Interfacial Tension between Molten Iron and CaO–SiO₂ Based Fluxes*

Haiping SUN, Kunihiro NAKASHIMA and Katsumi MORI

Department of Materials Science and Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka, Fukuoka-ken, 812 Japan.

(Received on June 26, 1996; accepted in final form on September 9, 1996)

Flux–metal interfacial tension has been examined by X-ray photography of a metal drop melted in a molten flux. The experiments were carried out at 1580°C using a zirconia crucible with low solubility in the fluxes. The systems used in the investigation were as follows:

Metal phase: Fe–O alloy, oxygen content in the alloys varied from 0.002 to 0.070 mass%.

Flux phase: Ternary system: CaO–SiO₂–M_x(F,O)_y, where M_x(F,O)_y represents NaF, CaF₂, Al₂O₃, Na₂O, MgO, Li₂O or ZrO₂ and concentrations varied from 2 to 40 mass%.

Multicomponent system: CaO–SiO₂–Al₂O₃–Fe₂O₃–Na₂O–NaF–CaF₂–MgO–Li₂O–ZrO₂.

The interfacial tension was observed to increase with increasing NaF, CaF₂, Na₂O, MgO or Li₂O contents, while only minor changes in the values were observed with varying Al₂O₃ or ZrO₂ contents in CaO–SiO₂ or CaO–SiO₂–Al₂O₃ systems. The interfacial tensions between flux and molten iron decreased with increasing oxygen activity in iron,

$$\gamma = \gamma_0 - 0.324 \ln(1 + 116a_O)$$

KEY WORDS: interfacial tension; flux; liquid iron; continuous casting; sessile drop.

1. Introduction

Interfacial tension between flux and liquid iron is an important property in the production of higher quality steel since low interfacial tension values increase the likelihood for flux entrainment at a flux–metal interface resulting in liquid slag entrapment in the metal phase and eventually to a product defect. Alternatively, if the interfacial tension is high, gaseous bubbles generated in the metal phase during solidification can be easily jammed at flux–metal interface, and these bubbles also lead to a surface defect of the product. In the process of continuous casting, the flux–metal interfacial tension can affect the formation of (a) the initial solidification at the meniscus level, and (b) a flux film between the mould and slab. In order to interpret various phenomena occurring in casting processes, numerous studies have been carried out on the subject over the last several decades. However, there is a considerable disagreement between the measured values, because of flux contamination due to (i) the dissolution of the crucible materials into fluxes and (ii) the difficulties in controlling the oxygen content in the metal resulting from the reaction between slag and molten iron. In the present study, the effect of (i) component in the flux was investigated using a zirconia crucible since ZrO₂ has an insignificant effect

on the interfacial tension as will be mentioned later to Fig. 10 and also, the contents of ZrO₂ dissolved into the flux within the duration of the measurement are rather lower compared with those of other commercial crucible materials, and (ii) oxygen contents on the interfacial tension were examined.

2. Experimental

The experiments were performed using the X-ray sessile drop technique at 1580°C. The metal and flux system were contained in zirconia crucibles resting in an electrical resistance furnace under an argon atmosphere. An X-ray unit was employed to determine the shape of sessile iron drops immersed in the fluxes. Interfacial tensions were obtained from the contour of the droplets on the X-ray pictures by numerical solution of the Young–Laplace equation. The experimental setup, image processing, and numerical resolution are detailed in the previous work.¹⁾ Initial iron samples were prepared by melting electrolytic iron (0.0015 mass% C, 0.0009 mass% S, <0.0010 mass% P, <0.0005 mass% Si, 0.0001 mass% Mn, 0.0001 mass% Cu, 0.0002 mass% N, 0.010 mass% O) in an induction furnace under a vacuum atmosphere. Initial fluxes were prepared by premelting mixtures of desired quantities of reagents in a platinum crucible,

* This paper was presented in the “International Workshop on Thermophysical Data for the Development of Mathematical Models of Solidification” held at Gifu City from 6–8 October, 1995.

and then crushed to <12 mesh after quenching the liquid flux on a stainless plate.

The flux compositions obtained by the chemical analysis of the quenched flux samples after the experiments are shown in **Table 1**. The CaO/SiO₂ ratio for these fluxes is close to unity. The composition of the fluxes was varied by adding NaF, CaF₂, Al₂O₃, Na₂O, MgO and Li₂O from 0 to 40 mass%, respectively. Several percent of ZrO₂ was also contained in the final fluxes due to the dissolution of the crucible materials. The density of the molten iron used in these calculations was taken as $6.94 \times 10^3 \text{ kg m}^{-3}$. Table 1 also shows the densities of the molten fluxes used in the measurement of the interfacial tension in the present study. These density values for the molten fluxes were estimated from final flux composition by the regular solution approximation model proposed by Nakajima²⁾; it was assumed that the interaction effects of CaF₂, NaF and ZrO₂ with other components in the flux were negligible. The molar volumes of NaF provided by Bloom and Burrows,³⁾ and those of ZrO₂ from the data obtained by Matsuyama⁴⁾ for the CaO–SiO₂–Al₂O₃–Na₂O–F[–]–Li₂O–ZrO₂ system were used in the density determination. From the measurements of the interfacial tension as a function of time, the tension was found to be independent of time after molten fluxes were in contact with the iron droplet for 10 min. The average of several measured values after 10 min was used as the interfacial tension of the measured system.

3. Results and Discussion

3.1. Effect of Oxygen in Molten Iron

The interfacial tension is markedly reduced by the oxygen in the molten iron due to its strongly surface active nature. In the present study, a graphite protection crucible was used to reduce any oxygen presented in the atmosphere during the measurements, consequently great attention was paid in the preparation of

the samples for the measurements and the prevention of the oxygen pickup of the iron during the measurements. However, as seen in Table 1, 20–200 ppm of oxygen were contained in the final metal samples. These oxygen levels are considered to be generated from the decomposition of the oxides in the slag and the contamination by air during the flux addition. The interfacial tension is plotted against the oxygen content in **Fig. 1**. Although it was found that the dependence of the interfacial tension on the oxygen content was not very clear, a decrease in the interfacial tension with increasing oxygen content was obvious for each flux system. This indicates that the interfacial tension obtained in the present study depends not only on the flux composition but also upon the oxygen content in the molten iron. Therefore the effect of the oxygen in the molten iron should be taken into account in order to make clear the flux composition effect on the interfacial tension.

A literature survey shows that many investigations on the oxygen effect^{5–8)} have been carried out since the past several decades, but a numerical relation between interfacial tension and oxygen content has not been established yet. This is because the slag system and composition were not identical and the variation of the interfacial tension with slag composition was not taken into consideration in these studies. In the present study, the effect of oxygen content on the interfacial tension between flux and molten iron was investigated using 35CaO–35SiO₂–30Al₂O₃ flux and pure molten iron in an alumina crucible. The oxygen content in the molten iron was controlled by adding a certain amount of FeO (0–12.1 mass%) into the flux. The observed interfacial tensions, oxygen contents, and estimated flux densities are given in **Table 2**. The oxygen activities referred to the infinite dilution for oxygen in metal based on the Henrian law were calculated from oxygen contents and the interaction parameter $e_o^o = -0.17$,⁹⁾ and were also given in the table. The relation between interfacial tension and oxygen content in metal is shown in **Fig. 2**. A decrease in the interfacial tension with increasing the oxygen content was observed.

The relation between surface tension of molten iron

Table 1. Flux compositions and interfacial tensions between the fluxes and molten iron.

Flux Type	flux compositions				oxygen activity in metal, a_o	flux density 10^3 kg m^{-3}	interfacial tension	
	CaO	SiO ₂	ZrO ₂	additions mass %			γ N m ⁻¹	γ_o N m ⁻¹
A-1	47.1	45.4	6.7		0.0056	2.541	1.314	1.476
A-2	41.1	38.1	11.8	NaF:6.40	0.0023	2.501	1.362	1.437
A-3	36.0	34.8	12.4	NaF:15.0	0.0039	2.393	1.384	1.504
B-1	42.2	38.6	9.4	CaF ₂ :7.60	0.0040	2.568	1.372	1.496
B-2	36.6	35.3	10.8	CaF ₂ :15.8	0.0060	2.568	1.344	1.515
C-1	43.0	41.5	4.5	Al ₂ O ₃ :9.60	0.0029	2.593	1.388	1.481
C-2	38.6	38.4	1.4	Al ₂ O ₃ :19.2	0.0044	2.637	1.315	1.447
C-3	34.4	33.0	1.6	Al ₂ O ₃ :29.0	0.0055	2.721	1.257	1.416
C-4	29.5	28.5		Al ₂ O ₃ :41.7	0.0083	2.805	1.222	1.441
D-1	37.2	40.6	8.8	Na ₂ O:3.50	0.0108	2.517	1.331	1.594
D-2	41.8	41.7	4.7	Na ₂ O:9.20	0.0021	2.455	1.523	1.594
D-3	35.9	36.0	6.1	Na ₂ O:17.5	0.0048	2.406	1.395	1.539
E-1	42.1	40.7	3.1	MgO:9.4	0.0035	2.563	1.487	1.599
E-2	36.7	35.9	4.7	MgO:17.8	0.0024	2.618	1.570	1.651
G-1	45.0	43.0	6.7	Li ₂ O:1.5	0.0042	2.458	1.445	1.572
G-2	41.6	42.0	8.6	Li ₂ O:4.2	0.0026	2.482	1.464	1.550
G-3	40.2	42.6	8.1	Li ₂ O:8.3	0.0175	2.411	1.446	1.805
G-4	42.8	42.2	7.7	Li ₂ O:1.7	0.0035	2.520	1.485	1.597
G-5	47.7	47.4	8.0	Li ₂ O:4.6	0.0199	2.475	1.375	1.763
J-1	27.6	27.9	5.2	Al ₂ O ₃ :38.6	0.0051	2.823	1.166	1.318
J-2	26.7	27.0	9.5	Al ₂ O ₃ :36.1	0.0052	2.842	1.190	1.343
J-3	25.1	25.2	14.2	Al ₂ O ₃ :34.8	0.0085	2.876	1.170	1.393

Fig. 1. Interfacial tension vs. oxygen content in molten iron at 1580°C.

Table 2. Effect of oxygen in metal on the interfacial tension between 35CaO–35SiO₂–30Al₂O₃ + FeO flux and Fe–O metal at 1 580°C.

oxygen mass%	a_o	flux density 10 ³ kg m ⁻³	γ N m ⁻¹
0.0055	0.0055	2.793	1.168
0.0066	0.0066	2.794	1.230
0.0069	0.0069	2.795	1.180
0.0073	0.0073	2.795	1.183
0.0073	0.0073	2.795	1.211
0.0073	0.0073	2.795	1.223
0.0081	0.0080	2.796	1.143
0.0081	0.0080	2.796	1.184
0.0081	0.0081	2.796	1.218
0.0085	0.0085	2.797	1.137
0.0088	0.0088	2.797	1.146
0.0106	0.0106	2.799	1.152
0.0130	0.0130	2.802	1.050
0.0147	0.0146	2.805	1.080
0.0162	0.0161	2.806	1.081
0.0181	0.0180	2.809	1.014
0.0183	0.0182	2.809	0.992
0.0188	0.0186	2.810	1.015
0.0197	0.0195	2.811	0.992
0.0211	0.0209	2.812	0.986
0.0247	0.0244	2.817	0.931
0.0270	0.0267	2.820	0.933
0.0281	0.0278	2.821	0.945
0.0313	0.0309	2.825	0.884
0.0333	0.0329	2.827	0.881
0.0363	0.0357	2.831	0.847
0.0400	0.0393	2.836	0.798
0.0410	0.0403	2.838	0.791
0.0436	0.0428	2.844	0.821
0.0438	0.0430	2.846	0.847
0.0443	0.0435	2.848	0.807
0.0522	0.0510	2.850	0.754
0.0586	0.0572	2.858	0.709
0.0598	0.0583	2.859	0.705
0.0705	0.0684	2.872	0.705

Fig. 2. Dependence of 35CaO–35SiO₂–30Al₂O₃ + FeO (=0–12.1 mass%) flux and Fe–O molten iron interfacial tension on oxygen content in molten iron at 1 580°C.

and oxygen content in the melt proposed by Belton¹⁰⁾ indicated that,

$$\gamma_o - \gamma = RTT^0 \ln(1 + K_O a_o) \quad \text{.....(1)}$$

where, γ_o : the surface tension of the pure liquid, N m⁻¹,
 T^0 : the surface excess quantity at full coverage, mol m⁻²,
 a_o : activity of oxygen in the molten iron, and
 K_O : equilibrium constant of oxygen adsorption reaction at surface.

This relation was also observed to be applied to the interfacial tension.^{1,7)} The values of the parameters, γ_o ,

Fig. 3. Measured interfacial tension values at 1 580°C against oxygen activity based on Eq. (2).

RTT^0 and K_O in Eq. (1) for the data presented in Table 2 were determined by an iteration calculation involving several steps: (i) the values of the γ_o and RTT^0 are calculated using a given value of K_O obtained by least squares method, and (ii) then this calculation was repeated by changing the value of K_O until the maximum value of the correlation coefficient was obtained. The relation for 35CaO–35SiO₂–30Al₂O₃ flux and molten iron at 1 580°C was found as follows,

$$\gamma_o - \gamma = 0.324 \ln(1 + 116a_o) \quad \text{.....(2)}$$

$$\gamma_o = 1.386 \text{ N m}^{-1}$$

Figure 3 shows the measured values plotted against the activity of oxygen, based on Eq. (2).

If the adsorption of oxygen, in the form of ion, at the flux–molten iron interface is a single layer and in most dense configuration, the value of $RTT^0 = 0.417 \text{ N m}^{-1}$ can be calculated from the radius¹¹⁾ of oxygen ion (1.32 Å). If the adsorption of oxygen at the flux–molten iron interface is a single layer of FeO and in most dense configuration, the value of $RTT^0 = 0.272 \text{ N m}^{-1}$ is obtained from the radii¹¹⁾ of oxygen (1.32 Å) and iron ions (0.83 Å). The value of RTT^0 obtained in the present study (0.324 N m⁻¹) is between these two values. The values of RTT^0 and K_O , respectively, reported by Ogino *et al.* at 1 600°C,¹²⁾ Jimbo *et al.* at 1 550°C¹³⁾ and Kasama *et al.* at 1 600°C¹⁴⁾ for the surface tension of molten iron–oxygen alloy were 0.358 and 210, 0.279 and 140, and 0.299 and 110, respectively. The values of RTT^0 and K_O for interfacial tension compares reasonably well with those reported for the surface tension.

In the measurement of the interfacial tensions between flux and molten iron, the variation of the oxygen content in the metal phases could not be avoided (Table 1). Assuming that the surface excess quantity at full coverage and equilibrium constant of oxygen adsorption are independent of the flux composition, hypothetical interfacial tensions (where oxygen activity in the molten iron is zero, γ_o), were calculated for the fluxes using Eq. (2). The values of γ_o , which is independent on the oxygen content in the melt, is used to examine the effect of flux composition on the interfacial tension

between the flux and the molten iron. The effect of sulfur was ignored in the present study, since sulfur content in the metal phase (0.0009 mass%) was much lower compared with that of oxygen, and the interfacial tension was less sensitive to sulfur in the metal phase than surface tension was, as seen in the previous results.^{1,29)}

3.2. Interfacial Tension for Ternary System

Effect of NaF

The results on the influence of NaF content in the flux are shown in Fig. 4. The NaF content in the CaO-SiO₂ flux was varied from 0 to 20 mass%. The solid circles show the measured values of the interfacial tension and the vertical bars show the standard deviation of the measurement. The values given in the brackets are the oxygen content where the interfacial tensions were measured. The open circles are the values corrected with respect to the oxygen content in the iron based on Eq. (2). A slight increase in the interfacial tension was observed as the NaF content in the flux increases. The results for the CaO-Al₂O₃ flux reported by Evseev and Filippov,¹⁵⁾ which show a strong effect of NaF, are also presented in the figure to provide a comparison with the present results for the CaO-SiO₂ flux.

Effect of CaF₂

The variation of the interfacial tension with CaF₂ content in the CaO-SiO₂ flux is shown in Fig. 5. A slight increase in the interfacial tension was observed as the CaF₂ content in the flux increases similar to that of NaF. The same trend was also shown in the results due to Shinozaki *et al.*¹⁶⁾ for CaO-SiO₂-Al₂O₃ flux using alumina or magnesia crucibles ($a_O = 0.0010-0.0031$). The values obtained by Gaye *et al.*¹⁷⁾ for this flux are also presented in the figure. Their results are consistent with those of the present work when the higher oxygen contents of the metal in their measurement ($a_O = 0.0047-0.0186$) are taken into account. The results due to Ogino *et al.* using a slag lens method¹⁸⁾ for CaO-Al₂O₃ flux also show an increasing trend with CaF₂ addition. The similar trends observed by the additions of NaF and

Fig. 4. Effect of NaF in flux on the interfacial tension between liquid iron and flux.
this work: CaO-SiO₂ flux, zirconia crucible, 1580°C
Evseev and Filippov: CaO-Al₂O₃ flux

CaF₂ to the flux are considered to be due to the weak interaction between fluorine and the molten iron.

Effect of Al₂O₃

Figure 6 shows the influence of Al₂O₃ content in the CaO-SiO₂ flux on the interfacial tension. The measured interfacial tension was increased when 10% Al₂O₃ was added to the flux but decreased with further increasing Al₂O₃ content, and remained unchanged when Al₂O₃ was more than 30%. This complicated behavior is considered to be caused by the variation of the oxygen content in the melt. As shown in the figure, γ_0 was slightly decreased with addition of Al₂O₃ to the flux. The values measured by El Gammal and Stracke¹⁹⁾ using drop weight method are lower than those in the present study. This is not surprising since the metal sulfur

Fig. 5. Effect of CaF₂ in flux on the interfacial tension between liquid iron and flux.
this work: CaO-SiO₂ flux, zirconia crucible, 1580°C
Ogino *et al.*: CaO-Al₂O₃ flux lens method, 1600°C
Shinozaki *et al.*: CaO-SiO₂-Al₂O₃ flux, alumina or magnesia crucible, 1600°C
Gaye *et al.*: CaO-SiO₂-Al₂O₃ flux, alumina crucible, 1600°C

Fig. 6. Effect of Al₂O₃ in flux on the interfacial tension between liquid iron and flux.
this work: CaO-SiO₂ flux, zirconia crucible, 1580°C
El Gammal and Stracke: CaO-SiO₂-Al₂O₃ flux, drop weight method, 1570°C
Sharan and Cramb: CaO-SiO₂-Al₂O₃ flux and Fe-20%Ni alloy, alumina crucible, 1550°C

content of their measurement was as high as about 0.038 mass%, which was much higher than that of the present study.

Effect of Na₂O

The influence of Na₂O content of the flux on the interfacial tension is shown in Fig. 7. An increase in the interfacial tension was observed as the Na₂O content in the flux increases. This trend is in agreement with the results obtained by Shinozaki *et al.*¹⁶⁾ for CaO–SiO₂–Al₂O₃ flux. However, an opposite trend was obtained in the study of Adachi *et al.*²⁰⁾ The values provided by Gaye *et al.*¹⁷⁾ for CaO–SiO₂–Al₂O₃ flux show an increasing trend although they are lower than those of the present study because the oxygen content in their

Fig. 7. Effect of Na₂O in flux on the interfacial tension between liquid iron and flux.
this work: CaO–SiO₂ flux, zirconia crucible, 1580°C
Shinozaki *et al.*: CaO–SiO₂–Al₂O₃ flux, magnesia crucible, 1600°C
Adachi *et al.*: CaO–MgO–Al₂O₃ flux, lens method, 1540°C
Gaye *et al.*: CaO–SiO₂–Al₂O₃ flux, lens method, 1600°C

Fig. 8. Effect of MgO in flux on the interfacial tension between liquid iron and flux.
this work: CaO–SiO₂ flux, zirconia crucible, 1580°C
Yoneda *et al.*: CaO–SiO₂ flux, zirconia crucible, 1580°C
El Gammal and Stracke: CaO–SiO₂–Al₂O₃ flux, drop weight method, 1570°C

measurements was relative high.

Effect of MgO

Figure 8 shows the interfacial tension variation with MgO content in flux which is similar to that of Na₂O, i.e., an increase in the MgO content increases the interfacial tension. The γ_0 values for this system measured by Yoneda *et al.*²¹⁾ using a zirconia crucible also show the increasing trend with MgO additions. The lower interfacial tension obtained by El Gammal and Stracke¹⁹⁾ in CaO–SiO₂–Al₂O₃ flux where CaO/SiO₂=1 and Al₂O₃=15 mass% may be due to the higher sulfur content in their metal.

Effect of Li₂O

As can be seen from Fig. 9, an increase in the interfacial tension was observed with increasing Li₂O content in the flux. The decreasing trend with increasing Li₂O content in the flux by more than 5% is considered to be due to the higher oxygen content in the melt. The increase of γ_0 with Li₂O content in the flux was obvious. This agrees with the results of Shinozaki *et al.*¹⁶⁾ for CaO–SiO₂–Al₂O₃ flux containing less than 8 mass% of Li₂O.

Effect of ZrO₂

In the investigation of flux containing zirconia, a CaO–SiO₂–Al₂O₃ flux and alumina crucibles were used. The results are presented in Fig. 10. γ and γ_0 points at ZrO₂=0 mass% and at ZrO₂=1.6 mass% are from C-3 and C-4 fluxes, respectively, and the γ_0 value obtained for 35CaO–35SiO₂–30Al₂O₃ as given in Fig. 3 was also shown in Fig. 10 at ZrO₂=0 mass%. Although relatively large scatters were observed in the Fig. 10 for γ_0 values, the interfacial tension slightly decreased with increasing ZrO₂ in the content range below 5 mass% ZrO₂ and slightly increased with increasing ZrO₂ when flux contains more than 5 mass% ZrO₂. Considering the relatively small effect of ZrO₂ on the interfacial tension and the nearly same low level of ZrO₂ dissolution in each flux system, ZrO₂ dissolution is considered to have a negligible effect on the evaluation of the variation of the interfacial tension with certain component

Fig. 9. Effect of Li₂O in flux on the interfacial tension between liquid iron and flux.
this work: CaO–SiO₂ flux, zirconia crucible, 1580°C
Shinozaki *et al.*: CaO–SiO₂–Al₂O₃ flux, magnesia crucible, 1600°C

content in the flux. An insignificant effect of ZrO_2 on the interfacial tension was also observed by Yoneda *et al.*²¹⁾ for this flux system.

Figure 11 shows the summary of the effect of the additions in the CaO-SiO_2 and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ flux on the interfacial tension, γ_0 , obtained from Eq. (2) for each experiment. It was found that, the interfacial tension (i) increased with increasing concentration of basic oxides and fluorides in the flux but (ii) slightly decreased with increasing Al_2O_3 content in the flux, and (iii) slightly decreased with increasing ZrO_2 content in the range of $\text{ZrO}_2 < 5$ mass% while increased slightly with increasing ZrO_2 in the range of $\text{ZrO}_2 = 5\text{--}15$ mass%.

3.3 Interfacial Tension of Industrial Fluxes

The interfacial tension measurement was carried out for several practical flux compositions. The final flux compositions and the interfacial tensions are given in

Fig. 10. Effect of ZrO_2 in flux on the interfacial tension between liquid iron and flux.
this work: $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ flux, alumina crucible, 1580°C
Yoneda *et al.*: $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ flux, alumina crucible, 1580°C

Table 3. Since only the total fluorine ion was analyzed for these fluxes, the NaF and CaF_2 contents in the fluxes were simply estimated to be proportional to the molar fraction ratio between Na^+ and 2Ca^{2+} . As can be seen from the table, Al_2O_3 and fluorine were varied for the fluxes Nos. 1–8. About 10 mass% of Na_2O was contained in the fluxes ND 1–5 and NE 1–4, and CaO/SiO_2 was also varied in these fluxes. In the fluxes NF 4–8, small amounts of MgO and Li_2O were added, and the CaO/SiO_2 ratio was varied. The interfacial tensions obtained for these multicomponent fluxes showed similar trends to those demonstrated in the ternary system described previously, *i.e.*, the interfacial tension slightly increases with increasing fluorine and Na_2O content in the flux. A slight increase in the interfacial tension with increasing CaO/SiO_2 ratio of flux was observed in these fluxes. The viscosities of several initial fluxes (ND, NE and NF, $\text{ZrO}_2 = 0$ mass%) were measured at 1410°C using the rotation method⁴⁾ and were also given in Table 3.

Fig. 11. Influence of additions in CaO-SiO_2 flux (% $\text{CaO}/\text{\%SiO}_2 = 1$) on the interfacial tension between liquid iron and flux at 1580°C .

Table 3. Flux compositions, viscosities and interfacial tensions between flux and molten iron.

Flux	flux compositions									oxygen activity in metal, a_o	flux viscosity* poise	flux density 10^3 kg m^{-3}	interfacial tension	
	CaO	SiO ₂	Al ₂ O ₃	Na ₂ O	ZrO ₂	F ⁻	FeO	MgO	Li ₂ O				γ N m^{-1}	γ_0 N m^{-1}
	mass %													
No.1	42.0	37.7	1.9	6.4	10.1	3.1	0.54			0.0032		2.527	1.377	1.481
No.2	40.5	36.4	1.8	7.6	9.7	4.8	0.36			0.0028		2.499	1.325	1.416
No.3	39.7	34.7	1.6	8.8	11.0	4.4	0.27			0.0039		2.503	1.334	1.454
No.4	37.6	33.2	1.7	10.4	11.7	6.1	0.27			0.0025		2.480	1.330	1.413
No.5	40.6	36.5	5.5	5.0	9.5	3.2	0.36			0.0026		2.556	1.351	1.435
No.6	39.4	35.4	5.3	7.3	9.1	3.5	0.54			0.0024		2.532	1.338	1.418
No.7	38.0	33.7	5.1	7.5	10.7	4.0	0.45			0.0040		2.538	1.348	1.471
No.8	36.2	32.8	4.8	10.1	10.4	6.5	0.36			0.0026		2.489	1.332	1.418
ND-1	28.4	45.1	0.8	8.6	12.7	4.9	0.91			0.0036	6.80	2.442	1.360	1.474
ND-2	34.0	41.1	0.5	9.1	11.2	4.7	0.63			0.0029	3.10	2.456	1.388	1.481
ND-3	38.8	36.0	0.5	9.0	11.7	4.8	0.36			0.0036	1.80	2.489	1.379	1.493
ND-4	40.8	34.6	0.5	9.5	10.7	5.2	0.27			0.0056	1.10	2.486	1.408	1.569
ND-5	45.9	31.9	0.5	8.6	10.0	4.6	0.27			0.0037	0.90	2.518	1.437	1.554
NE-1	36.6	32.6	1.3	12.3	11.9	6.7	0.36			0.0035	0.85	2.459	1.292	1.403
NE-2	45.7	32.3	0.5	9.1	8.9	5.6	0.27			0.0066	0.85	2.497	1.456	1.639
NE-3	35.2	30.6	10.6	11.3	9.5	5.8	0.27			0.0032	2.30	2.519	1.395	1.498
NE-4	41.4	37.0	2.0	5.8	10.1	2.9	0.36	1.6		0.0032	2.30	2.540	1.398	1.501
NF-5	37.0	31.4	8.9	2.4	10.5	7.0	0.27	1.4	2.1	0.0032	2.00	2.563	1.260	1.363
NF-6	40.8	36.4	3.3	3.4	7.4	3.7	0.45	0.6	0.0	0.0059	4.00	2.542	1.268	1.438
NF-7	36.3	36.6	5.2	2.7	10.2	3.3	0.36	0.4	0.9	0.0045	6.00	2.553	1.287	1.423
NF-8	33.9	42.5	5.1	2.7	7.1	3.7	0.90	1.0	0.0	0.0066	8.00	2.519	1.223	1.406

* viscosity values at 1410°C for initial flux

4. Prediction of Interfacial Tension

In order to obtain an empirical relation between interfacial tension and flux composition, the following relation was derived on the assumption of the additivity of the contribution of each component in the flux and metal oxygen to the interfacial tension.

$$\gamma = \sum_{i=1}^n A_i X_i + \sum_{i=1}^{n-1} \sum_{j=i+1}^n B_{ij}^I X_i X_j - 0.324 \ln(1 + 116a_o) \quad \dots\dots\dots(3)$$

where, A_i : the interfacial tension factor of component i in the flux, N m^{-1} ,

B_{ij}^I : the interaction factor of the interfacial tension between component i and j in the flux, N m^{-1} , and

X_i : molar fraction of component i in the flux.

The values of A_i and B_{ij}^I are determined by the trial and error method from the observed results of present study and are shown in **Tables 4** and **5**. Larger interfacial tension factors were obtained for the strong basic components in the fluxes and the minus values were obtained for the interaction factors of the interfacial tension. The standard deviation, as seen in **Fig. 12a**), between the value calculated by Eq. (3) and the observed was 0.047 N m^{-1} .

In **Fig. 12b**), the same comparison of interfacial tensions between molten iron and fluxes was made for the experimental results obtained by Shinozaki *et al.*,¹⁶⁾ Gaye *et al.*,¹⁷⁾ Bretonnet *et al.*,²²⁾ and Riboud and Lucas²³⁾ for which oxygen contents in the metal were reported. The standard deviation was increased to 0.074 N m^{-1} . Although there exists some overestimation of the interfacial tension for the fluxes containing more than 15 mass% Na_2O , the values for $\text{CaO-SiO}_2\text{-CaF}_2$ -

Table 4. Interfacial tension factors, A_i , standard free energy changes of formation an oxide, ΔG_i^0 , surface tension factors, σ_i , ion-oxygen attraction, I_i ($= Z/r_i r_o$), interaction energies with iron ion in flux, $\alpha_i \text{Fe}^{++}$.

i	A_i $\text{N m}^{-1} \text{mol}^{-1}$	ΔG_i^0 kJ mol^{-1}	σ_i $\text{N m}^{-1} \text{mol}^{-1}$	I_i	$\alpha_i \text{Fe}^{++}$ kJ mol^{-1}
CaO	1.868	-433.6	0.747	0.70	-31.35
SiO ₂	1.477	-290.3	0.293	2.44	-41.80
Al ₂ O ₃	1.561	-360.6	0.759	1.66	-1.76
MgO	2.380	-350.4	0.750	0.95	33.44
Li ₂ O	4.190	-316.5	0.430	0.50	--
Na ₂ O	2.870	-85.3	0.366	0.36	19.23
CaF ₂	1.980	--	0.280	--	--
NaF	2.360	--	--	--	--
ZrO ₂	1.910	-376.4	--	--	--

Table 5. Interaction interfacial factors, B_{ij}^I , $\text{N m}^{-1} \text{mol}^{-1}$.

$i \setminus j$	CaO	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	Li ₂ O	ZrO ₂	NaF	CaF ₂
CaO	--	-0.98	-1.22	-0.90	-0.40	-0.40	-1.00	-3.45	-0.50
SiO ₂	-0.98	--	-0.20	-0.39	-1.20	-0.40	-0.70	-0.50	-0.10
Al ₂ O ₃	-1.22	-0.20	--	-15.0	-3.50	-14.5	-2.60	-7.00	-1.75
MgO	-0.90	-0.39	-15.0	--	-3.00	-18.0	0	-12.0	-3.05
Na ₂ O	-0.40	-1.20	-3.50	-3.00	--	-14.5	-0.50	-4.00	-3.45
Li ₂ O	-0.40	-0.40	-14.5	-18.0	-14.5	--	-1.00	-18.0	-18.0
ZrO ₂	-1.00	-0.70	-2.60	0	-0.50	-1.00	--	-6.00	-2.00
NaF	-3.45	-0.50	-7.00	-12.0	-4.00	-18.0	-6.00	--	-3.10
CaF ₂	-0.50	-0.10	-1.75	-3.05	-3.45	-18.0	-2.00	-3.10	--

$\text{Na}_2\text{O-Al}_2\text{O}_3$ flux reported by Gaye *et al.* are in general agreement with the predictions using Eq. (3). For the ternary system $\text{CaO-CaF}_2\text{-Al}_2\text{O}_3$, the measurements by Riboud *et al.* agree well with Eq. (3) if CaF_2 in the fluxes is below 70 mass%. In spite of a larger scatter in the values for fluxes with more than 15 mass% MgO and more than 30 mass% CaF_2 , there is a general agreement with those observed for the $\text{CaO-SiO}_2\text{-CaF}_2\text{-Na}_2\text{O-Li}_2\text{O-MgO-Al}_2\text{O}_3$ system reported by Shinozaki *et al.* The variation of the predicted interfacial tension compares reasonably well with those measured by Bretonnet *et al.* for the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system using slag lens method. But the interfacial tensions reported in their study are, in general, smaller than the measurements obtained in the present investigation.

The physical concepts of the interfacial tension factors, A_i , and interaction interfacial factors, B_{ij}^I , are not yet clear at present stage. A more extensive study on the multicomponent system is considered to be necessary in the future to upgrade the accuracy of these factors. It is instructive to examine the correlation of these factors with other properties of the flux to establish their physical

Fig. 12. Calculated vs. observed interfacial tension values for flux-iron system.

present work: $\text{CaO-SiO}_2\text{-NaF-CaF}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-MgO-Li}_2\text{O-ZrO}_2$, 1580°C, zirconia crucible
 Gaye *et al.*: $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-CaF}_2$, alumina crucible, 1600°C
 Bretonnet *et al.*: $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$, lens method, 1600°C
 Riboud and Lucas: $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$, alumina crucible, 1600°C
 Shinozaki *et al.*: $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-Li}_2\text{O-CaF}_2$, alumina crucible, 1600°C

Fig. 13. Relations of interfacial tension factors, A_i , with standard free energy changes of oxide formation (a), ΔG_i^0 , surface tension factors (b), σ_i , ion-oxygen attraction (c), I_i , and interaction energies with iron ion in flux (d), $\alpha_i^{Fe^{++}}$.

Fig. 14. Relations of interaction interfacial factors, B_i^j , with interaction surface factors (a), ω_{ij} , and interaction energies between cations (b), α_i^j .

meaning. Figure 13a) shows a slight increasing trend of interfacial tension factors with standard free energy changes²⁴⁾ for a pure solid oxide formation from one mole of oxygen gas and pure solid metal elements at 1580°C. Any significant trend can not be seen in Fig. 13b) between the interfacial tension factors and the surface tension factors.²⁵⁾ Figures 13c) and 13d), respectively, show the decreasing trend of the interfacial factors of a pure component with the ion-oxygen attraction²⁶⁾ and the increasing trend of those with interaction energies with iron ion in the fluxes.²⁷⁾ For the interaction interfacial factors, as seen in Figs. 14a) and 14b), respectively, there was an increasing trend of interaction interfacial factors with (a) interaction surface factors²⁵⁾ and (b) interaction energies between cations.²⁷⁾

Figures 15 and 16, respectively, show the relations of the interfacial tension, γ_0 , between molten iron and fluxes with optical basicity²⁸⁾ and with the viscosity of the fluxes. An increasing tendency of the interfacial tension with optical basicity of the fluxes and a slightly decreasing tendency of those with viscosity of the fluxes were observed.

5. Conclusions

The effects of (a) NaF, CaF₂, Al₂O₃, Na₂O, MgO, Li₂O and ZrO₂ in CaO-SiO₂ and CaO-SiO₂-Al₂O₃

Fig. 15. Relation between optical basicity of flux and interfacial tension.

Fig. 16. Relation between viscosity of flux at 1410°C and the interfacial tension between liquid iron and flux at 1580°C.

fluxes and (b) oxygen in the metal on the interfacial tension between molten iron and fluxes were investigated at 1580°C by the sessile drop method using zirconia or alumina crucibles. It was found that the interfacial tension between 35CaO-35SiO₂-30Al₂O₃ flux and liquid iron with various oxygen content could be expressed by the following equation.

$$\gamma_0 - \gamma = 0.324 \ln(1 + 116a_O) \quad \text{.....(2)}$$

where a_O is the activity of oxygen in liquid iron, and γ_0 is a hypothetical interfacial tension at infinitesimally low a_O .

In the examination of the variation of the interfacial tension with flux composition, the effect of oxygen in the melt was taken into account. The variation of the interfacial tension with flux composition has shown up the varying effects of some individual components of these flux. Minor changes in the interfacial tension were observed with varying ZrO₂ content in the fluxes. A slight decrease of the interfacial tension was found as the Al₂O₃ content in flux increased. The interfacial tension was markedly increased with the additions of Na₂O, MgO and Li₂O to the fluxes, and slightly increased with the

additions of the fluorides NaF and CaF_2 to the fluxes. An empirical relation, Eq. (3), for the prediction of the interfacial tension was derived from considering the effect of the flux components and oxygen content in the melt.

Acknowledgements

The authors wish to thank Mr. T. Matsuyama, Nippon Steel Metal Products Co., Ltd., for providing the several types of fluxes and chemical analyses of the fluxes. This work was sponsored by The Iron and Steel Institute of Japan and Nippon Steel Corporation.

REFERENCES

- 1) H. Sun, R. Ito, K. Nakashima and K. Mori: *Tetsu-to-Hagané*, **81** (1995), 888.
- 2) K. Nakajima: *Tetsu-to-Hagané*, **80** (1994), 593.
- 3) H. Bloom and B. W. Burrows: Proc. First Australian Conf. Electrochem., Pergamon Press, New York, (1963), 882.
- 4) T. Matsuyama: private communication.
- 5) K. Ogino, S. Hara, R. Mitsuwa and K. Kimoto: *Tetsu-to-Hagané*, **65** (1979), 2012.
- 6) K. Mukai, T. Kato and H. Sakao: *Tetsu-to-Hagané*, **59** (1973), 55.
- 7) N. Shinozaki, T. Kurashige, K. Mori and Y. Kawai: *J. Jpn. Inst. Met.*, **46** (1982), 60.
- 8) S. I. Popel and G. F. Kononov: *Izv. V.U.Z. Chernaya. Metall.*, **8** (1959), 3.
- 9) The Japan Society for the Promotion of Science, The 19th Comm. on Steelmaking: Steelmaking Data Sourcebook, Revised Edition, Gordon and Breach Science Publisher, Tokyo, (1988), 273.
- 10) G. R. Belton: *Metall. Trans. B*, **7B** (1976), 35.
- 11) Handbook of Physico-chemical Properties at High Temperatures, ed. by Y. Kawai and Y. Shiraishi, ISIJ, Tokyo, September, (1988).
- 12) K. Ogino, N. Nogi and C. Hosoi: *Tetsu-to-Hagané*, **69** (1983), 1989.
- 13) I. Jimbo, A. Sharan and A. W. Cramb: *Steelmaking Conf. Proc.*, **76** (1993), 485.
- 14) A. Kasama, A. McLean, W. A. Miller, Z. Morita and M. J. Ward: *Can. Metall. Q.*, **22** (1983), 19.
- 15) P. P. Evseev and A. F. Filippov: *Izv. VUZ.*, **6** (1965), 72.
- 16) N. Shinozaki, H. Fujiike, K. Mori and Y. Kawai: *Tech. Rep. Kyushu Univ.*, **62** (1989), 575.
- 17) H. Gaye, L. D. Lucas, M. Olette and P. V. Riboud: *Can. Metall. Q.*, **23** (1984), 179.
- 18) K. Ogino and S. Hara: *Tetsu-to-Hagané*, **63** (1977), 2141.
- 19) T. El Gammal and P. Stracke: Proc. 3rd Int. Conf. on Molten Slags and Fluxes, Glasgow, 1988: Inst. Met., London, (1989), 207.
- 20) A. Adachi, K. Ogino, T. Suetaki and T. Saito: *Tetsu-to-Hagané*, **51** (1965), 1857.
- 21) N. Yoneda, H. Sun and K. Mori: *CAMP-ISIJ*, **8** (1995), 1110.
- 22) J. L. Bretonnet, L. D. Lucas and M. Olette: *C. R. Hebd. Seances Acad. Sci.*, Paris **280C** (1975), 1169 and **285** (1977), 45.
- 23) P. V. Riboud and L. D. Lucas: *Can. Metall. Q.*, **20** (1981), 199.
- 24) Handbook of Iron and Steelmaking, ed. by ISIJ, Maruzen, Tokyo, (1983).
- 25) K. Nakajima: *Tetsu-to-Hagané*, **80** (1994), 599.
- 26) R. C. Ward: An Introduction to the Physical Chemistry of Iron and Steelmaking, Edward Arnold Ltd., London, (1962).
- 27) S. Ban-ya: *ISIJ Int.*, **33** (1993), 2.
- 28) J. A. Duffy: *Ironmaking Steelmaking*, **17** (1990), 411.
- 29) H. Sun, N. Yoneda, K. Nakashima and K. Mori: *Tetsu-to-Hagané*, **83** (1997), 1.