Effect of Alloy Elements on Interfacial Tension between Slag and Molten Iron

Haiping Sun, Naoya Yoneda, Kunihiko Nakashima and Katsumi Mori
Department of Materials Science & Engineering
Faculty of Engineering, Kyushu University
6-10-1 Hakozaki, Fukuoka, Japan 812-81
092-642-3666

ABSTRACT

The interfacial tensions between 35mass%CaO-35mass%SiO_2-30mass%Al_2O_3 slag and molten iron with varying oxygen, sulfur, carbon, silicon, aluminum, chromium, nickel and phosphorus contents were investigated at 1580°C by the sessile drop method. It was found that the interfacial tension (γ) between slag and molten iron decreased with increasing oxygen and sulfur contents and could be expressed by the following relation for the melts of [S]>0.07 mass%:

$$\gamma_{\text{pure iron}} - \gamma = RT\Gamma^{\circ} \ln(1+K_S a_S + K_O a_O)$$

Minor changes in the interfacial tension were observed with varying carbon and nickel contents in the molten iron. The interfacial tension markedly decreased with increasing chromium content while was increased with increasing aluminum, silicon and phosphorus contents in the molten iron.

1. INTRODUCTION

Interfacial tension between two phases is one of the important factors for improving the process operation since it influences on slag-metal reactions. In the casting processes, a better surface quality and less inclusion defect of steel products are considered to be partly related to flux/metal or inclusion/metal interfacial tension. Measurement of interfacial tension of various systems have been carried out to provide fundamental information for optimizing metallurgical processes. One of the critical reasons for the scattering of the interfacial values in the literatures could be the different oxygen levels in the metals. However, mutual reactions between slag and metal and then the variation of the oxygen in the melt can not be avoided in the high temperature measurement. In the present study, the variation of slag-metal interfacial tension with the contents of the interfacial active elements, oxygen and sulfur, in the metal was examined using Fe-O and Fe-O-S melts. The effect of the carbon, silicon, aluminum, chromium, nickel and phosphorus contents in the metal on the interfacial tension were also examined considering the coexist of oxygen in the melt.

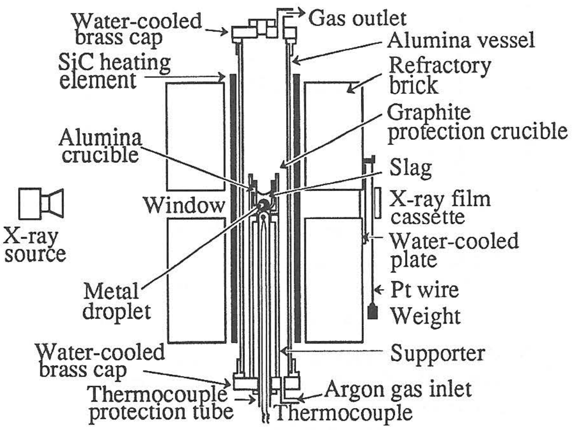

Fig. 1. Schematic diagram of the experimental apparatus.

2. EXPERIMENTAL PROCEDURES

An electrical resistance furnace, as shown in Fig. 1, was used for heating and melting iron and slag. The vertical alumina tube closed with water-cooled brass caps was purged with a purified argon gas during the experiments. The sessile iron droplet in the molten slag was observed using an X-ray device. The horizontal direction of the immersed droplet was determined using a vertical platinum wire hanging between the crucible and the film.

About 20 grams of iron alloy was melted in an alumina crucible (30 mm ID with a round bottom) under an argon atmosphere. After the temperature, which was measured with a thermocouple placed just below the crucible, reached 1580°C, about 25 grams of the slag was added on the surface of the liquid iron. The time when the slag fully melted was taken as the starting point of the contact of molten iron with the liquid slag. 20 minutes was allowed for slag/metal system to reach the equilibrium or steady state to avoid any changes of slag or metal compositions due to the slag/crucible and slag/metal reactions during the measurement. The X-ray photographs of the iron droplet were taken at every 2 minutes until 32 minutes after this starting point. The final metal sample was withdrawn using a quartz tube after the last photograph was taken. The metal compositions were determined by chemical analysis of these metal samples.

Initial iron samples were prepared by melting electrolytic iron (Fe>99.9%) in an induction furnace under a vacuum atmosphere, the alloying elements were added to this iron sample before the experiment. Slag (35mass%CaO -35 mass% SiO_2 -30 mass% Al_2O_3) was prepared by premelting mixtures of desired quantities of reagents in a platinum crucible, and then crushed to <12 mesh.

3. DETERMINATION OF INTERFACIAL TENSION

A profile of molten iron droplet in the slag, as shown schematically in Fig. 2, obtained from the X-ray photograph, was determined by measuring the diameters of the droplet in the horizontal direction at several arbitrary heights from the vertex of the droplet. In the present study, 7~13 points were read from the photograph. The interfacial tension was calculated using curve the fitting method as

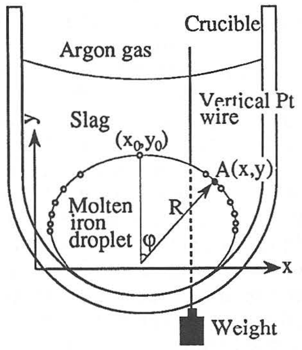

Fig. 2. Schematic of the profile of a sessile drop in molten slag.

follows.

Young and Laplace relation shown by the Equation (1) is derived from the balance of forces acting on the interface between two phases,

$$R = b\left(\beta\frac{y_0 - y}{b} + 2 - \frac{b\sin\varphi}{x}\right)^{-1} \quad (1)$$

where

$$\beta = \frac{g\,b^2}{\gamma}(\rho_m - \rho_s) \quad (2)$$

For a point A at the contour of the droplet, the small changes of abscissa, x, and ordinate, y, due to small change in the angle between a vertical direction and the normal direction at point A, φ, are given by,

$$dx = R\cos\varphi\, d\varphi \quad (3)$$
$$dy = -R\sin\varphi\, d\varphi \quad (4)$$

Where

R is radius of curvature at point A, m.
b is radius of curvature at vertex of the droplet, m.
β is the shape parameter for a sessile droplet.
γ is the interfacial tension between two phases, N m^{-1}.
ρ_m and ρ_s are the densities of the melt and slag, kg m^{-3}.
g is the acceleration of gravity, kg m^{-1} s^{-2}.

Taking the values at the vertex of the droplet ($x=x_0$, $y=y_0$, $\varphi=0$ and $R=b$) as the initial conditions, the shape of the droplet can be calculated based on the numerical integration of Equations (1), (3) and (4) for the given values of the parameters β and b. The solid line in Fig. 2 shows the calculated shape of the droplet, which was compared with the measured values as shown by the points in the figure. The error, ε, was calculated as the sum of the distance between the computed and measured points ($(x,y)_{cal} - (x,y)_{obs}$) using equation (5)

$$\varepsilon = \frac{1}{N}\sum_{i=1}^{N}\{(x,y)_{cal} - (x,y)_{obs}\}^2 \quad (5)$$

The numerical integration was repeated with varying the values of b and β for several hundreds times. The values of b and β with which the minimum ε was obtained were selected as the values for the observed shape of the droplet. The interfacial tension was then determined using the values of b and β in the Equation (2) with the densities of two phases. In the present study, ε was generally less than 10^{-10} m^2, which corresponds the tolerances of the b and β to be ±0.62 % and ±1 %, respectively, and subsequently a tolerance of the interfacial tension to be ±1.25 % and ±1.00%, respectively.

The density of the pure iron used in these calculations was taken as 6.94 g cm^{-3}. Effects of oxygen, aluminum and carbon on the melt density were not taken into consideration since their contents in the present study were negligible low, while the densities of the other alloys were estimated by the literature values[1,2]. Density for 35mass% CaO-35mass%SiO_2-30mass%Al_2O_3 slag at 1580 °C was estimated to be 2.704 g cm^{-3} by the regular solution approximation model proposed by Nakajima[3]. The variation of the slag composition by the reaction with melt was also taken into account in the slag density estimation with the model.

4. RESULTS

4.1 Variation of interfacial tension with time

The variation of interfacial tension with time were observed in the measurements for entire systems investigated. Several examples were shown in Fig. 3, the values of interfacial tension were essentially independent with the time in the time period of 20~32 minutes after liquid slag contacting with the melt, which indicates that the equilibrium or steady state had been reached before the X-ray photographs were taken. The average value of these points was taken as the interfacial tension value for the system concerned. The smaller deviation of the points of lower interfacial tension system (curve 3) is because the shape of the sessile droplet is more sensitive to the interfacial tension than higher interfacial tension system (curve 1 and 2) thus to be easier measured.

4.2 Effect of interfacial active element

Oxygen and sulfur are well known as the interfacial active element and frequently presented in the melt during

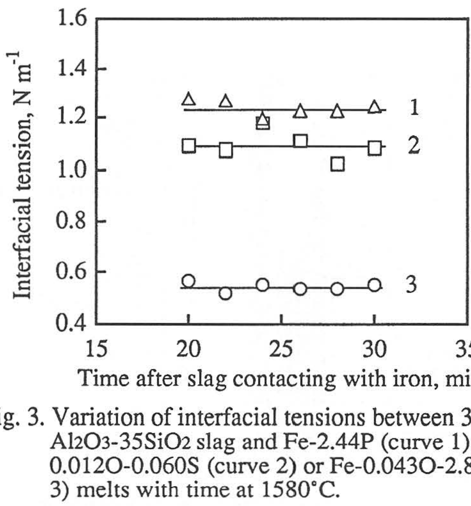

Fig. 3. Variation of interfacial tensions between 35CaO-30 Al_2O_3-35SiO_2 slag and Fe-2.44P (curve 1), Fe-0.012O-0.060S (curve 2) or Fe-0.043O-2.87S(curve 3) melts with time at 1580°C.

the steelmaking precesses. Many investigations have been carried out on the oxygen or sulfur effect[4,7-11,15-17], but a numerical relation between interfacial tension and oxygen and/or sulfur content has not yet well understood. This is because the slag system and composition were not identical and the oxygen present in the melt during the investigation of sulfur effect was not taken into account in those studies.

The surface tension (γ, N m^{-1}) for Fe-O melts can be expressed as a function of oxygen activity, a_O, by the following equation, which was derived by combining the Gibbs' and Langmuir adsorption isotherm with a given oxygen adsorption constant K_O.

$$\gamma_0-\gamma=RT\Gamma_O^0 \ln(1+K_O a_O) \qquad (6)$$

where γ_0 is the surface tension for the pure liquid and Γ^0 (mole m^{-2}) is the surface excess quantity at full coverage. This relation was applied to the interfacial tension[4,5] by substituting surface tension with interfacial tension.

For Fe-O-S system, assuming interfacial excess quantity of iron $\Gamma_{Fe}=0$ and the interfacial excess quantity at full coverage of oxygen is equal to that of sulfur, $\Gamma_O^0=\Gamma_S^0\equiv\Gamma^0$, following equation can be obtained,

$$\gamma_0-\gamma=RT\Gamma^0 \ln(1+K_O a_O+K_S a_S) \qquad (7)$$

There is an alternative approach[12] to the surface tension of Fe-O-S system assuming the additivity of the contribution of oxygen and sulfur to the surface tension,

$$\gamma_0-\gamma=RT\Gamma_O^0 \ln(1+K_O a_O)+RT\Gamma_S^0 \ln(1+K_S a_S) \qquad (8)$$

These three relations will be discused later with the observed values of the interfacial tension.

In the present study, the effect of oxygen and sulfur contents on the interfacial tension between slag and molten iron was investigated using $35CaO-35SiO_2-30Al_2O_3$ slag and pure molten iron. The oxygen and sulfur contents for Fe-O and Fe-O-S systems, as obtained from the chemical analysis of the quenched metal samples after the experiments, are shown in Table I. For Fe-O system, oxygen content and interfacial tension varied from 0.0055 to 0.0598 mass%, and 1.230 to 0.705 N m^{-1}, respectively. For Fe-O-S system, oxygen and sulfur varied from 0.0058 to 0.0643 mass%, and, from 0.056 to 6.09 mass%, respectively, and interfacial tension changed from 0.453 to 1.100 N m^{-1}. The oxygen and sulfur activities in the table were calculated using the interaction parameters[6], $e_O^O=-0.17$, $e_O^S=-0.133$, $e_S^S=-0.046$ and $e_S^O=-0.27$.

Fe-O system

The results for Fe-O system are shown in Fig. 4. A decrease in the interfacial tension with increasing the oxygen content was observed. The present results agreed well with those for $47CaO-53Al_2O_3$/Fe-O system at 1580 °C by Krinochkin et al.[7] and $CaO-SiO_2$ based slag/Fe-O system at 1580 °C by Ogino et al.[8] and were about 0.1 N m^{-1} greater than the $50CaO-50Al_2O_3$/Fe-O system at 1570 °C by Mukai et al.[9]. Fig. 5 shows the semi-logarithmic relation between interfacial tension and oxygen content. The linear relation was observed in the range ln a_O>-4.5. The excess oxygen quantity, 1.63×10^{-9} mol cm^{-2} was calculated from Gibbs adsorption isotherm in this range. For the comparison, the results reported by Ogino et al.[10] and Olette[11] for the similar slag systems are also shown in the figure.

Table I Interfacial tensions (γ)between $35CaO-35SiO_2-30Al_2O_3$ slag and Fe-O or Fe-O-S alloys at 1580°C.

Fe-O alloy			Fe-O-S alloy				
[O] mass%	a_O	γ N m^{-1}	[O] mass%	[S] mass%	a_O	a_S	γ N m^{-1}
0.0055	0.0055	1.168	0.0065	0.067	0.0064	0.067	1.058
0.0066	0.0066	1.230	0.0151	0.057	0.0148	0.056	1.016
0.0069	0.0069	1.180	0.0122	0.060	0.0119	0.059	1.100
0.0073	0.0073	1.183	0.0270	0.060	0.0262	0.059	0.893
0.0073	0.0073	1.211	0.0176	0.077	0.0171	0.076	0.940
0.0073	0.0073	1.223	0.0262	0.103	0.0251	0.100	0.837
0.0081	0.0080	1.143	0.0329	0.126	0.0312	0.122	0.833
0.0081	0.0080	1.184	0.0058	0.127	0.0056	0.125	0.978
0.0081	0.0081	1.218	0.0230	0.160	0.0217	0.155	0.798
0.0085	0.0085	1.137	0.0356	0.136	0.0337	0.131	0.743
0.0088	0.0088	1.146	0.0086	0.317	0.0078	0.305	0.862
0.0106	0.0106	1.152	0.0092	0.941	0.0069	0.847	0.709
0.0130	0.0130	1.050	0.0089	1.034	0.0065	0.922	0.693
0.0147	0.0146	1.080	0.0105	1.300	0.0070	1.125	0.656
0.0162	0.0161	1.081	0.0133	0.327	0.0120	0.313	0.874
0.0181	0.0180	1.014	0.0081	0.552	0.0068	0.518	0.777
0.0183	0.0182	0.992	0.0105	0.981	0.0077	0.878	0.675
0.0187	0.0186	1.015	0.0637	5.870	0.0103	3.030	0.461
0.0197	0.0195	0.992	0.0460	4.250	0.0123	2.633	0.495
0.0211	0.0209	0.986	0.0427	2.870	0.0174	2.062	0.542
0.0247	0.0244	0.931	0.0207	1.990	0.0112	1.591	0.593
0.0270	0.0267	0.933	0.0643	6.090	0.0097	3.070	0.453
0.0281	0.0278	0.945	0.0439	4.840	0.0098	2.821	0.463
0.0313	0.0309	0.884	0.0421	4.380	0.0108	2.683	0.480
0.0333	0.0329	0.881	0.0097	0.160	0.0092	0.156	0.902
0.0363	0.0357	0.847	0.0082	0.254	0.0076	0.246	0.893
0.0400	0.0394	0.798	0.0084	0.358	0.0075	0.343	0.854
0.0410	0.0404	0.791	0.0104	0.484	0.0089	0.457	0.856
0.0436	0.0429	0.821	0.0109	0.602	0.0090	0.561	0.832
0.0438	0.0430	0.847	0.0165	0.684	0.0133	0.630	0.759
0.0443	0.0436	0.807	–	–	–	–	–
0.0522	0.0511	0.754	–	–	–	–	–
0.0586	0.0573	0.709	–	–	–	–	–
0.0598	0.0584	0.705	–	–	–	–	–

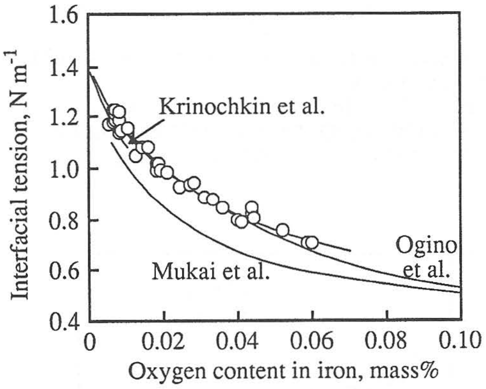

Fig. 4. Variation of iron-slag interfacial tension with sulfur content in iron.
this work: 35CaO-30Al2O3-35SiO2/Fe-O, 1580°C
Krinochkin et al.(ref.7):47CaO-53Al2O3/Fe-O, 1570-600°C
Ogino et al.(ref.8):CaO-SiO2 based slag/Fe-O, 1580°C
Mukai et al.(ref.9):50CaO-50Al2O3/Fe-O, 1570°C

The values of parameters, γ_0, $RT\Gamma^0$ and K_O in equation (6) for the data of Fe-O system were determined by an iteration calculation involving several steps: (i) the values of the γ_0 and $RT\Gamma^0$ are calculated using a given value of K_O obtained by least square method, and (ii) then this calculation was repeated by changing the value of K_O until the maximum value of the correlation coefficient for the relation between γ and $\ln(1+K_O a_O)$ was obtained. The relation for $35CaO$-$35SiO_2$-$30Al_2O_3$ slag and Fe-O melt at 1580°C was found as follows,

$$\gamma_0-\gamma=0.324\ \ln(1+116a_O) \qquad (9)$$

The measured values based on Equation (9) are shown by open triangular mark in Fig. 6. A hypothetical interfacial tension, γ_0, at infinitesimally low a_O for this system was found to be 1.386 N m^{-1}. If the adsorption of oxygen, in the form of ion, at the slag-molten iron interface is a single layer configuration, the value of $RT\Gamma^0$=0.417 N m^{-1} can be calculated from the radius of oxygen ion. If the adsorption of oxygen at the slag-molten iron interface is a single layer configuration of FeO, the value of $RT\Gamma^0$ =0.272 N m^{-1} is obtained from the radii of oxygen and iron ions. When compared with the value of $RT\Gamma^0$ obtained in present study (0.324 N m^{-1}), the adsorption of oxygen at the slag-molten iron interface is more likely to occur as a single layer configuration of FeO. The values of $RT\Gamma^0$ and K_O, respectively, reported by Ogino et al.[12] at 1600 °C, Jimbo et al.[13] at 1550 °C and Kasama et al.[14] at 1600 °C 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 $RT\Gamma^0$ and K_O for interfacial tension agree comparably well with those reported for the surface tension.

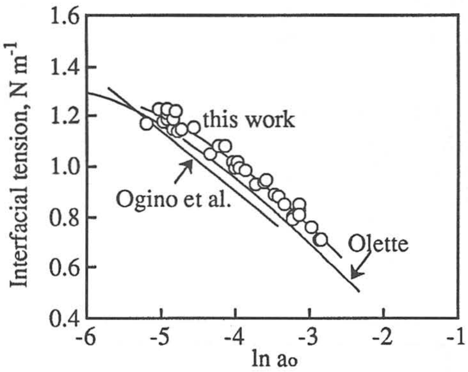

Fig.5. Iron-slag interfacial tension as function of sulfur activity in iron.
this work: 35CaO-30Al2O3-35SiO2/Fe-O, 1580°C
Ogino et al.(ref.10):40CaO-20Al2O3-40SiO2/Fe-O,1600°C
Olette(ref.11):CaO-Al2O3-SiO2-FeO/Fe-O, 1600°C

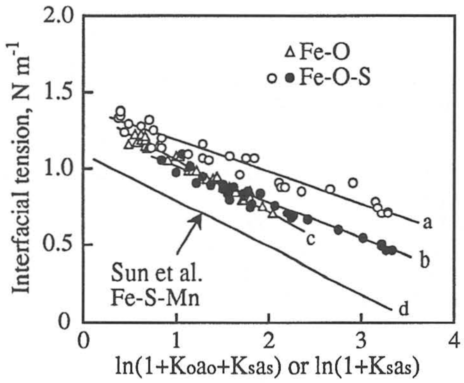

Fig. 6. Iron-slag interfacial tensions versus sulfur and oxygen activities in iron.
this work: 35CaO-30Al2O3-35SiO2, 1580°C
Fe-O (line c): γ=1.386-0.324 ln(1+116ao)
Fe-O-S(line b): γ=1.238-0.236 ln(1+116ao+8.5as)
Fe-O-S(line a): γ =1.381-0.204 ln(1+8.5as)
or γ^0=1.381-0.324 ln(1+116ao)-0.204 ln(1+8.5as)
Sun et al.(ref.4): MnO-30Al2O3-SiO2/Fe-S-Mn, 1550°C
(line d): γ=1.07-0.235 ln(1+120ao+10as)

Fe-O-S system

The results on the influence of sulfur content in the melt are shown in Fig. 7. A decrease in the interfacial tension was observed as the sulfur content in the melt increases. The results for the $47CaO$-$23Al_2O_3$-$27SiO_2$ slag reported by Popel et al.[15], MnO-Al_2O_3-SiO_2 slag reported by Sun et al.[4], showing a lower interfacial values, are also presented in the figure to provide a comparison with the present results. Fig. 8 shows the semi-logarithmic relation between interfacial tension and sulfur activity. The present results are in fairly good agreement with those by Cramb and Jimbo[16], and Olette[17] for the similar system but are somewhat larger than those for MnO-Al_2O_3-SiO_2 slag by Sun et al.[4]. The linear relation was observed for the measured values, γ, in the range $\ln a_S>-1.2$, while a large scatter of the points was observed when $\ln a_S<-1.2$. This indicates that the effect of oxygen in the melt on the interfacial tension can not be ignored at lower sulfur contents. With the consideration of the Equation (8) assuming the additivity of the effect of two elements, the interfacial tensions where oxygen activity in the molten iron is zero, γ_0, were calculated for the Fe-O-S with relation (9). The values of γ_0, which take oxygen content in the melt into account, were also given in the Figs 6 through 8. The excess sulfur quantity, 1.01×10^{-9} mol cm^{-2} is calculated from open points in Fig. 8 where the effect of oxygen was not included.

Experimental results of the melts containing oxygen and sulfur treated with relations (7) and (8) are given by solid and open circles, respectively, in Fig.6. The relations were found to be,

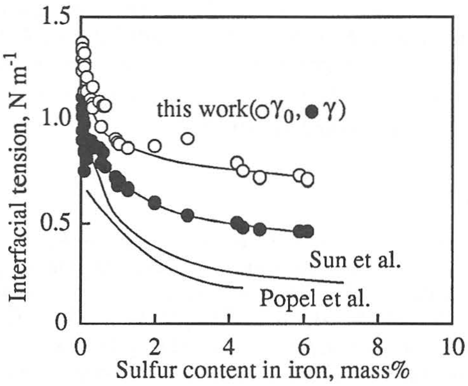

Fig. 7. Variation of iron-slag interfacial tension with sulfur content in iron.
this work: 35CaO-30Al2O3-35SiO2/Fe-S-O, 1580°C
Popel et al.(ref.15): 47CaO-23Al2O3-27SiO2-1FeO/ Fe
Sun et al.(ref.4): MnO-Al2O3-SiO2/Fe-S-Mn,1580°C

$$1.241-\gamma=0.252\ln(1+116a_O+8.5a_S) \qquad (10)$$
$$1.381-\gamma=0.324\ln(1+116a_O)+0.204\ln(1+8.5a_S) \qquad (11)$$

Smaller deviation was found for the relation by equation (10) than by equation (11). The values of $RT\Gamma^0$, K_O and K_S used in equation (10) were in good agreement with those for MnO-Al_2O_3-SiO_2 slag reported by Sun et al.[4] because of the nearly constant oxygen contents of melts used by them. However, the values of γ_0 and $RT\Gamma^0$ estimated by equations (9) and (10) are different. This is because equation (10) was obtained by fitting the data of relatively higher sulfur region. Therefore, the data points of Fe-O-S melts with sulfur contents below 0.07mass% can be expressed by modifying equation (9) as

$$1.386-\gamma=0.324\ln(1+116a_O+8.5a_S) \qquad (12)$$

The iso-interfacial tension diagram for Fe-O-S system with slag at 1580 °C was drawn in Fig. 9. The interfacial tension is sensitive to the oxygen and sulfur if their content in the melt are lower.

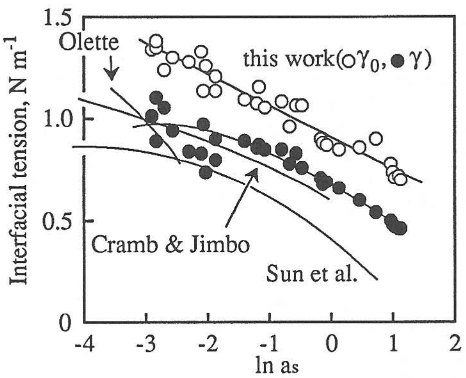

Fig.8. Iron-slag interfacial tension as function of sulfur activity in iron.
this work: 35CaO-30Al2O3-35SiO2/Fe-S-O, 1580°C
Cramb & Jimbo(ref.17):CaO-Al2O3-SiO2/Fe-S,1600°
Olette(ref.16):30CaO-30Al2O3-35SiO2/Fe-S-Si (ao=0.016), 1600°C
Sun et al.(ref.7):35MnO-30Al2O3-35SiO2/Fe-S-Mn, 1550°C

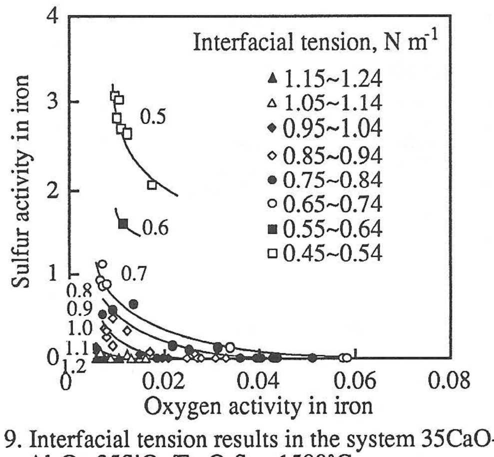

Fig. 9. Interfacial tension results in the system 35CaO-30 Al2O3-35SiO2/Fe-O-S at 1580°C.

4.3 Effect of alloying element

The interfacial tension measurement was carried out for Fe-Si, Fe-Al-Si, Fe-C, Fe-P, Fe-Cr and Fe-Ni alloys. The final melt compositions and the interfacial tensions are summarized in Table II. In these measurements, the variation of the oxygen content in the metal phases can not be avoided. Therefore, the surface excess quantity at full coverage and equilibrium constant of oxygen adsorption were assumed to be independent of alloying elements, and hypothetical interfacial tensions (where oxygen activity in the molten iron is zero, γ_0), were calculated using Equation (9). The values of γ_0, which is independent of the oxygen content in the melt, is used to examine the effect of alloying elements on the interfacial tension between the slag and the molten iron alloys. Oxygen activities of the melt, a_O, were calculated from final melt compositions with the interaction parameters[6], $e_O^O=-0.17$, $e_O^{Si}=-0.066$, $e_O^{Al}=-1.17$, $e_O^{C}=-0.421$, $e_O^{P}=0.07$, $e_O^{Cr}=-0.055$ and $e_O^{Ni}=0.006$.

Fe-Si system

The variation of the interfacial tension with silicon content in the melt is shown in Fig. 10. The solid and open circles show the measured values, γ, and the values corrected with respect to the oxygen activity, γ_0, respectively. An increase in the interfacial tension was

Table II Interfacial tensions (γ) between iron based alloys and $35CaO$-$35SiO_2$-$30Al_2O_3$ slag at 1580 ℃.

Content in metal (mass%) Element		[O]	a_O	ρ_m g cm^{-3}	γ N m^{-1}	γ_0 N m^{-1}
pure iron						
0		0.0073	0.0073	6.94	1.183	1.386
Fe-Si, [Si]						
0.964		0.0017	0.0015	6.89	1.355	1.408
1.52		0.0029	0.0023	6.86	1.357	1.433
3.19		0.0024	0.0015	6.76	1.531	1.582
4.17		0.0060	0.0032	6.71	1.452	1.554
6.34		0.0050	0.0019	6.59	1.450	1.515
1.81		0.0014	0.0011	6.84	1.438	1.476
Fe-Al, [Al]	[Si]					
0.0027	0.148	0.0037	0.0035	6.93	1.350	1.466
0.0016	0.057	0.0053	0.0052	6.94	1.271	1.424
0.0002	0.280	0.0040	0.0039	6.92	1.260	1.380
0.0105	0.575	0.0066	0.0058	6.91	1.259	1.426
0.0010	0.404	0.0037	0.0034	6.92	1.343	1.451
0.0172	0.780	0.0032	0.0027	6.90	1.461	1.549
Fe-C, [C]						
0.069		0.0072	0.0071	6.94	1.179	1.374
0.381		0.0084	0.0079	6.94	1.118	1.329
Fe-P, [P]						
7.07		0.0038	0.0117	6.59	1.223	1.501
8.55		0.0053	0.0211	6.51	1.131	1.532
5.48		0.0089	0.0214	6.68	1.269	1.673
4.08		0.0083	0.0160	6.76	1.259	1.599
9.64		0.0057	0.0268	6.45	1.211	1.669
Fe-Cr, [Cr]						
9.96		0.0088	0.0025	6.81	1.110	1.192
12.8		0.0076	0.0015	6.80	1.110	1.162
18.5		0.0101	0.0010	6.75	1.071	1.105
24.2		0.0154	0.0007	6.73	1.041	1.067
34.1		0.0256	0.0003	6.66	0.983	0.995
34.3		0.0147	0.0002	6.66	0.977	0.984
Fe-Ni, [Ni]						
14.3		0.0062	0.0076	7.10	1.108	1.313
43.6		0.0041	0.0074	7.31	1.075	1.275
45.9		0.0034	0.0065	7.33	1.073	1.255
50.1		0.0027	0.0055	7.36	1.049	1.208
8.09		0.0072	0.0080	7.06	1.133	1.346

observed as the silicon content in the melt increases. The interfacial tension values obtained in the present work are at similar level with those reported by Dumay and Cramb[18] for Fe-Si system, while values provided by other investigators[7,19-21] are generally lower than the present work. The same increasing trend was also seen in the results for Fe-Cr by Bairamov et al.[20], and Ooi et al.[21], where the slag compositions were close to the present work. For $CaO-Al_2O_3$ based slag measured by Ogino et al.[19] and Krinochkin et al.[7], however, show an opposite trend as silicon content increases.

Fe-Al system

Fig. 11 shows the interfacial tension variation with aluminum content in the melt which shows the similar trend to that of silicon, i.e., an increase in the aluminum content increases the interfacial tension. Due to the stronger affinity of aluminum with oxygen than that of silicon, the reduction of SiO_2 by aluminum in the melt occurred after SiO_2 bearing slag contacted with the melt containing aluminum. As

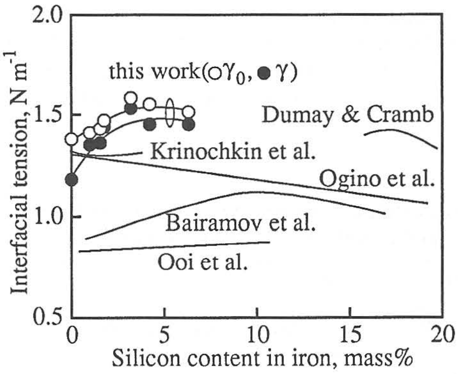

Fig. 10. Variation of iron-slag interfacial tension with silicon content in iron.
this work: 35CaO-30Al2O3-35SiO2/Fe-Si, 1580°C
Dumay & Cramb(ref.18): 29CaO-12Al2O3-59SiO2/Fe-Si, 1450°C
Ogino et al.(ref.19): 46CaO-49Al2O3-5.3MgO/Fe-Si,1540°C
Krinochkin et al.(ref.7): 47CaO-53Al2O3/Fe-Si, 1550-1600°C
Bairamov et al.(ref.20):43CaO-15Al2O3-8MgO-32SiO2/Fe-Cr,1700°
Ooi et al.(ref.21):40CaO-20Al2O3-40SiO2/Fe, 1570°C

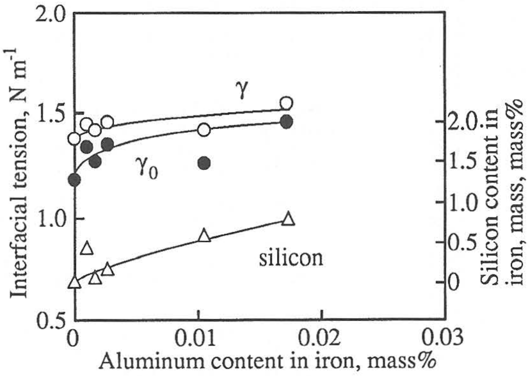

Fig. 11. Variation of interfacial tension between 35CaO-30Al2O3-35SiO2 slag and Fe-Al melt with aluminum content in iron at 1580°C

shown in the figure, an increase in the silicon content in the melt was found with increasing final aluminum content. The increase in the interfacial tension in Fe-Al system could be possibly partly attributed to this increase in silicon content in the melt. Compared with the results shown in Fig.10 for Fe-Si system, the interfacial tension is considered to be increased with increasing aluminum content in the melt even with taking account of the contribution of the increase in the silicon content.

Fe-C system

As can be seen from Fig. 12, a slight decrease in the interfacial tension was observed with increasing carbon content in Fe-C melt. The values obtained by Mukai et al.[9] and Popel[22] for $CaO-Al_2O_3$, and $CaO-SiO_2-Al_2O_3$ slag, respectively, are also presented in the figure. Their results are consistent with those of the present work. The values for $CaO-SiO_2-Al_2O_3$ slag by Gaye et al.[23], however, show the increasing trend with carbon additions. A gas bubble attached to the iron drop was observed between slag/melt interface when more than 0.5 mass% carbon was contained. Equation (1) can not be applied to such a system. So, the interfacial values could not be measured beyond this carbon content in the present work.

Fe-P system

The influence of phosphorus content in the Fe-P melt on the interfacial tension is shown in Fig. 13. An increase in the interfacial tension was observed as the phosphorus content in the melt increases. However an opposite trend was obtained in the studies of Popel[22] and Ogino et al.[19] for $CaO-SiO_2-Al_2O_3$ and $CaO-SiO_2-MgO$ slag, respectively.

Fe-Cr system

Fig. 14 shows the influence of chromium content in the Fe-Cr melt on the interfacial tension. The measured interfacial tension was slightly decreased with increasing chromium content, while a stronger decreasing trend was observed for γ_0. This can be explained that the difference between γ_0 and γ become smaller due to the lower oxygen activity in the higher chromium melt. For the binary CaO-

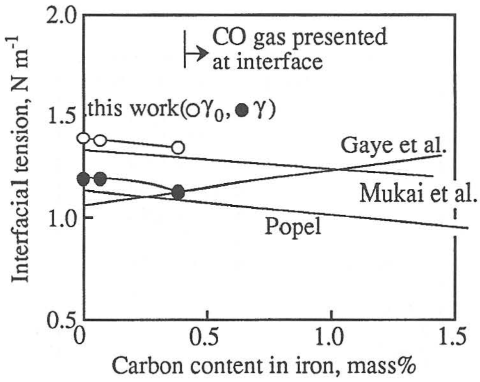

Fig. 12. Variation of iron-slaginterfacial tension with carbon content in iron.
this work: 35CaO-30Al2O3-35SiO2/Fe-C, 1580°C
Mukai et al.(ref.9): CaO-Al2O3/Fe-C, 1570°C
Popel(ref.22): 39CaO-26Al2O3-35SiO2/Fe-C, 1560°C
Gaye et al.(ref.23): CaO-Al2O3-SiO2/Fe-C

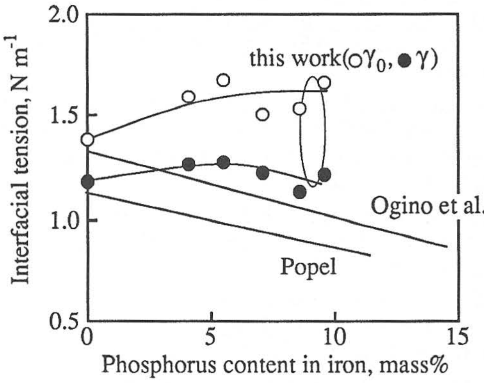

Fig. 13. Variation of iron-slag interfacial tension with phosphorus content in iron.
this work: 35CaO-30Al2O3-35SiO2/Fe-P, 1580°C
Ogino et al.(ref.19): 46CaO-49Al2O3-5.3MgO/Fe-P, 1540°C
Popel(ref.22): 39CaO-26Al2O3-35SiO2/Fe-P, 1560°C

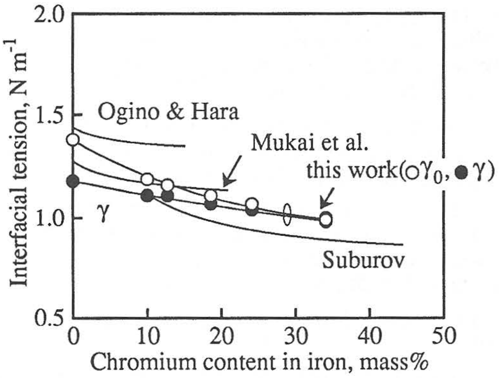

Fig. 14. Variation of iron-slag interfacial tension with chromium content in iron.
this work: 35CaO-30Al2O3-35SiO2/Fe-Cr, 1580°C
Ogino & Hara(ref.24): 50CaO-50Al2O3/Fe-Cr, 1600°C
Saburov et al.(ref.25): 40CaO-60Al2O3/Fe-Cr, 1650°C
Mukai et al.(ref.9): CaO-Al2O3/Fe-Cr, 1570°C

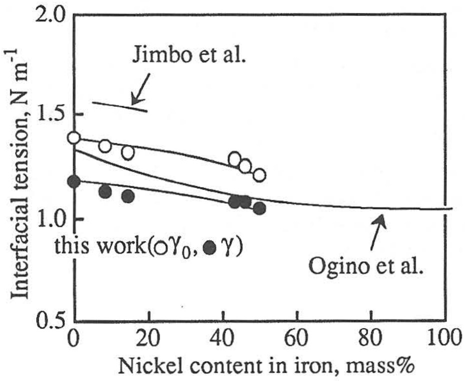

Fig. 15. Variation of iron-slag interfacial tension with nickel content in iron.
this work: 35CaO-30Al2O3-35SiO2/Fe-Ni, 1580°C
Jimbo et al.(ref.26): CaO-Al2O3 flux, Fe-Ni, 1550°C
Ogino et al.(ref.19): 46CaO-49Al2O3-5.3MgO/Fe-Ni, 1540°C

Al_2O_3 slag, the measurements by Mukai et al.[9], Ogino and Hara[24], and Suburov et al.[25] also show a slightly decrease of interfacial tension with chromium addition. The results of Mukai et al. and Suburov agree well with present work since the metal oxygen activity could be easier kept at a lower level in Fe-Cr melt and the variation of the interfacial tension due to the different oxygen content could be essentially eliminated, especially for higher chromium melt.

Fe-Ni system

The results on the influence of nickel content in the Fe-Ni melt are shown in Fig. 15. The nickel content in the Fe-Ni melt was varied from 0 to 45 mass% and a slight decrease in the interfacial tension was observed as the nickel content in the melt increases. This is in agreement with the results for the $CaO\text{-}Al_2O_3\text{-}MgO$ based slag reported by Ogino et al.[19] but much lower than that obtained by Jimbo et al.[26] for $CaO\text{-}Al_2O_3$ slag.

γ_0-solute content relation

As mentioned previously, since interfacial tension of any system is very sensitive to the oxygen activity in the melt the values of γ_0 which the effect of oxygen was taken into account are used for the comparison between various systems. Fig. 16 shows the summary of the effect of the additions in the melt on the interfacial tension, γ_0, obtained for each system. The measured interfacial value, γ, was used for oxygen curve in the figure. The interfacial tension increased with increasing concentration of aluminum, phosphorus and silicon, slightly decreased with increasing carbon and nickel contents, and decreased by adding oxygen, sulfur and chromium to the melt.

5. CONCLUSION

The interfacial tensions of $35mass\%CaO\text{-}35mass\%SiO_2\text{-}30mass\ \%Al_2O_3$ slag with Fe-O, Fe-O-S, Fe-Si, Fe-Al-Si, Fe-C, Fe-P, Fe-Cr or Fe-Ni alloys were investigated at 1580°C by the sessile drop method. The interfacial tension (γ_0) for Fe-O and Fe-O-S systems decreased with increasing oxygen and/or sulfur contents and

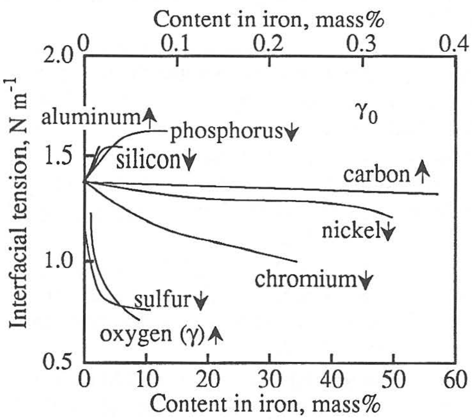

Fig. 16. Effect of content of element in molten iron on interfacial tension for 35CaO-30Al2O3-35SiO2 /iron system at, 1580°C

their values (N m^{-1}) were found to follow Gibbs' relation. A hypothetical interfacial tension (γ_0) at infinitesimally low a_O, for the Fe-(S, Si, Al, C, P, Cr or Ni) melt systems were estimated using $\gamma_0 - \gamma = 0.324 \ln (1 + 116 a_O)$ with measured interfacial tension (γ) and oxygen activity (a_O). By examining the variation of γ_0 with contents of impurity or alloying elements in the melt, it was found that minor changes in the interfacial tension were observed with varying carbon and nickel contents in the molten iron. The interfacial tension markedly decreased with increasing sulfur and chromium contents while was increased with increasing aluminum, silicon and phosphorus contents in the molten iron.

REFERENCES

1. Iron and Steel Institute of Japan, "Densities", Handbook of the Properties of Molten irons and slags, Iron and Steel Institute of Japan, Tokyo, Japan, January 1972, pp.1-31
2. S. Watanabe, K. Ogino and Y. Tsu, "Density and Compressibility", Handbook of Physico-chemical Properties at High Temperature, Edited by Y. Kawai and Y. Shiraishi, The Iron and Steel Institute of Japan, Tokyo, Japan, September 1988, pp.1-43
3. K. Nakajima, "Estimation of Molar Volume for Multicomponent Silicate Melts", Tetsu-to-Hagane, Vol. 80, No.8, August 1994, pp.593-598
4. H. Sun, R. Ito, K. Nakashima and K. Mori,"Interfacial Tension between Mutual Interfaces of Liquid Iron, SiO_2-Al_2O_3-MnO-MnS slags and MnS Based Sulfide", Tetsu-to-Hagane, Vol.81, No.9, 1995, pp.888-893
5. N. Shinozaki, T. Kurashige, K. Mori and Y. Kawai, " The Effect of Oxygen and Manganese on the Interfacial Tension between Liquid Iron and Slag", Journal of the Japan Institute of Metals,Vol.46, No.1, 1982,pp.60-66
6. The Japan Society for the Promotion of Science, The 19th Committee on Steelmaking, "Recommended Values of Activity Coefficients and Interaction Parameters of Elements in Iron Alloys", Steelmaking Data Sourcebook, Revised Edition, Gordon and Breach Science Publisher, Tokyo, Japan, 1988, pp.273-325
7. E.V.Krinochkin, K.T. Kurochkin, P.V. Umrikhin:Nauchn. Trudy. Mosk. Inst.Stali. Splav. Vol. 79, 1973, p.31
8. K. Ogino, S. Hara, T. Miwa and S. Kimoto,"The Effect of Oxygen Content in Molten Steel on the Interfacial Tension between Molten Steel and Slag", Tetsu-to-Hagane, Vol.65, No.14, 1979, pp.2012-2021
9. K. Mukai, T. Katou and H. Sakao, "On the Determination of Interfacial Tension between Liquid Iron Alloy and CaO-Al_2O_3 Slag", Tetsu-to-Hagane, Vol.59, No.1, 1973, pp.55-62
10. K. Ogino, S. Hara, T. Miwa and S. Kimoto, "The Effect of Oxygen Content on the Interfacial Tension between Molten Iron and Slag", Transactions ISIJ, Vol.24, No.6, 1984, pp.522-531
11. M. Ollette,"Interfacial Phenomena and Mass Transfer in Extracting Metallurgy", Steel Research, Vol.59, No.6,1988, pp.246-256
12. K. Ogino, N. Nogi and C. Hosoi, "Surface Tension of Molten Fe-O-S Alloy", Tetsu-to-Hagane, Vol.69, No.16, 1983, pp.1989-1994
13. I. Jimbo, A. Sharan and A. W. Cramb, "Recent Measurements of Surface and Interfacial Tensions in Steels", Proceedings of 76th Steelmaking Conference of the Iron and Steel Society, Dallas, TX, 1993, pp. 485-494
14. A. Kasama, A. McLean, W. A. Miller, Z. Morida and M. J. Ward, "Surface Tension of Liquid Iron and Iron-Oxygen Alloys", Canadian Metallurgical Quarterly, Vol.22, No.1, 1983, pp.9-17
15. S.I. Popel, O.A.Esin, G.F.Konovalov and N.S.Smirnov, Proc. Acad. Sci. USSR (Phys. Chem.), Vol.112, 1957, p.27
16. A.W.Cramb and I.Jimbo, "Interfacial Considerations in Continuous Casting", Transaction of the ISS, Vol.16, No.6, June 1989, pp.43-55
17. M. Olette, "Surface Phenomena: A Cornerstone of Iron and Steelmaking Processes", ISIJ International , Vol.33, No. 10, 1993, pp.1113-1124
18. C.Dumay and A.W.Cramb, "Density and Interfacial Tension of Liquid Fe-Si Alloys", Metallurgical and Materials Transactions B, Vol. 26B, February 1995, pp.173-176
19. K. Ogino, T. Suetaki, K. Niioka and A. Adachi, "Effect of Alloying Elements on Interfacial Tension between Molten Steel and Slag", Tetsu-to-hagane, Vul.53, No.7, 1967, pp.769-771
20. B.I.Bairamov, S.I. Popel and A.A. Deryabin, "Exact Calculation of Interfacial Tension",(in Russian), Izu. VUz. Chern Metall., No.1, 1979, pp.5-8
21. H. Ooi, T. Nozaki and Y. Yoshii, "The Effect of Chemical Reaction on the Interfacial Tension between Molten Iron and CaO-SiO_2-Al_2O_3 Slag", Tetsu-to-hagane, Vol.58, No.7, 1972, pp.830-841
22. S.I.Popel, Sb. Nauchn. Tr. Ural'sk Polit. Vol. 126, 1963, p.5
23. H. Gaye, L. D. Lucas, M. Olette and P. V. Riboud, "Metal-Slag Interfacial Properties Equilibrium Values and 'Dynamic' Phenomena", CIM International Symposium on Interface Phenomena in Metallurgical Systems, Hamilton, August 23-27, 1981 and Canadian Metallurgical Quarterly, Vol.23, No.2, April 1984, pp.179-191
24. K. Ogino and S. Hara, "Density, Surface Tension and Electrical Conductivity of Calcium Fluoride Based Fluxes for Electroslag Remelting", Tetsu-to-Hagane, Vol.63, No.13, 1977, pp.2141-2151
25. L.N.Saburov, S.I.Popel, and A.A.Deryabin, "Densities and Surface Properties of Molten Ferroalloy and Slag", (in Russian), Izu. Akad. Nauk. SSSR Metally., No.3, 1973, pp.49-55
26. I.Jimbo, A.Sharan and A.W.Cramb, "The Surface and Interfacial Tensions of Steel Alloys Containing Nickel or Carbon and Sulphur", Transaction of the ISS, June 1994, pp.48-55