Interfacial Energy between CaO-SiO_2-Al_2O_3 Slag and Iron in Equilibrium and Reaction Conditions

Matti Liukkonen, Lauri E.K.Holappa, Dong Mu

Laboratory of Metallurgy
Helsinki University of Technology
Vuorimiehentie 2, FIN-02150 Espoo,
Phone: 358-9-4512754, Finland

ABSTRACT

Interfacial phenomena have a very significant role in metallurgical processes where reactions and mass transfer take place between slag, metal and gas phases as well as ceramic materials.

In this study interfacial energy between a liquid iron droplet and surrounding liquid CaO-SiO_2-Al_2O_3 based slag was measured by applying transmission X-ray technique, image analysis and solving Young-Laplace equation to calculate the interfacial energy.

The highest interfacial energy 1700 mN/m was measured for pure CaO-Al_2O_3/Fe system the value decreasing with increasing SiO_2 content in the slag.

Dynamic interfacial energy was measured between Fe-Al alloy and several SiO_2-containing slags. The exchange reaction between aluminium in the metal phase and silica in the slag caused abrupt lowering of the $\gamma_{s/m}$ and the metal droplet fell down quite flat. When the reaction rate slackened the droplet recovered and the interfacial energy reached its common value corresponding to the equilibrium condition.

1. INTRODUCTION

Interfacial phenomena in metallurgical systems have been of great interest in recent years, several reviews and numerous research papers have been published on research activities performed e.g in France, Japan and the United States.[1-6]

Surface and interfacial properties of metal and slag in the high temperature area play a very important role in the operations in iron and steelmaking. The formation of solid inclusion clusters, coalescence of liquid inclusions and their removal into the slag or onto the refractories are much affected by surface phenomena. Dissolved surface active elements have a great influence on reactions like decarburization, desulphurization, denitrogenization, nitrogen and oxygen pick up. The character, shape and area of an interface between liquid metal and slag is strongly related to surface phenomena, through-interface reactions, dispersion of neighbouring phases in each others, interfacial motion, Marangoni flow etc[2]. The interfacial phenomena affect to reaction kinetics, but they have not any effect to thermodynamic equilibrium values.

Nowadays, two main principles have been applied to measure interfacial energy between two liquids, metal and slag: Sessile drop of metal immersed in liquid slag observed with transmission X-rays and optical observation of slag droplet resting on a liquid metal substrate. Recently, the X-ray technique combined with digital image processing and computer aided calculation methods has been applied[7-8]. In this work the X-ray transmission technique was adopted too.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Pure iron samples (Table I) were prepared by melting electrolytic iron in an Al_2O_3 crucible under vacuum and deoxidised with aluminium.

Table I. Impurities in Fe [ppm].

O	S	Al	C	Mn	Si	P
12	50	800	125	42	500	48

Iron-aluminium alloys were prepared by melting iron and reagent grade Fe-Al alloy under CaO-Al_2O_3 slag in vacuum. The aluminium content in the final alloy was analysed to be 4.5 wt% Al.

Slag samples were synthesised by melting mixtures of reagent grade powders $CaCO_3$, SiO_2, and Al_2O_3 in a graphite crucible under vacuum with subsequent grinding and oxidation treatment at 800° C to remove eventual carbon pick up. The sample sizes were 1.5-2.3 g iron and 7-17g slag.

2.2 Experimental technique

The furnace was heated up by $LaCrO_3$ elements to experimental temperature 1550° C. In the case of pure iron the crucible with the slag and metal sample was loaded from the furnace bottom and slowly raised up to a temperature below the melting point in purified argon atmosphere. Then the crucible was brought up to the final temperature zone and melting of the slag and metal sample occurred in less than 1 min. In the case of Fe-Al alloy only the slag was raised to the final temperature zone and the metal sample was introduced to the melt from the upper side of the furnace. X-ray photographing was performed up till the reaction had reached the equilibrium state again. The sample behaviour was followed continuously at max voltage 110 kV with tube current 60 mA. For accurate recording the generator was used in pulse mode with voltage 80-90 kV and current range 125-200 mA, the exposure time being 1-2 sec.

2.3 Calculation procedure and data acquisition

A droplet profile can be indicated by group of intersections and the corresponding height. The data acquisition needs three steps. Firstly, an image was captured by DT-2851 image grabber installed in a PC 486 computer. Secondly, the image was treated by IPPLUS image processing software for contrast improvements and determining the droplet profile. The third step was to convert an image file from an image format to a data file by a file format converting program. Finally, the data was delivered to a computer program solving the Young-Laplacian equation to calculate the interfacial energy.

To calculate the interfacial energy the computer program developed at the Moscow State University was used in the present work. The software package uses the curve-fitting method, the basic strategy of which is to first construct an object function which expresses the error between the experimental points and a theoretical Young-Laplacian curve. This object function, which is actually a sum of squares of distance from each experimental point to the curve, is minimized numerically by using e.g. the Newton-Raphson or the Newton-Gauss method.

3. RESULTS

Equilibrium interfacial energy between CaO-SiO_2-Al_2O_3 slags and pure iron droplets was studied as a function of SiO_2 content. In the case of iron-aluminium droplet immersed in SiO_2-Al_2O_3-CaO slag the interfacial energy was measured as a function of time.

3.1 Interfacial energy between pure iron and CaO-SiO_2-Al_2O_3 slag

The results are shown in a ternary diagram in Fig. 1. They are comparable with the highest values in the literature obtained by using corresponding technique with X-ray radiography, computer aided image treatment and calculation[7,8,11,12]. Results are 250-400 mN/m higher than the earlier studies which were based on different experimental technique or a different calculation method using the Bashworth-Adams tables[1,9].

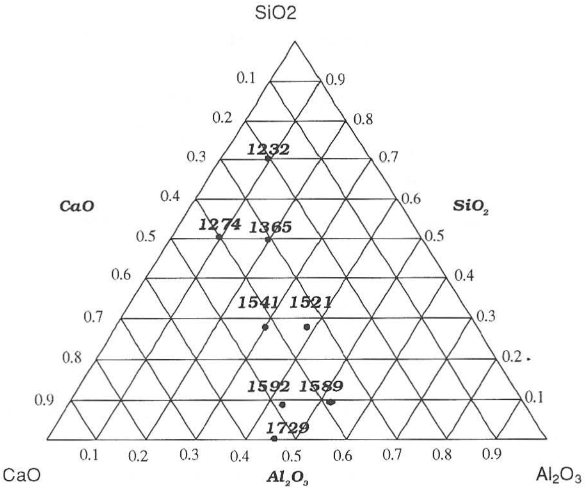

Figure 1. Interfacial energy in mN/m between pure iron and CaO-SiO_2-Al_2O_3 slag.

3.2 Dynamic interfacial energy between Fe-Al alloy and SiO_2-Al_2O_3-CaO slag

Dynamic interfacial energy was measured earlier a.o. by Gaye et al.[1], Ooi et al.[10] and Cramb & Jimbo[12]. In this work dynamic interfacial energy was measured between the metal droplet and surrounding SiO_2-Al_2O_3-CaO slag with various compositions. The slag was melted down in an Al_2O_3 or MgO crucible in argon atmosphere. The metal sample was laid down and let fall through the slag onto the crucible bottom. There it melted rapidly and exchange reaction between the metal and slag phases commenced. The droplet behaviour was monitored and at certain intervals accurate exposure was taken for profile measurement.

3.2.1 Results of dynamic interfacial energy measurements

Figures 2a and b show two examples of the iron droplet behaviour when immersed in liquid slag. In Figure 2c is a cross section of the crucible in run I-9-1. The calculated apparent interfacial energy has been presented in Figure 3. The experimental and calculated results of six runs have been compiled in Table II.

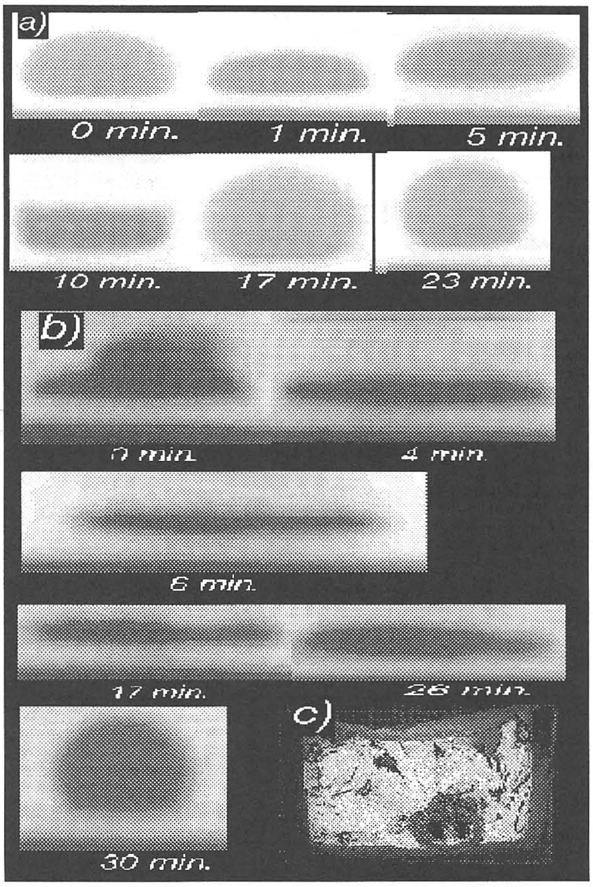

Figure 2. X-ray image showing the changing shape of an iron droplet during its reaction with the surrounding slag. Run a) I-6-2. b) I-9-1. c) Photograph of the cross-section of the crucible after the experiment. Run I-9-1.

There can be seen clearly (Fig.2) how the droplet starts to collapse and flatten, thus resulting in a very low $\gamma_{s/m}$ value (Fig 3). When the reaction starts to approach its equilibrium the reaction rate will slow down, the interfacial energy will increase again and the droplet will rise up and attain its stationary equilibrium shape.

3.2.2 Thermodynamics of interfacial exchange reaction

When an Al-containing iron melt is in contact with a slag with high SiO_2 activity the following exchange reaction will take place i.e. aluminium will reduce SiO_2 from the slag.

$$2[Al]_{Fe} + \tfrac{3}{2}(SiO_2)_s(l) \rightarrow (Al_2O_3)_s(l) + \tfrac{3}{2}[Si]_{Fe} \qquad (1)$$

By using the thermodynamic data from the literature[13] the Gibbs energy for the corresponding reaction with solid oxides (SiO_2 and Al_2O_3) is obtained :

$$\Delta G^{\circ} = -360340 + 66.5T \qquad /J \qquad (2)$$

The equilibrium constant for the reaction (1) is respectively

$$K = \frac{a_{(Al_2O_3)} * a_{[Si]}^{3/2}}{a_{[Al]}^{2} * a_{(SiO_2)}^{3/2}} \qquad (3)$$

By applying the activity diagrams in the literature[14] for the examined slag systems, pure solid oxides as the references, and by introducing the obtained data to Eq.(3) the final (residual) Al-activity in the metal droplet after the reaction is obtained for the experimental runs. (Table II)

Owing to the various slag compositions with different activities of Al_2O_3 and SiO_2, the driving force for the exchange reaction as well as the final equilibrium state is different for each run. As quite evident, the lowest equilibrium Al-content should be obtained in the run I-8-1 with the highest SiO_2 and lowest Al_2O_3 in the slag. The highest equilibrium $a_{[Al]}$ is in the Run I-9-1 with a high Al_2O_3 and fairly low SiO_2 in the slag. Anyway, the driving force should be high enough for all the experimental runs to cause the reaction to proceed quite intensively.

4. DISCUSSION

Exchange reaction occured between SiO_2 in the slag and Al in the metal phase causing abrupt lowering of the $\gamma_{S/m}$ and collapsing of the metal droplet quite flat. When the reaction rate slackened the droplet recovered and the interfacial energy reached its common value corresponding to the equilibrium condition. The reaction ceased when most of the aluminium in the metal droplet was consumed.

The exchange reaction could be verified by analysing the metal and slag samples afterwards. The results for Al and Si contents in the metal droplets after the experiment are given in Table II. The results show that Al was oxidized and transferred from the metal phase to the slag phase as Al_2O_3, and SiO_2 was reduced from the slag phase and silicon was dissolved to the metal droplet, respectively. According to the reaction stoichiometry 4.5 wt% [Al] should correspond to 3.5 wt% [Si]. Most of the results in Table II agree fairly well with this assumption.

According to the reaction equilibrium the final Al-content in the metal phase should be very low around 10^{-3}-10^{-4} wt% Al. These values are at the lower detection limit of the standard acid dissolution-AAS analysing method used in this work. However, the analysed residual Al-contents coincide with the calculated $a_{[Al]}$ values and thus show that the reaction had proceeded close to the equilibrium.

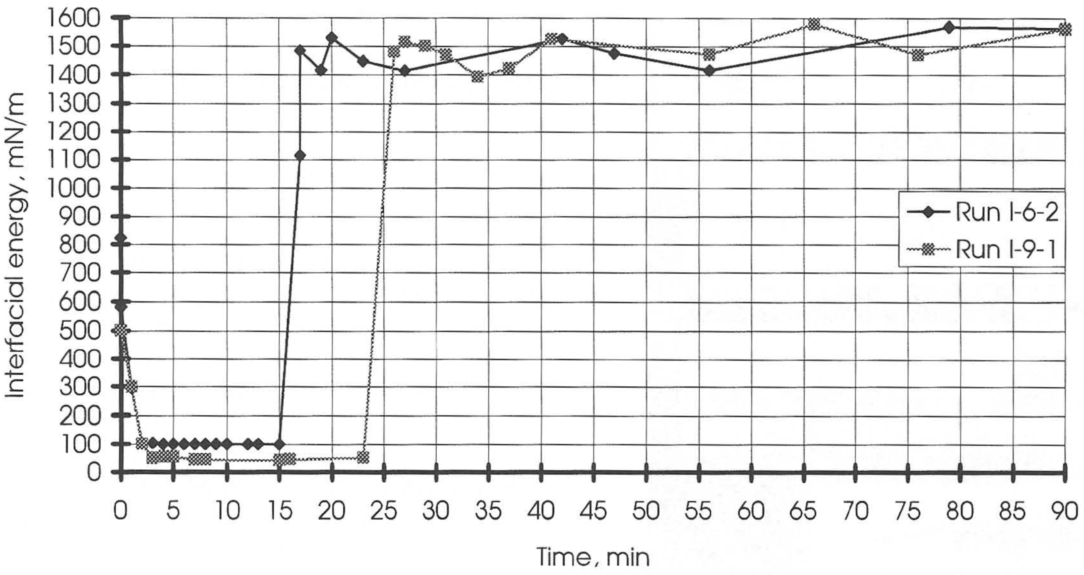

Figure 3. Example of dynamic interfacial energy between Fe-Al alloy and SiO_2-Al_2O_3-CaO slag as a function of time.

Table II. Results of the dynamic interfacial reaction experiments. Al_2O_3 crucible was generally used, except runs I-6-3 and I-7-2 with MgO crucible.

	I-6-2	I-6-3	I-7-1	I-7-2	I-8-1	I-9-1
Slag	Analysis after and *before the run/wt%, density/g/cm^3 and weight/g.					
SiO_2	39.6	31.6	44.7	34.6	*69.9/69.8	*41.0/35.9
Al_2O_3	28.1	14.7	26.0	9.1	*10.2/11.4	*22.4/32.9
CaO	32.3	20.4	29.3	28.3	*19.9/18.9	*36.0/31.2
MgO	0	33.3	0	28.0	0	0
ρ_{slag}	2.6645	2.6645	2.6808	2.6808	2.5006	2.7294
W_{slag}	7	7	17	7	17	17
Metal droplet	Analysis after the run/wt%, weight/g, density 6.928g/cm^3 and Al-activity.					
Si	3.19	2.48	3.30	2.42	4.27	3.19
Al_{tot}	0.002	0.016	0.014	0.002	0.009	0.002
$Al_{soluble}$	0.001	0.004	0.001	< 0.001	< 0.001	0.001
O	0.0075	0.0248	0.00263	0.0063	0.0123	0.0049
W_{metal}	1.6863	1.5322	1.7691	1.5485	1.7009	2.2515
$a_{[Al]}$	$1.2*10^{-3}$	-	$9.0*10^{-4}$	-	$3.8*10^{-4}$	$1.6*10^{-3}$
X-ray image	Observed interfacial phenomena					
Behaviour of metal droplet	Distinct flattening	No flattening	No distinct flattening	No flattening	Distinct flattening	Distinct flattening
"Dynamic" $\gamma_{S/m}$ mN/m	< 100	~1200	~1300	~1300	<< 100	< 100
"Equilibrium" $\gamma_{S/m}$ mN/m	1450	1300	1400	1350	1350	1500

When MgO crucible was used there occured no drastic lowering of the interfacial energy. Somehow the existence of MgO will affect the interfacial reaction between the slag and the metal. The analysis results show that the reaction has occured only partly; the Si-content of the metal droplets had increased to 2.5 wt%, but anyway being markedly below the values of the experiments in Al_2O_3 crucibles and the theoretical maximum value 3.5 wt% Si. The slag analyses after the runs I-6-3 and I-7-2 show quite high MgO contents around 30 wt%. This means dissolution of the crucible material into the slag. The most severe attack against the crucible was observed at the slag-atmosphere-crucible triple point (slag line). The "stabilizing" effect of MgO in the slag on the interfacial behaviour needs, however, more investigations.

5. CONCLUSIONS

The sessile drop method combined with computer aided X-ray transmission technique is a reliable and reproducible way to measure interfacial energy between slag and metal. The highest measured values 1700mN/m were obtained for $CaO-Al_2O_3$/pure Fe system at 1550 ° C. The $\gamma_{s/m}$ values decreased with increasing SiO_2 content being between 1200-1300 mN/m with 70 wt% SiO_2 in the slag.

In non-equilibrium system with chemical reactions and mass transfer processes at the slag-metal interface, the interface can be in highly activated state and the shape of the interface can greatly change due to the reactions. In these experiments "dynamic" interfacial phenomena were qualitatively observed between the metal droplet and the surrounding slag. When the exchange reaction between the dissolved aluminium in the metal droplet and SiO_2 in the slag phase occured intensively, the metal droplet collapsed down and became quite flat, the $\gamma_{s/m}$ value falling down close to zero. When the reaction rate slowed down the droplet shape recovered and the $\gamma_{s/m}$ reached its stationary equilibrium value. The described behaviour was observed in most of the cases with high driving force for the exchange reaction to occur. However, there were some diverging phenomena especially when using MgO crucibles which led to heavy interaction at the three phase contact point and thus to different behaviour of the metal droplet.

ACKNOWLEDGEMENTS

The authors like to thank A.S.Krylov and A.V.Vvedensky from Faculty of Computational Mathematics and Cybernetics, Moscow State University for their Sesdrop-computer-program for calculation of interfacial energy as well as Rautaruukki Oy and Fundia Koverhar for analysing metal and slag samples. The financial support from Technology Development Centre of Finland is gratefully acknowledged.

REFERENCES

1. H.Gaye, L.D.Lucas, M.Olette, P. V.Riboud, "Metal-Slag Interfacial Properties Equilibrium Values and "Dynamic" Phenomena", Can. Met. Quart., 23 (1984)2, pp. 179-191.
2. M.Olette, "Surface Phenomena: A Cornerstone of Iron and Steelmaking Processes" , ISIJ International, Vol 33, (1993), No. 10, pp. 1113-1124.
3. A.W.Cramb, I.Jimbo, "Interfacial Considerations in Continuous Casting", I & SM, June (1989), pp. 43-55.
4. K.Nakashima, K.Mori, "Interfacial Properties of Liquid Iron Alloys and Liquid Slags Relating to Iron- and Steelmaking Processes", ISIJ Intern., Vol. 32, (1992), pp. 11-18.
5. M.Tokuda, "The Background of the Special Issue on Interfacial Phenomena in Refining and Casting Processes of Iron and Steel", ISIJ Inter., Vol.32, (1992), pp. 1-2.
6. K.Ogino, "Interfacial Phenomena in Metallurgical Processes and Interfacial Properties of Slags", 4th International Conference on Molten Slags and Fluxes, June 8-11, 1992, Sendai, Japan, ISIJ, pp. 314-317.
7. I.Jimbo, A.W.Cramb, "Computer Aided Interfacial Measurements, ISIJ Intern.,Vol 32, (1992), pp. 26-35.
8. D.Mu, M.Liukkonen, L.Holappa, "Interfacial Energy between Slag and Metal in Equilibrium and Reaction Conditions", International Symposium on Science and Technology of Metallurgical Processing, The Morita Symposium, Osaka, October 12-13, 1994, pp. 13-18.
9. K.Ogino, S.Hara, T.Miwa, S.Kimoto,"The Effect of Oxygen Content in Molten Iron on the Interfacial Tension between Molten Iron and Slag", Transactions ISIJ.Vol. 24, (1984), pp. 522-531
10. H.Ooi, S.Nozaki, H.Yoshii, "The Effect of Chemical Reactions on the Interfacial Tension between Iron and $CaO-SiO_2-Al_2O_3$ Slag", Transactions ISIJ, Vol. 14, (1974), pp. 9-16.

11. A.Sharan, A.W.Cramb, "Interfacial Tension of Liquid Fe-Ni Alloys and Stainless Steels in Contact with CaO-SiO_2-Al_2O_3 Based Slags at 1550° C ", Metallurgical and Materials Transactions B , vol.26B, 1995, pp. 87-94.

12. A.W.Cramb, I.Jimbo,"Ladle Metallurgy: Fundamentals of the Slag-Metal Interface", Scaninject VII, Part I, 7 th International Conference on Refining Processes, MEFOS, Luleå, Sweden, June 7-8, (1995), pp. 89-107.

13. Steelmaking Data Sourcebook, The Japan Society for the Promotion of Science, The 19th Committee on Steelmaking, Gordon and Breach Science Publishers, Montreux 2, Switzerland, 1988.

14. SlagAtlas, 2nd Edition, Stahleisen, Dusseldorf, Germany, 1995, pp. 235-240.