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Direct observation of spontaneous emulsification and associated interfacial phenomena at the slag–steel interface

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Interfacial tension decreases drastically when an intense chemical reaction occurs at a steel–slag interface. This phenomenon results in spontaneous droplet spreading during the initial period of reaction and droplet recovery as the rate of reaction decreases. In the present work, spreading tendency was found to be associated with spontaneous emulsification of both steel in slag and slag in steel. Spontaneous emulsification was observed at 1550 °C when a liquid Fe–3.28%Al alloy droplet was placed in contact with liquid $CaO–SiO_2–Al_2O_3$ (40:40:20 by weight) slag.

Surface turbulence induced metal emulsification and droplet spreading was observed by X-ray photography. Spontaneous droplet spreading was noted at alloy aluminium contents as low as 0.25%. Spontaneous emulsification was steel into slag was documented at aluminium contents greater than 3%. From the observation of quenched Fe–3.28%Al alloy droplets by optical and scanning electron microscopy, slag entrapment and metal emulsification were documented and the metal–slag interface was shown to be extremely perturbed during the reaction of aluminium with silica.

Keywords: X-ray photography; spontaneous emulsification; interfacial tension; steel–slag interface; casting

1. Introduction

When a chemical reaction takes place between a droplet of a liquid steel alloy and a liquid slag a number of investigators (Kozakevitch *et al.* 1955; Ooi *et al.* 1974; Riboud & Lucas 1981; Sharan & Cramb 1995; Liukkonen *et al.* 1997; Gaye *et al.* 1984) have found that the droplet spontaneously spreads on its substrate and then, after an amount of time, spontaneously recovers its equilibrium shape. Most investigators have calculated the apparent interfacial energy of the droplet during spreading by assuming that the Young–Laplace equation still holds during spreading and that the droplet remains symmetrical. Under these assumptions it appears that the interfacial energy is decreasing rapidly during reaction.

This phenomenon may be important when aluminium is added to a molten steel in contact with silicate slag, a common occurrence during either steel deoxidation or slag 'killing' (when aluminium is added in bulk to the slag covering on top of a steel ladle to reduce the iron and manganese oxide content of the slag). Few studies of dynamic interfacial phenomena have been carried out on steel alloys with less than 4% aluminium in contact with silicate slags. In this study, observation of dynamic interfacial phenomena was carried out with the aid of X-ray photography at a range

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Table 1. *Reactions for which a drastic decrease of interfacial tension has been observed (Riboud & Lucas 1981)*

metallic alloys	slag	reaction
Fe–Al	$CaO–SiO_2$ (or $–Al_2O_3$)	$2\underline{Al} + \frac{3}{2}SiO_2 = Al_2O_3 + \frac{3}{2}\underline{Si}$
Fe–Al	$CaO–Al_2O_3–Fe_2O_3$	$2\underline{Al} + Fe_2O_3 = Al_2O_3 + 2\underline{Si}$
Fe–C–S	$CaO–Al_2O_3–SiO_2$	$\underline{S} + (O) = (S) + \underline{O}$
Fe–Ti	$CaO–Al_2O_3–SiO_2$	$\underline{Ti} + SiO_2 = TiO_2 + Si$
Fe–P	$CaO–Al_2O_3–Fe_2O_3$	$2\underline{P} + \frac{5}{3}Fe_2O_3 = P_2O_5 + \frac{10}{3}Fe$
Fe–B	$CaO–Al_2O_3–SiO_2–Fe_2O_3$	$2\underline{B} + Fe_2O_3 = B_2O_3 + 2Fe$
Fe–Cr	$CaO–SiO_2–FeO$	$2\underline{Cr} + 3FeO = Cr_2O_3 + 3Fe$
Fe	Cu_2O	$Fe + Cu_2O = 2\underline{Cu} + FeO$
Fe–Si	$Cu_2O–Al_2O_3$	$\underline{Si} + 2Cu_2O = SiO_2 + 4\underline{Cu}$

of aluminium contents (0.25–3.28%) in steel alloy droplets in contact with $CaO–SiO_2–Al_2O_3$ (40:40:20 by weight) at 1550 °C.

Dynamic phenomena (droplet spreading and recovery) was documented at aluminium contents as low as 0.25% and clear evidence of spontaneous emulsification was seen in steel alloys containing greater than 3% aluminium.

2. Background

Interfacial tension (or energy), an equilibrium thermodynamic quantity, has been determined by many investigators (Gaye *et al.* 1984; Ogino *et al.* 1984; Kawai *et al.* 1982; Gammal & Schoneberg 1992; Jimbo & Cramb 1992; Liu *et al.* 1993; Jimbo *et al.* 1995, 1996), and ranges from 300 to 1700 $mN\,m^{-1}$ when steels are in contact with slags. The lowest values are found when oxygen saturated iron is in contact with an FeO containing slag (Ogino *et al.* 1984; Kawau *et al.* 1982). Apparent interfacial tensions, calculated during droplet spreading, decrease to lower than 100 $mN\,m^{-1}$ where a reaction between an element in the alloy and a slag component occurs. Since Kozakevitch *et al.* (1955) first reported this dynamic interfacial phenomenon between an iron, carbon and sulphur alloy and a blast furnace type slag in 1955, several investigators have reported dynamic droplet spreading in steel–slag systems (Ooi *et al.* 1974; Riboud & Lucas 1981; Sharan & Cramb 1995; Liukkonen *et al.* 1997). Riboud & Lucas (1981) measured the apparent interfacial tension between a number of metallic alloys in contact with slag systems. They observed the lowering of interfacial tension for the reactions between metallic alloys and slags shown in table 1.

Recently the effect of sulfur transfer has been shown to affect results of equilibrium interfacial energy determinations even when no droplet spreading can be determined (Jimbo *et al.* 1995, 1996).

Due to its industrial significance, a number of investigators have focused on the dynamic phenomena that can be observed when an liquid Fe–Al alloy droplet is in contact with a silicate slag. Figure 1 shows the summarized results of previous investigators (Ooi *et al.* 1974; Riboud & Lucas 1981; Sharan & Cramb 1995; Liukkonen *et al.* 1997). As can be seen in figure 1, three distinct periods can be observed: (1)

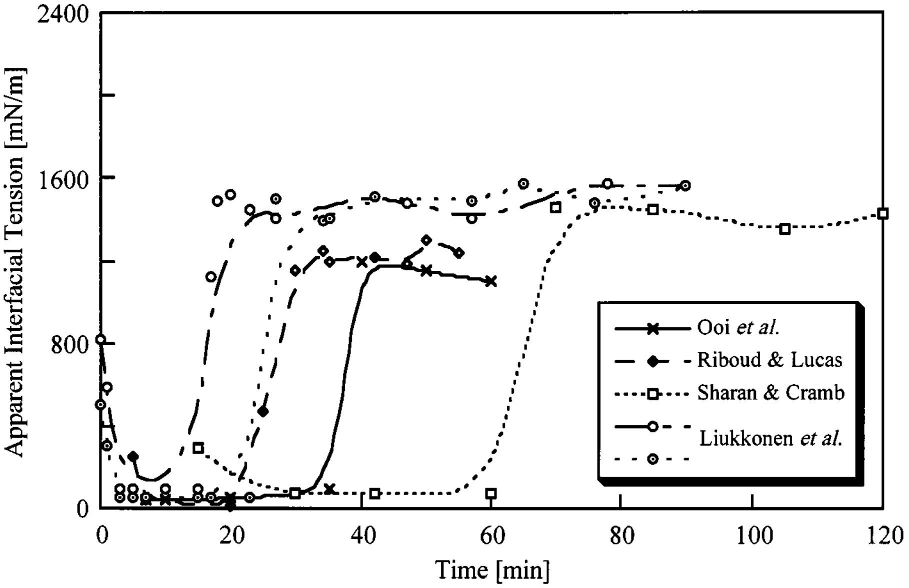

Figure 1. Dynamic interfacial phenomena observed by previous investigators.

an initial transient period where the droplet dynamically spreads and the apparent interfacial energy decreases; (2) a period of very low interfacial energy where droplet spreading stops, but the droplet remains flattened; and (3) a recovery period where the droplet returns to its equilibrium shape. In most cases, the transient period finishes within 5 min. The duration time of the period of low interfacial energy ranges from 15 min up to 1 h and during this time apparent interfacial tension values were measured to be less than 100 mN m^{-1}. The recovery period has a different start time depending on the study; however, in all cases the recovering rate was very rapid (less than 5 min). Ooi *et al.* (1974) were the first to observe spontaneous droplet spreading and an apparent lowering of the interfacial tension for Fe–Al alloy droplets containing more than 4% initial aluminium content in contact with $CaO–SiO_2–Al_2O_3$ slags. They determined that an aluminium content of greater than 2% was necessary to induce dynamic interfacial phenomena. They also suggested that droplet dynamic phenomena were due to the reduction of silica in the slag by aluminium dissolved in the iron and that the rate controlling step was the chemical reaction at the interface. They did not observe dynamic phenomena between an Fe–Al droplet containing 9.8% aluminium and a $CaO–Al_2O_3$ slag which indicated that the following reaction was responsible for the dynamic effects:

$$4\underline{\mathrm{Al}} + 3(\mathrm{SiO_2}) = 3\underline{\mathrm{Si}} + 2(\mathrm{Al_2O_3}) \tag{2.1}$$

Riboud & Lucas (1981) also reported droplet spreading between Fe–4.45%Al alloys and a $CaO–SiO_2–Al_2O_3$ slag and suggested that the apparent interfacial tension tends to zero when the oxygen flux is larger than about 0.1 g atom m^{-2} s^{-1}. Under this condition, they also suggested that dispersion of one phase into the other may occur spontaneously. By microscopic observation after quenching of a capillary slag–metal interface, the following features were observed by Riboud & Lucas (1981).

(1) The metal–slag interface had a very irregular outline with roughness of all sizes from millimeters down the limit of the resolution of the optical microscope (micrometres).

(2) Numerous metallic droplets were found in the slag phase near the metal–slag interface. Droplet sizes ranged from 1–100 μm in diameter. For the metallic droplet formation, they suggested a 'diffusion and stranding' mechanism.

Sharan & Cramb (1995) confirmed these phenomena in iron based alloys containing 20% nickel and 2.39% aluminium in contact with a CaO–SiO_2–Al_2O_3 (40:40:20 by weight) slag. The interfacial tension within 15 min was measured to be 296 mN m^{-1}, between 15 and 60 min it decreased to be less than 100 mN m^{-1}, and then significantly recovered to a value of about 1500 mN m^{-1} after 1 h, when equilibrium between the metal and slag was attained. As can be seen in figure 1, the long transient period followed by an even longer period of lowered interfacial energy may result from the nickel effect and/or the lower content of aluminium. Sharan suggested that the slag phase surrounding the metal droplet had a higher oxygen potential than the metal, which lead to an imbalance in the oxygen level in the two phases and was the driving force for the reaction.

Liukkonen *et al.* (1997) verified the above findings by using Fe-4.5% Al alloy in contact with a CaO–SiO_2–Al_2O_3 slag. They also verified the reaction between aluminium and silica by chemical analysis before and after experiments. However, they reported that droplet flattening was not observed when using MgO crucibles.

Due to these interesting results and the lack of data at lower aluminium contents, it was decided to further study this phenomena at aluminium contents ranging from 0.25–3.3% in order to determine the limits of dynamic droplet spreading.

3. Experimental method

Determination of the apparent and equilibrium interfacial tension between a liquid Fe–Al alloy and CaO–SiO_2–Al_2O_3 slag was carried out by using a combination of the sessile drop and X-ray photography techniques. After taking an X-ray photograph of the specimen droplet at 1550 °C, the image contour was digitized. The interfacial tension was determined numerically by finding a solution to Laplace's equation which was the best fit for the measured data points. The procedures for experimental and calculation methods are given elsewhere in detail (Jimbo & Cramb 1992).

(*a*) *Sample preparation for dynamic interfacial tension measurement*

Five Fe–Al master alloys were prepared to investigate the phenomena of dynamic interfacial tension. In order to prepare master alloys that have a different initial aluminium content, solid iron (99.95% purity obtained from Noah Technology) and solid aluminium (99.999% purity obtained from Alfa AESAR) were melted in contact with CaO–Al_2O_3 (1:1 by weight) slag.

Table 2 shows the chemical composition of five Fe–Al alloys analysed by LECO for oxygen and by Spectrolab S for the other elements from RIST (Research of Industrial Science Technology in Korea) before and after experiments. Master alloys were cut to be 1.5–3 g, polished and washed with acetone. The prepared specimen was contained under slag in an alumina crucible and charged into an electric furnace with Ar–CO (3:1 by volume) atmosphere at 1550 °C. The CaO–SiO_2–Al_2O_3 (40:40:20 by weight) slag (10 g) was prepared in the induction furnace with an air atmosphere. After the furnace reached 1550 °C, the crucible containing the metal–slag specimen was placed in the middle of the furnace. It took about 4 min to melt the sample after it charged, as confirmed by X-ray observation.

Table 2. *The chemical composition of alloys before and after experiments*
(Top row, before experiments; bottom row, after experiments (wt%).)

sample	Al	Si	O	S	C
1	0.25	0.03	0.024	0.002	0.001
	0.002	0.316	0.020	0.005	0.011
2	0.73	0.017	0.019	0.002	0.013
	0.002	0.536	0.015	0.006	0.052
3	0.77	0.012	0.007	<0.001	—
	< 0.001	< 0.39	0.11	—	—
4	1.84	0.036	0.012	0.003	0.041
	0.006	1.31	0.075	0.005	0.031
5	3.28	0.03	0.005	<0.001	—
	<0.01	1.53	0.13	—	—

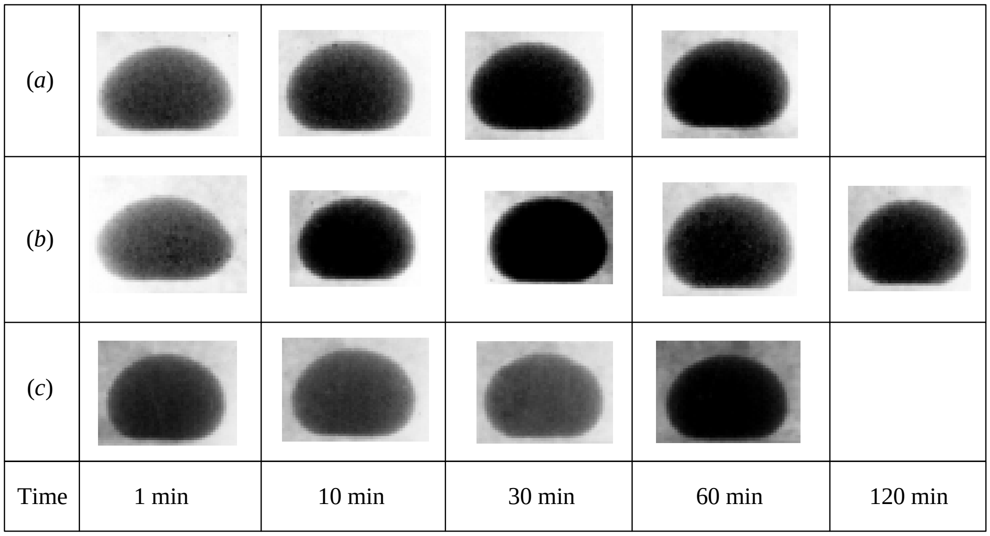

Figure 2. The scanned X-ray photographs of Fe–Al alloys in contact with CaO–SiO_2–20%Al_2O_3 (basicity, $B = 1{:}1$) slag as a function of time: (*a*) Fe–0.25% Al; (*b*) Fe–0.73% Al; (*c*) Fe–0.77% Al.

4. Results and discussion

(*a*) *X-ray observation and interfacial tensions*

Figure 2 shows the Fe–Al (less than 1%Al) droplet shapes after immersion into a CaO–SiO_2–Al_2O_3 (40:40:20 by weight) slag as a function of time. As can be seen in figure 2*a*, the droplet shape at 1 min is flatter than after 10 min and indicates that the dynamic droplet spreading occurs even when aluminium contents are as low as 0.25%. Spreading was complete and the droplet recovered in 10 min. The droplet shape remains almost unchanged between 10 min and 1 h. A similar trend can be seen in the case of the Fe–0.73% Al alloy in figure 2*b*; however, the droplet shape at 1 min is much flatter than the one for the Fe–0.25% Al alloy. In this case the photograph

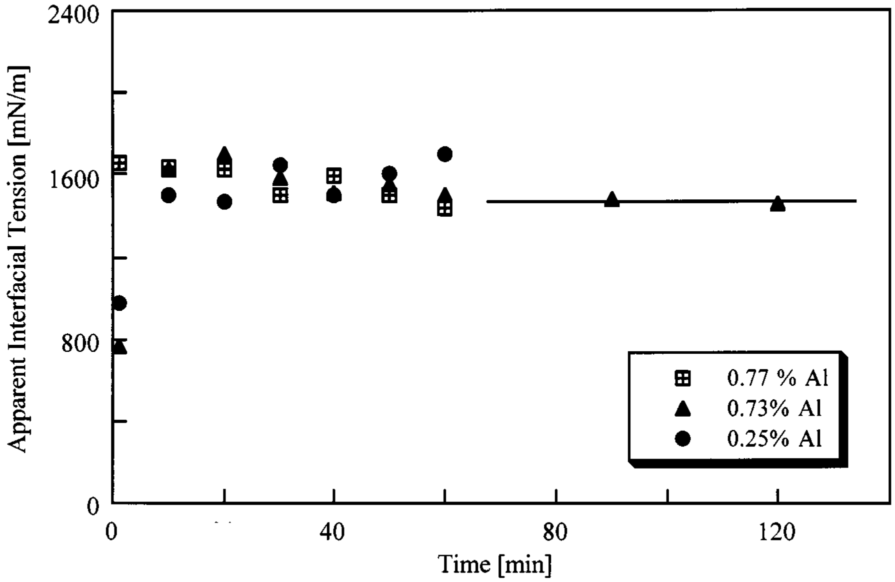

Figure 3. The variation of apparent interfacial tension between Fe–(< 1%)Al alloy and $CaO–SiO_2–20\%Al_2O_3$ (B = 1:1) slag.

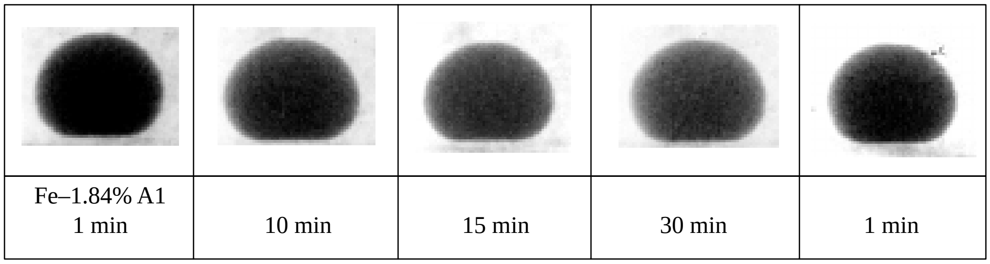

Figure 4. The scanned photographs of Fe–1.84% Al alloys in contact with $CaO–SiO_2–20\%$ Al_2O_3 (B = 1:1) slag as a function of time.

was taken for 2 h. The droplet shape at 2 h is similar to the one at 10 min. In the case of 0.77% Al alloy (figure 2*c*), droplet spreading was not observed.

Figure 3 shows the calculated variations of apparent interfacial tension based on the droplets of figure 2. As can be expected from the observation, interfacial tensions at 1 min in two of the samples are lower than the other measurements. The interfacial tension of Fe–0.73% Al (760 mN m^{-1}) is lower than that of Fe–0.25% Al (980 mN m^{-1}). For the Fe–0.25% Al alloy, the interfacial tension values are initially scattered; however, after 30 min the scatter in the values decreased. In the case of Fe–0.73% Al alloy the interfacial tension increases initially and converges on an equilibrium value after 30 min. For this alloy the measurement was carried out for 2 h and the value of interfacial tension did not significantly vary from 30 min to 2 h.

Figure 4 shows the droplet shapes of an Fe–1.84% Al alloy in contact with $CaO–SiO_2–Al_2O_3$ slag system with time. Unlike previous cases, there was no droplet spreading observed even at 1 min.

Figure 5 shows the calculated interfacial tensions for these droplets. In the case of Fe–1.84% Al alloy, the apparent interfacial tensions do not come to an equilibrium value but increase with time. This result was quite surprising as the final values for

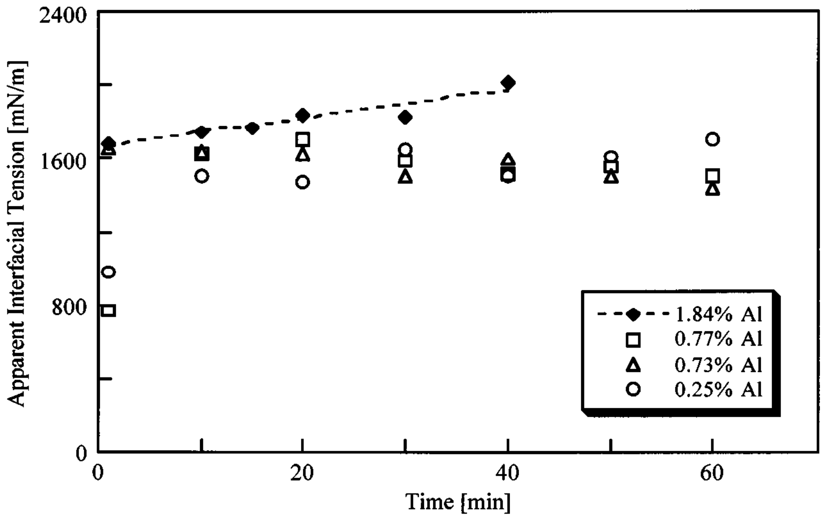

Figure 5. The variation of apparent interfacial tension between Fe–1.84% Al alloy and $CaO–SiO_2$–20% Al_2O_3 (B = 1:1) slag (previous values shown for comparison).

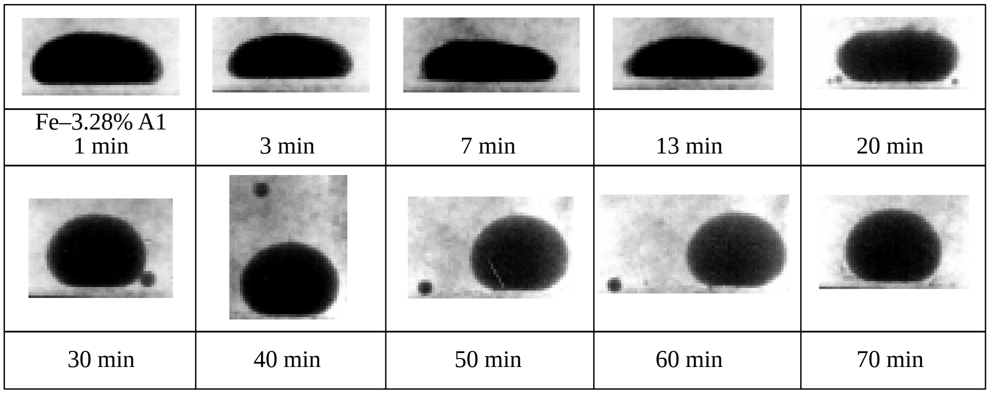

Figure 6. The scanned X-ray photographs of Fe–3.28% Al alloy in contact with $CaO–SiO_2$–20% Al_2O_3 slag as a function of time.

the apparent interfacial tension were higher than any equilibrium measurements and indicative of droplet swelling (increase in height) rather than spreading (decrease in height).

Figure 6 shows the appearance of the Fe–3.28% Al droplets as a function of time. The droplet shape at 3 min is much flatter than that at 1 min. From 7 to 13 min the droplet image is blurred especially at the left-hand side and at the interface on the top side of the droplet. The time for the exposure is 4 s. This indicates that the interface is disturbed and a vigorous reaction between the alloy and the slag occurs in this time period. At 20 min the edge becomes sharp; however, perturbation of the top interface still occurs and leads to blurring in the photograph. At this time, in addition to the main droplet, there are three small droplets that have spontaneously separated from the main droplet. This figure clearly shows spontaneous metal emulsification due to reaction between the metal and a slag.

Between 30 and 70 min the droplet shape recovered. It was also observed that the small droplet that exists between 30 and 60 min is travelling around the large

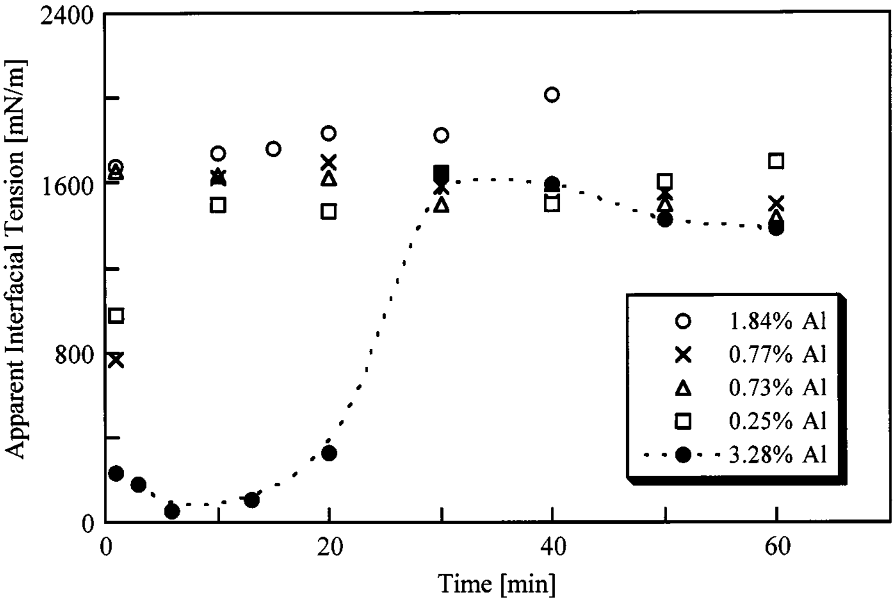

Figure 7. The variation of apparent interfacial tension between Fe–3.28% Al alloy and CaO–SiO_2–20% Al_2O_3 (B = 1:1) slag.

droplet. This movement indicates that fluid flow exists in the slag phase even under apparent constant temperature conditions. After 1 h only one droplet could be seen and on quenching the sample only one droplet could be found in the crucible.

Figure 7 shows the measured apparent interfacial tension values for the above system. The apparent interfacial tensions are calculated at 1 min to be 230 $mN\,m^{-1}$ and at 3 min to be 180 $mN\,m^{-1}$. Between 7 and 20 min, it is difficult to capture the contour of the interface from X-ray images owing to the blurred interface. For those cases, the interfaces are selected as a smooth curved line from a clear interface and apparent values are 57, 106 and 328 $mN\,m^{-1}$ at 6, 13 and 20 min, respectively. The interfacial tension after 30 min reaches an equilibrium value ranging from 1500 to 1600 $mN\,m^{-1}$. Apparent droplet densities have been calculated from X-ray photographs and their values (approximately 7000 $kg\,m^{-3}$) did not significantly change with time after 30 min, even though spontaneous emulsification can be seen in the photograph. However, at 20 min, the apparent density is calculated to be 5180 $kg\,m^{-3}$ and indicates that the volume of metal has significantly expanded. Both results may be due to emulsification of both slag and metal into each other which could result in a higher apparent volume of the droplet.

The cause of dynamic interfacial phenomena during mass transfer, although well documented, is not well understood. In this discussion, basic thermodynamic and kinetic aspects will be considered. In table 2 results of chemical analysis before and after experiments is given. Silicon was picked up by the iron while aluminium was transferred into the slag and mass balance indicates that the following overall reaction occurred:

$$4\underline{\mathrm{Al}}_{\mathrm{metal}} + 3(\mathrm{SiO_2})_{\mathrm{slag}} = 3\underline{\mathrm{Si}}_{\mathrm{metal}} + 2(\mathrm{Al_2O_3})_{\mathrm{slag}} \tag{4.1}$$

Figure 8 shows that the exchange relationship between the decrease in aluminium and the increase in silicon of the alloy before and after the experiments. The straight line presents the stoichiometric relationship between aluminium and silicon from

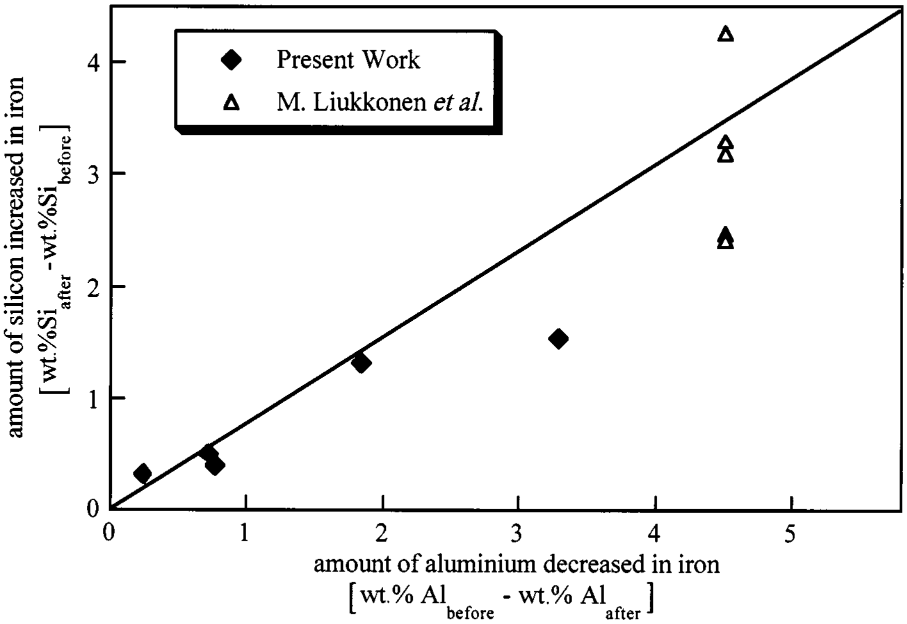

Figure 8. The relationship between the amount of aluminium decrease and the amount of silicon increase in iron from chemical analysis before and after experiments.

equation (4.1). The data qualitatively fit the line, which indicates that the overall reaction (4.1) could be responsible for the dynamic phenomena.

(*b*) *Micro-observation after quenching*

To observe the metal–slag interface during reaction, the samples were quenched at 5, 10, 20 and 25 min after taking X-ray photographs. Figure 9 shows the X-ray photographs and their calculated apparent interfacial tension values. The apparent interfacial tension at 5 min represents a higher value than the previous experiment. This may be due to a delayed initiation of the reaction. The other values are consistent with previous results. A quenched sample can allow a direct observation of the steel–slag interface. Two quenched samples at 5 and 10 min were observed using an optical and scanning electron microscope (SEM), where quenching occurred immediately after taking an X-ray photograph.

Figure 10*a* shows the overall shape of the alloy surrounded by slag at 5 min after quenching. As can be expected from the X-ray photographs, the droplet is almost spherical in shape. However, a deformed part was observed by optical microscopy. This part is magnified in figure 10*b* where entrapped slag could be seen close to the interface. Figure 11 shows an SEM image of the entrapped slag where its chemistry was verified by EDS analysis. These Al, Ca and Si mappings clearly verify that there is entrapped slag within the droplet. From the observation by optical microscopy (figure 10*b*), the entrapped slags are aligned normal to the interface and their lengths vary from 10 µm up to 0.4 mm and widths varying from 10 to 50 µm. The maximum penetration depth is 1.33 mm. This is believed by the authors to be the first indications of spontaneous emulsification of slag in steel during reaction.

Figure 12 shows a photograph of the quenched sample 10 min after the reaction started. Important metallurgical phenomena such as a significant surface creation and spontaneous metal and slag emulsification can be clearly observed. The overall

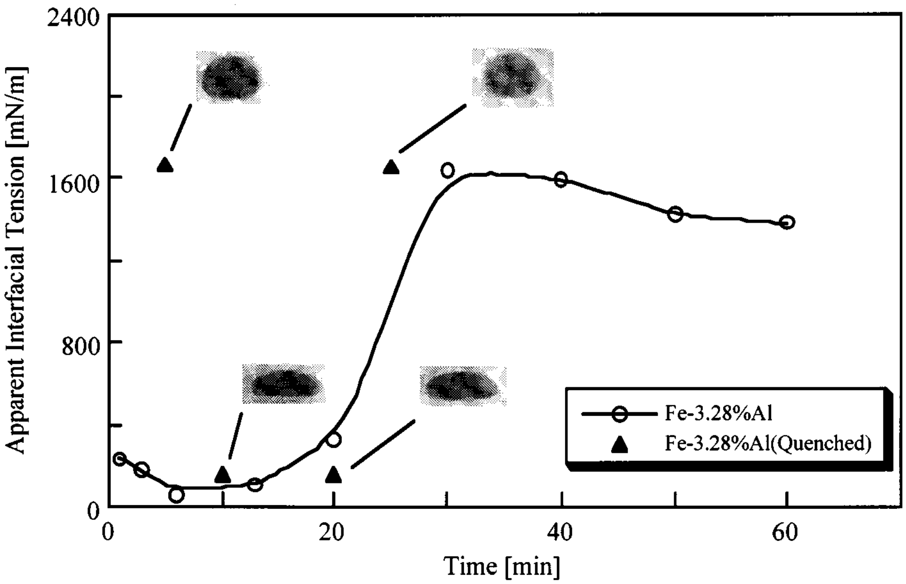

Figure 9. The variation of apparent interfacial tension between Fe–3.28% Al alloy and CaO–SiO_2–20% Al_2O_3 (B = 1:1) slag.

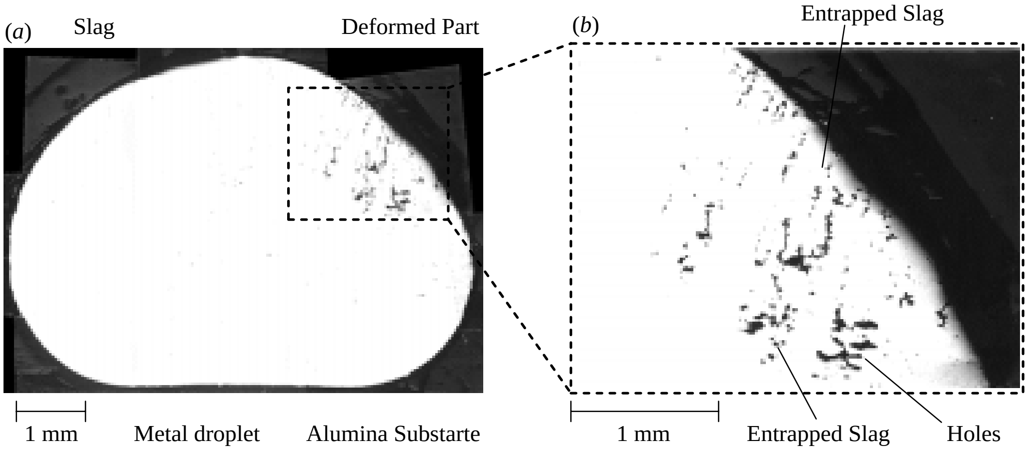

Figure 10. The appearance of the quenched Fe–3.28% Al alloy at 5 min (*a*) and the deformed and contaminated part with higher magnification (*b*).

shape of the metal droplet looks like the picture obtained by X-ray, but the interface has significant perturbations. Many small metal droplets (between 1 and 10 μm) as well as large droplets (from 10 to 100 μm) were observed near the interface. Even though both top and bottom interfaces are rough on the macroscale their features are quite distinct on the microscale.

Figure 13 shows the images of the top interfaces ((*a*) and (*b*)) and of the bottom interfaces ((*c*) and (*d*)) of the droplet of figure 12 observed by SEM. As can be seen in these phonographs, there are two distinct observations:

(1) No metallic fragments can be seen near the top interface while many fragments are found near the bottom interface (within 100 μm in size).

(2) The top interface is smooth while the bottom interface is highly perturbed.

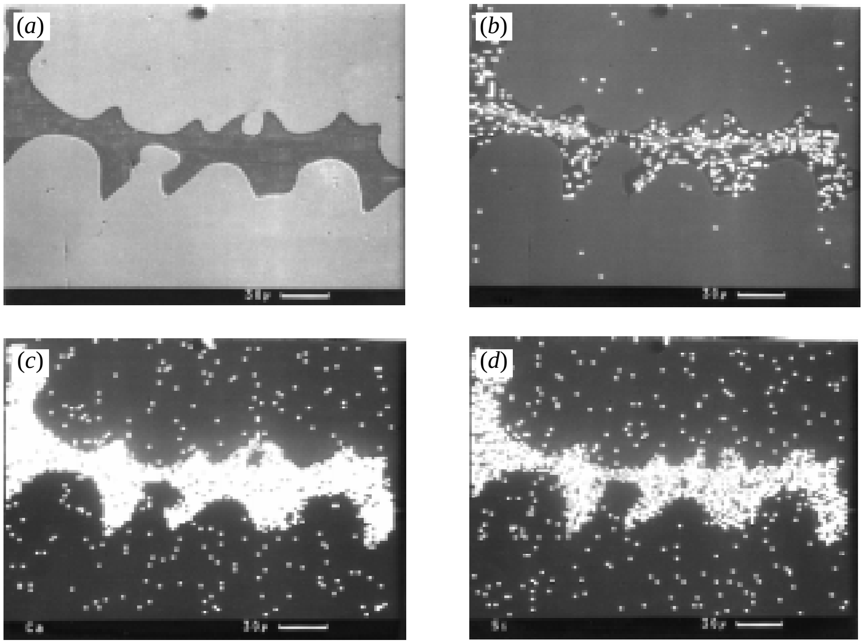

Figure 11. The SEM image of an entrapped slag and EDX analysis: (*a*) SEM image of entrapped part; (*b*) Al mapping; (*c*) Ca mapping; (*d*) Si mapping.

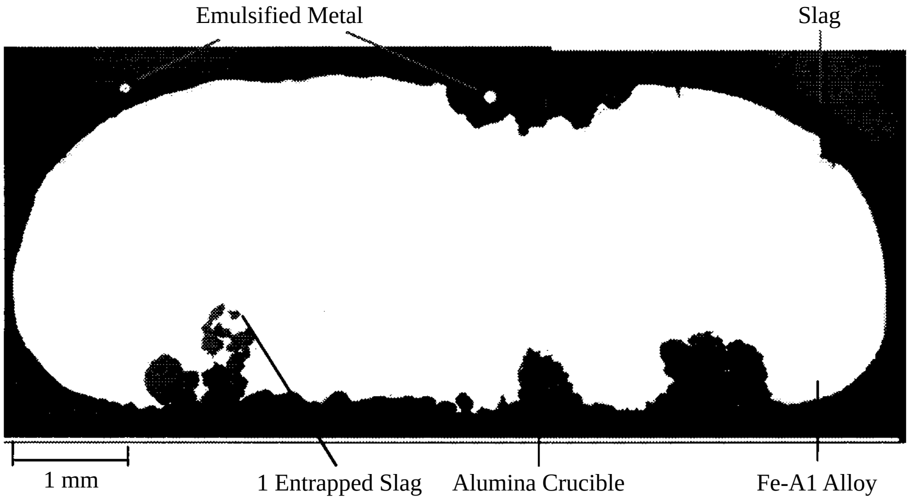

Figure 12. The photograph of Fe–3.28% Al alloy droplet in contact with $CaO–SiO_2–Al_2O_3$ quenched 10 min after melting.

It is clear that during reaction both spontaneous emulsification and droplet spreading occurs. The energy source responsible for bulk movement of slag into steel or steel into slag is not yet clear and may be related to Marangoni flows caused by local concentration gradients or local thermal gradients. The exothermic nature of aluminium reduction of silica will lead to significant thermal gradients; therefore, there will be local thermal gradients and the energy source for emulsification may be a combination of Marangoni flow by concentration and thermal gradients and natural convection.

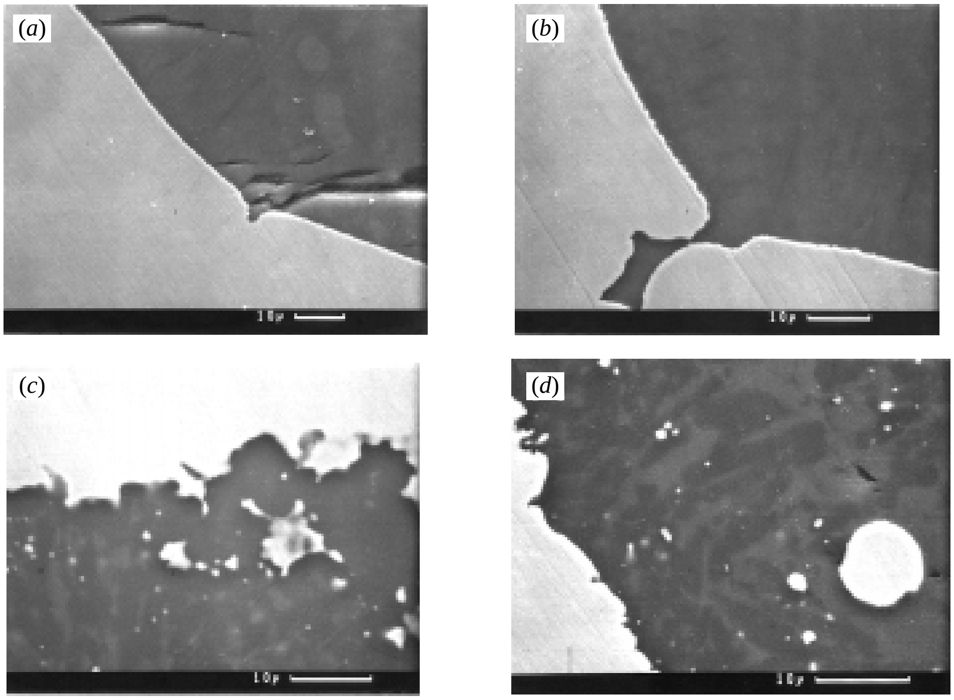

Figure 13. The features of top and bottom interfaces observed by SEM. (*a*) SEM image of top interface; (*b*) SEM image of top interface; (*c*) SEM image of low interface; (*d*) SEM image of low interface.

It is clear, however, that an understanding of dynamic phenomena can be confounded by spontaneous emulsification as droplet emulsification and swelling can be observed. Therefore, it is possible to calculate apparent interfacial energies that are lower than and also higher than equilibrium predictions depending upon the direction of emulsification.

5. Conclusions

Surface turbulence induced metal emulsification was observed by X-ray photography when an Fe–3.28% Al alloy droplet was in contact with a $CaO–SiO_2–Al_2O_3$ (40:40:20 by weight) slag. In addition, dynamic interfacial effects were noticed with aluminium contents as low as 0.25%. From observations using optical microscopy and SEM after quenching, both slag and metal emulsification phenomena were observed.

Dynamic interfacial phenomena, where spontaneous emulsification and droplet spreading and recovery are observed, may be more common than previously thought. Industrial processes where high levels of reactive alloys come into contact with reducible slags, for example during steel deoxidation, will be candidates for the observation of these phenomena.

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Discussion

A. Passerone (*ICTAM-CNR, Genoa, Italy*). With reference to the instabilities Professor Cramb has shown to appear at the liquid-iron–slag interface, which can sometimes destroy the drop axial-symmetric geometry, I would like to point out that recent studies in my laboratory on the interfacial tension evolution with tin in the presence of mass transfer across the interface, have demonstrated that deep interfacial tension minima can appear, depending on the conditions of the system.

I would like to suggest that this kind of study is taken into consideration when explaining the phenomena reported here in metal–slag systems.

A. W. Cramb. We have also seen deep minima in interfacial tension at high rates of reaction between the droplet and the slag phase and that during this condition it is possible to observe spontaneous emulsification of both phases. These minima are shown in figures 7 and 9.