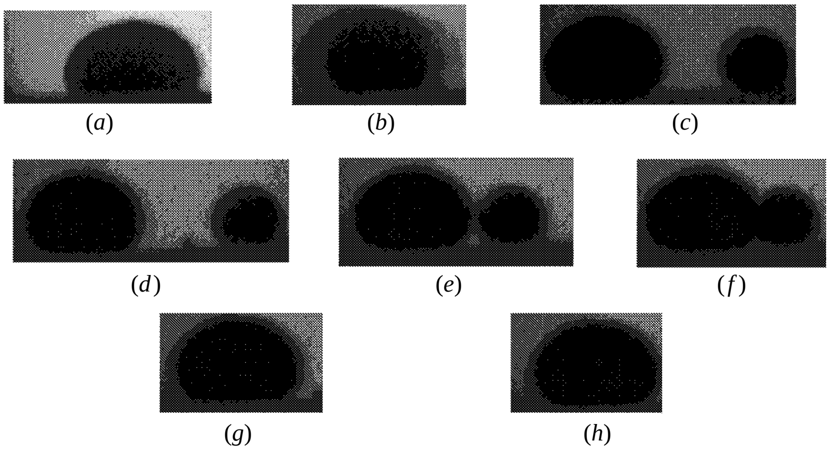
(*a*) (*b*) (*c*) (*d*) (*e*) (*f*) (*g*) (*h*)

Figure 6. X-ray images of an coppar drop with 0.2 wt% O and 0.56 wt% As in an Na_2CO_3 melt kept in an Al_2O_3 crucible at 1200 °C at various time intervals in a CO_2 atmosphere (solid Na_2CO_3 was added to liquid slag).

communication) by sampling and analysis, it was found that at the initial oxygen and arsenic levels in the copper metal, the arsenic removal was over within the first 100 s, which explains the difficulty in reproducing the rapid changes in the drop shape. In one of the experiments where CO_2 atmosphere was used, the splitting of the drop was noticed (figures 6*a*–*h*), which indicates the excessive mass-transfer reaction. The observations in the case of de-antimonisation were somewhat similar.

5. Summary

Dynamic interfacial tension studies are found to be very useful tools in following the metal–slag reactions and correlating the changes in the interfacial tensions and the reaction mechanisms. It was found that, with a sensitive sessile-drop unit, it should be possible to record the reaction sequences even during very short intervals of time. This provides an entirely new perspective of the micromechanisms of metal–slag reactions. It is hoped that, with parallel work at different laboratories in the world to ensure the reliability of the technique and the accuracy of the results, the sessile-drop technique will enable a better understanding of the kinetics and mass transfer phenomena in metal–slag reactions.

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