Dynamic Wetting of Graphite by Slag Containing Iron Oxide

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ABSTRACT

Wettability of graphite by the CaO-SiO_2-Al_2O_3-MgO-FeO_x slag have been investigated using the sessile drop technique. The focus of this presentation is on the coal/slag interfacial phenomena in the relation to direct iron smelting. Coal/slag interfacial properties are of importance for the kinetics and mechanism of iron reduction from the molten slag by char.

In this study wettability of graphite by slags of different compositions has been investigated at 1600°C. Experiments were performed in a horizontal super-kanthal tube furnace. Slag droplets on a graphite substrate were placed into the hot isothermal zone of the furnace and examined using a CCD camera. The camera assembly was connected to a computer and video cassette recorder through a video distributor amplifier. The images captured were stored in computer memory and the reaction sequence during the experiment was recorded on video tape. The wettability of graphite by slag was determined by direct measurement of the interfacial contact angle as a function of time. An on-line date/time generator permitted image capturing as a function of time. The results indicated significant effect of slag composition on the slag/graphite interfacial interactions.

1. INTRODUCTION

In iron bath smelting processes about 40% of iron is reduced by coal char dispersed in the slag phase. Laboratory scale research relating to the reaction of liquid iron by carbon has been carried out since the early 1950's.[1-12] However, data on wettability of solid carbon by liquid slag are extremely limited. This causes difficulty in interpretation of data on iron reduction by char.

Reduction of iron oxide from molten slag by char was investigated in works.[12-14] Bafghi et al.[12] conducted a kinetic study on the reduction of iron oxide from the molten slag by graphite at 1300°C. They concluded that the reduction rate is significantly affected by the slag composition. For slags with higher basicity, the reaction rate was found to be controlled by mass transfer in the slag phase. Whereas chemical reaction resistance is predominant in slags with lower basicities. Chemisorption of surface active agents (silica and/or phosphorus) at the interface lowers the chemical reaction rate.

Sugata et al.[13] measured the reduction rate of various concentration of iron oxide contained in molten slags in a temperature range from 1350 to 1450°C by rotating solid carbon or coke rods. They found that at higher rotation speeds of the rods there is no effect on the reduction rate and the reduction rate obtained was proportional to the first order FeO activity in slags. At lower rotation speed, the rate was considered to be controlled by both the diffusion in molten slags and the chemical reaction.

Sarma et al.[14] investigated the reduction of slags containing less than 10 wt.% FeO by solid carbonaceous materials. They found that the iron oxide reduction reaction occurs through a gas halo (CO) formed around the coal particle. CO formation caused slag foaming and the system was strongly stirred by gas evolution. The reaction rate is a function of the FeO content of the slag and depends on the speed of the rotation of the rod. Bafghi et al.[15] investigated the coal/slag reaction and found in contrast to Sarma's[14] that the reduction reaction occurs directly at the coal/slag interface.

Such inconsistency in results of iron reduction by char may partly be attributed to the effect of slag carbon interface phenomena which depends on the slag chemistry and other factors.

Wettability of carbon by slag was investigated in a very few works.[16-20] Towers[16] measured the contact angle of molten slags (CaO-Al_2O_3-SiO_2) on platinum, alumina and graphite substrates. The contact angle was affected by the gas atmosphere. After melting, contact angle between slag and graphite was found to be around 160 degrees. It decrease down to 20-30 degrees as a result of silicon reduction from slag.

Raask[17] studied the slag-coal interfacial phenomena by observing the wetting properties of coal-ash slags on devolatilized coal in an atmosphere of pure dry nitrogen. In a few experiments a volatilized potassium sulfate was also introduced into the nitrogen stream. He detected that coal-ash iron free slags did not wet carbon or devolatilized coal, as the contact angle of the slag on carbon was 160° and the slag droplets did not adhere to carbon. When the slag of high iron content was kept on a carbon plate above 1400°C for several minutes a diffuse interface rich in iron was observed. This layer adhered both to the slag and to the carbon surface, the contact angle was lowered only to 140°. When a slag-carbon interface was exposed to the vapor of potassium sulfate, the contact angle changed from 160° to below 90°.

Sahajwalla et al.[18] studied the wettability of carbonaceous substrate by slags in the temperature range 1400 - 1600°C to investigate the influence of carbon type, slag composition and temperature on the phenomena at the slag-carbon interface. The results indicate that the slag-carbon interactions significantly depend on the carbon type and slag composition.

The aim of the present paper is to investigate the wettability phenomena in graphite/ slag systems to understand the fundamental mechanisms governing the direct iron smelting process. The wettability of graphite by liquid slag is examined as a function of slag composition.

2. EXPERIMENTAL

Slags of the $CaO-SiO_2-Al_2O_3-MgO-FeO_x$ system were prepared by the repeated smelting and grinding of a mixture of pure (>99.9%) oxides. Slags 2-4 have different iron oxide concentration with low MgO, slag 1 has high MgO concentration with low iron oxide content. Slag samples were analysed by XRF, their final compositions are given in Table 1. The substrate was made from graphite with less than 0.3% ash. Substrates of suitable sizes were cut, polished up to 600 µm, cleaned and dried. 0.25 g of slag sample was placed on the carbon substrate.

Table 1 Composition of Slags (Wt %)

Sample No.	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3
#1	33.0	37.7	23.8	5.19	0.21
#2	28.1	47.3	24.0	0.11	0.22
#3	28.6	47.5	21.5	0.14	2.15
#4	26.8	42.3	21.3	0.11	9.16

The experiments were conducted by the sessile method in the laboratory horizontal tube furnace at 1600°C under argon atmosphere. The internal tube diameter was 55 mm. The schematic diagram of the experimental set-up is given in Figure 1.

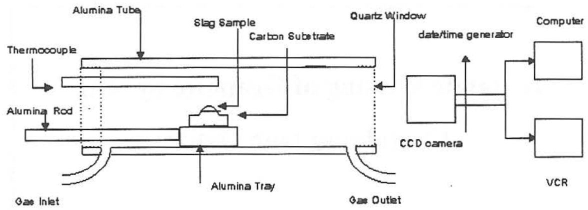

Figure 1. Schematic of sessile drop apparatus.

Temperature was controlled by the B-type thermocouple placed in the close vicinity of the sample. The graphite and slag sample were kept at the low temperature zone of the furnace tube initially, then, when the required temperature was achieved (1600°C) the sample was introduced into the hot zone.

The wettability of graphite by slag was determined by direct continuous measurement of the interfacial contact angle as a function of time. Droplet images were captured using CCD camera. The contact angle between the drop and graphite substrate was measured using image analysis software on the basis of curve fitting approach or the Laplace equation approach. The camera assembly was connected to a computer and video cassette recorder through a video distributor amplifier. The images captured were stored in a computer memory and the reaction sequence during the experiment was recorded on video tape. An on-line date/time generator permitted image capturing as a function of time. Examples of images for the slag no. 3 and 4 showing calculated contact angles are given in Figures 2-5. The contact angle was determined for both the left hand side (LHS) and the right hand side (RHS) of the drop and the best fit was used in the solution. In this figures SSR is the sum squares of residuals between the best fit polynomial and the drop profile; Ψ is the contact angle calculated from the tangent of the best fit polynomial and the top of the substrate.

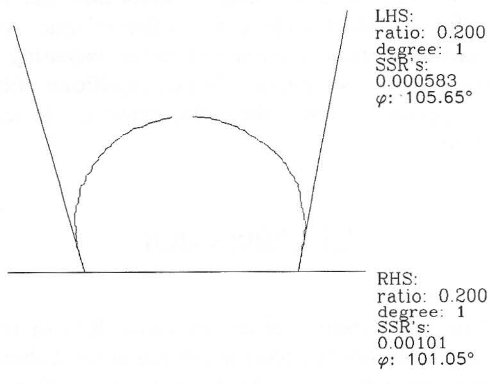

Figure 2 : Schematic depicting calculated profile, top of substrate and tangent associated with contact angle for slag #3.

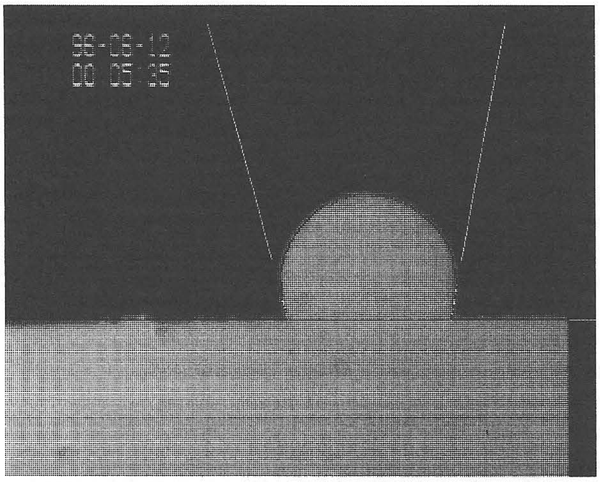

Figure 3 : Calculated droplet profile superimposed onto original captured image for slag #3 (40 seconds after melting).

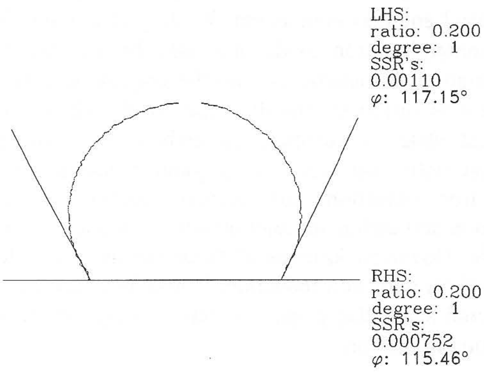

Figure 4 : Schematic depicting calculated profile, top of substrate and tangent associated with contact angle for slag #4.

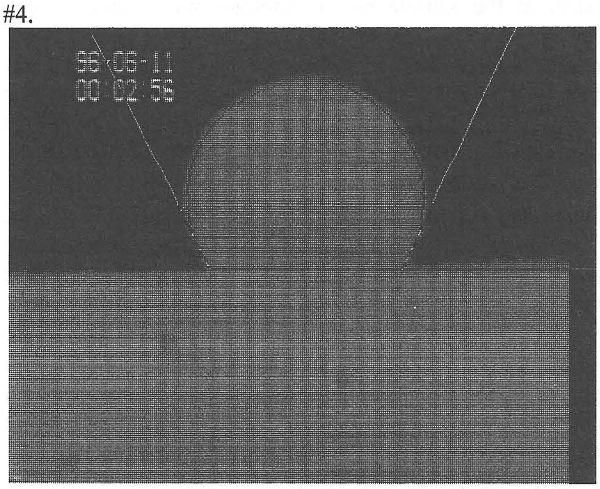

Figure 5 : Calculated droplet profile superimposed onto original captured image for slag #4 (40 seconds after melting).

3. RESULTS

Dynamic contact angles of slags on the graphite substrates at 1600°C are presented in Figures 6-9. Initially when the slag/graphite samples were introduced from the cold zone into the hot zone, the furnace temperature dropped by 120-150°C.

In the case of the slag no.1 (5.19 wt.% MgO, 0.21 wt.% FeO_x) the furnace temperature dropped from 1600°C to 1480°C. Slag started to melt immediately and formed a definite drop shape. Visibly the wettability was rather poor and drop did not show any sign of reaction. Slag started moving on the substrate and rolled out of it. For the first few seconds the contact angle was between 116 and 123° (Fig. 6). The wettability of graphite by slag no. 1 with high MgO content was poor at all times.

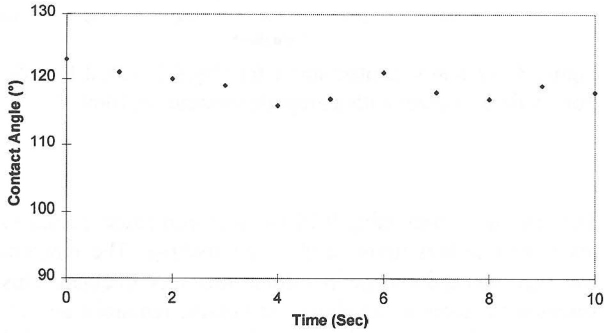

Figure 6: Dynamic contact angle for slag #1 with 0.2 wt% iron oxide in contact with a graphite substrate at 1600°C.

Slag no. 2 contained only 0.11 wt% MgO and the same initial concentration of iron oxide as slag no. 1. It started to melt at 1540°C. Figure 7 shows the change in the contact angle with time at 1600°C. During first 130 seconds contact angle fluctuated between 98 and 111°. Then contact angle slightly decreased and became steady at 102° for about 300 seconds.

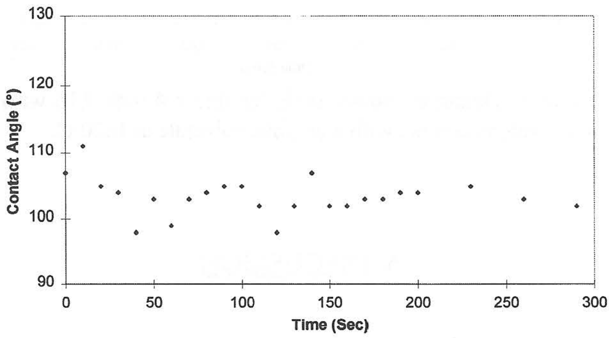

Figure 7 : Dynamic contact angle for slag # 2 with 0.2 wt% iron oxide in contact with a graphite substrate at 1600°C.

Slag no. 3 had low MgO concentration but higher content of iron oxide of 2.15%. This slag started to melt at 1530°C. Figure 8 shows that initially the contact angle was between 103° and 109°. There was no sign of reaction and the slag volume remained the same. The contact angle became steady after 380 seconds.

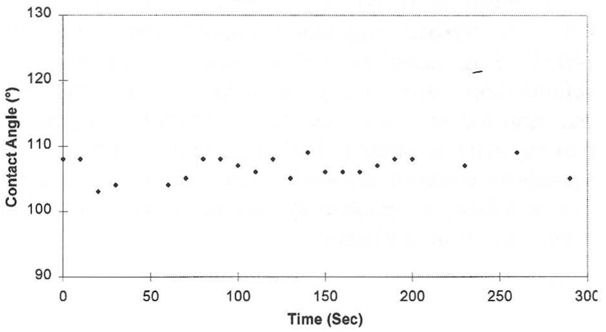

Figure 8 : Dynamic contact angle for slag # 3 with 2.15 wt% iron oxide in contact with a graphite substrate at 1600°C.

The slag no. 4 containing 9.16 wt.% of iron oxide started to react with carbon immediately after melting. The reaction was vigorous and change in volume was very frequent. This situation of reaction and change in volume remained up to 5 minutes and during this time the contact angle varied between 103-117° (Fig.9). After six minutes the reaction started to slow down but contact angle remained unchanged.

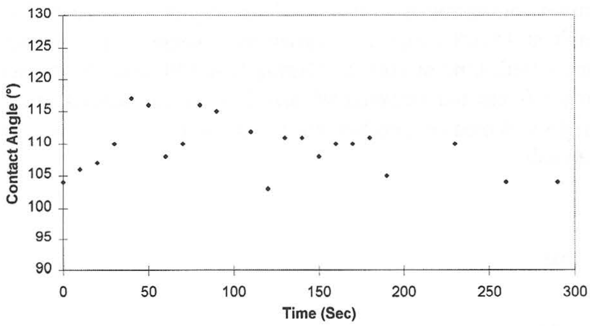

Figure 9: Dynamic contact angle for slag # 4 with 9.16 wt% iron oxide in contact with a graphite substrate at 1600°C.

5. DISCUSSION

It is generally accepted that wetting of carbon by slag is rather poor. Thus, contact angle between blast furnace type slag (40% CaO, 20% Al_2O_3 and 40% SiO_2) and graphite measured by Towers[16] was observed to be 160° and decreasing with time as a result of SiO_2 reduction. Raask[17] found the contact angle of coal ash (17.8%FeO) on the graphite substrate to be around 140°, while iron-free slag with approximately the same proportion of other components demonstrated worse wettability with contact angle ~160°. Wettability of graphite by slags examined in this research is also poor but better than reported by Raask[17] and Towers.[16]

The contact angle depends upon the coal/slag interfacial tension, slag and coal surface tension and the dynamic reaction occurring at the interface. The change in the wettability of graphite by slag containing iron oxide may be attributed[19] to the change in the interfacial energies brought about by the interfacial reaction (interfacial energies component) and to the change in the free energy per unit area released by the carbon / iron oxide reaction (the reaction component). The contribution of these processes in the wetting phenomena is unknown; Aksay[20] and Naidich[21] stated that the reaction components represents the predominant contribution of wetting; while Espie et al.[19] concluded that the reactive wetting is governed by the interfacial energies component. Wetting of graphite by the slag containing iron oxide may also be affected by the precipitation of metallic iron on the graphite/slag interface which was observed visually; and by the change in the physical state of substrate as carbon is consumed by reaction with iron oxide. Slag/graphite interaction apart from iron reduction may involve reactions of silicon reduction and carbon dissolution with formation of calcium carbide. However, kinetics of these reactions are slow in comparison with iron reduction; it may be assumed that at the initial stage slag/graphite reaction comprises only iron reduction by carbon.

The initial iron oxide in the slag was 0.2 wt.% in samples no. 1 and 2; 2.1 wt.% in the sample no. 3 and 9.1 wt.% in the sample no. 4. Samples no. 1 and 2 have different MgO concentration. Thus, the effect of iron oxide on the slag/graphite contact angle may be observed from Fig. 7, 8 and 9, which illustrate the dynamic contact for samples 2, 3 and 4 corresponding at 1600°C. Just after smelting, the sample with initial iron oxide content of 9.1 wt.% has contact angle about 105° lower than samples with 2.1 wt.% FeO_x and iron-free slag. This is illustrated by Fig. 10, where the contact angle is plotted vs. initial iron content after 10 seconds. Figure 10 shows that just after smelting (at 10 sec) the contact angle decreases and therefore, wetting improves with increasing initial iron oxide concentration. However, as the graphite/slag reaction proceeds, the effect of the initial iron oxide concentration changes : slags with higher iron oxide content have higher contact angle with graphite which means poorer wettability.

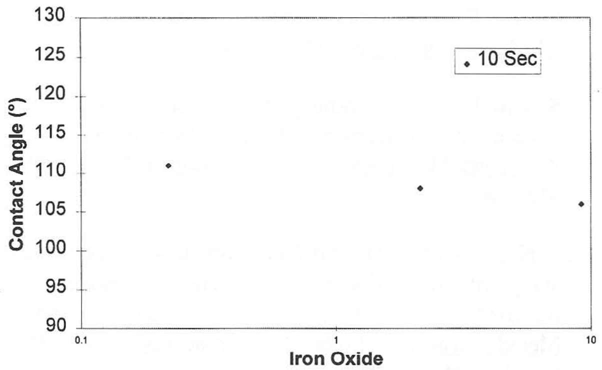

Figure 10: Variation of contact angle with iron oxide content at 1600°C, 10 seconds after melting

It may be presumed that after 10 seconds of reaction, iron oxide content in the slag is close to the initial concentration and affect the interfacial energies. It may also be expected that the higher iron oxide in the slag the faster rate of graphite/slag reaction, and therefore, greater contribution of the reaction component to the reactive wetting.

Data on surface tension of the $CaO\text{-}SiO_2\text{-}Al_2O\text{-}FeO_x$ system of compositions investigated in this work has not been found in literature. The surface tension of this system with high silica content (around 50 wt.%) was found decreasing with increasing iron oxide concentration.[22]

To evaluate the effect of iron oxide on the slag surface tension the contact angles of slags 2 and 3 were measured on the Pt substrate. It was revealed that wettability of Pt by slag containing 9.16% iron oxide is much better than the wettability of the iron-free slag. In the first case the average contact angle was 35°, while in the second case around 60°. It implies that surface tension of iron-free slag is higher than those of slag containing iron oxide (assuming that the work of adhesion is less affected by the slag composition than surface tension).

Thus, increasing wettability of graphite by slag with increasing iron oxide content after slag smelting may be attributed to both factors : effect of iron oxide on the interfacial energies and reaction component. As the reaction of iron reduction proceeds, concentration of iron oxide in the slag decreases. This causes increase in the surface tension and decrease in the reaction rate. As a result, the slag/graphite contact angle increases to about 113 degrees (Fig. 9) during the first 50 seconds, while contact angles for samples no. 2 and 3 slightly decrease during this time of reaction.

These results highlight the complexity of reactive interface phenomena. The contact angle between graphite and slag containing iron may be affected by the precipitated metallic iron, change in the physical state of substrate and other factors which are not considered by the model of reactive wetting.

Behaviour of iron free slags with different MgO content is illustrated by Figures 6 and 7. Slag with higher MgO has higher contact angle with graphite. This may be attributed to its higher surface tension.[23]

6. CONCLUSIONS

Experimental measurement of contact angles between polished graphite and $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}MgO\text{-}FeO_x$ slag revealed that wettability of graphite by slag is affected by slag chemistry, particularly initial iron oxide and magnesia content. Just after smelting slags with initial higher iron oxide content demonstrate better wettability of graphite. This may be attributed to the effect of iron oxide on the interfacial energies and to the reaction component. Experiments on Pt substrate showed that contact angle between Pt and slag with 9.1 wt.% iron oxide is less than in the case of iron free slag.

Increase in MgO content increases the contact angle between graphite and slag and therefore, decreases the wettability.

7. ACKNOWLEDGEMENT

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8. REFERENCES

1. Nagasaka, T., Banya, S., " Rate of reduction of liquid iron oxide", Tetsu-to-Hasane, Vol. 78, No. 12, December 1992, pp. 1-26.

2. Davies, M.W., Hazeldean, G.S.F., and Smith, P.N. "Kinetics of reaction between liquid iron oxide slags and carbon". Physical Chemistry of Process Metallurgy: The Richardson Conference, July 1973. The Institute of Mining and Metallurgy, p.95.

3. Philbrook, W.O. and Kirkbridge L.D. "Rate of FeO reduction from a $CaO\text{-}SiO_2\text{-}Al_2O_3$ by carbon saturated iron", J. Metals, N.Y., Vol. 8, 1956, p.351.

4. Tarby, S.K., and Philbrook, W.O., "The rate of mechanism of the reduction of FeO and MnO from

silicate and aluminate slags by carbon saturated iron", Trans Am. Inst. Min. Engrs. 239, 1967, p. 7005.

5. Krainer, H., Beer, H.P. and Brandl, H.' "Untersuchung uber die Reactionen flussiger hocheisen(II)- oxidhaltiger Schlacken mit festem kohlenstoff", Tech. Mitt. Krupp Forschungsber., Vol. 8B, 1977, p.279.

6. Kondakov, V.V., Ryzhonkov, D.I. and Golenko, D.M., "Kinetics of reduction of iron oxide with solid carbon at temperatures above 1400°C". Izv. vyssh. ucheb. zaved., Chern. Metall., No. 4, 1960, 23-8(Russian text)

7. Ershov, G.S., Popva, E.A., "Reduction of iron and silicon from slag melts by means of carbon", Izv. Akad. Nauk SSSR, Metall., Garu. Delo, No.1, 1964, 32-5, Chem. Abstr., 60, 1964, 14166.

8. Fay Fun. "Rates and mechanisms of FeO reduction from slags", Metall. Trans., 1, 1970, 2537-41.

9. Shavrin, S.V. and Zakharov, I.I. and Kulikov, G.S., "Reduction of molten iron oxide with carbon", Izv. Akad. Nauk SSSR, Metall., Garu. Delo, No.1, 1964, 26-31, Russ. Metall. Min., No. 1, 1964, 13.(Abstract)

10. Shavrin, S.V. and Zakharov, I.N. and Kulikov, "Reduction of iron oxides from fused slags". Fiz. Khim. Rasplav. Shlakov, 1970, 55-61, Chem. Abstr: 76, 1972, 16853.

11. Fruehan, R.J., "The rate of reduction of iron oxides by carbon", Metallurgical Transactions B, Vol. 8B, 1977, p.279.

12. Bafghi, M.S., Ito, Y., Yamada, S. and Sano, M., "Effect of slag composition on the kinetics of the reduction of iron oxide in molten slag by graphite", ISIJ International, 1992, Vol. 32, p. 1280.

13. Sugata, M., Sugiyama, T. and Kondo, S., "Reduction of iron oxide contained in molten slags with solid carbon", Transactions ISIJ, 1974, Vol. 14, p.88.

14. Sarma, B., Cramb, A.W. and Fruehan, R.J., "Reduction of FeO in smelting slags by solid carbon", Metall. Trans. B.

15. Bafghi, M.S., Fukuda, M., Ito, Y., Yamada, S. and Sano, M., "Effect of CO gas formation on reduction rate of iron oxide in molten slag by graphite", ISIJ International, 1993, Vol. 33, p. 1125.

16. Towers, H. "Contact Angle Measurements of Slags on Solid Surfaces", Trans. Brit. Ceram. Soc., 1954, Vol. 55, pp. 180-196.

17. Raask, E., "Slag-coal interphase phenomena", Trans. ASME. J. Eng. Power, 1966, No. 1, p.40.

18. Sahajwalla, V., Washington, B., and Taylor, I.F., "Wettability of Carbonaceous Substrates by Slags", 2nd Australian Melt Chemistry Symposium, February 1995, Melbourne.

19. Espie, L., Drevet, B., and Eustathopoulos, "Experimental study of the influence of interfacial energies and reactivity on wetting in metal/oxide systems", Metallurgical and Materials TransactionA, Vol. 25A, March 1994, p. 599.

20. Akssay, L.A., Hoge, C.E., and Pask, J.A. : J. Physc. Chem., 1974, Vol. 78 (12) pp. 1178-83.

21. Naidich, Ju., V., Prog. Surf. Membr. Sci., 1981, Vol. 14, pp. 353-484.

22. Turkdogan, E. T., "Phsicochemical properties of molten slags and glasses", The Metal Society, London, p 166.

23. Slag Atlas 2nd Edition, Verlag Stahleisen GmbH, 1995, p. 448.