The Wear of Tundish Stopper Refractories by Inclusion Slags

Dongsheng XIE, Craig GARLICK1) and Ty TRAN

CSIRO Minerals, Box 312, Clayton South, VIC 3169, Australia. E-mail: dongsheng.xie@csiro.au
1) OneSteel Market Mills, PO Box 245C, Newcastle, NSW 2300, Australia.

(Received on October 18, 2004; accepted in final form on November 26, 2004)

Liquid inclusions in the steel may play an important role in the wear of the stopper tip refractories in tundish operations. In the present study, the attack and wear of the tundish stopper refractories by inclusion slags in OneSteel Whyalla billet product have been investigated.

Three stopper tip refractories, Al₂O₃–C, ZrO₂–C and MgO–C, have been tested with inclusion slags (SiO₂–Al₂O₃–CaO–MnO–FeO) under argon at 1 570–1 610°C for 1–4 h using an in-situ gravimetric technique. The in-situ gravimetric data, combined with autopsy of the samples after the tests, provide valuable insights into the dynamic processes of the slag–refractory interactions and the mechanisms for refractory wear.

It was found that the performance of the three refractories differed considerably and was determined predominantly by the resistance to the chemical attack by the liquid inclusions and the extent of internal carbon–oxide reactions. The FeO in the inclusion had a detrimental effect on the oxidation of carbon in the refractory, causing vigorous reaction and severe wear. The MnO in the slag also reacted with carbon, but to a much lesser extent, while severe wear only occurred when slag attacked the refractory grains. The weight loss, due to internal carbon–oxide reactions, appeared to be an important issue.

Of the refractories tested, the MgO–C performed the worst, suffering from severe inclusion attack on both the carbon and the periclase grains, and considerable weight loss due to internal carbon reaction. The ZrO₂–C showed a reasonable resistance to the chemical attack from the inclusion, with MnO up to 33 wt%; but showed extensive weight loss due to internal carbon reaction. The Al₂O₃–C was the best performer in terms of resistance to both the inclusion attack and internal carbon reaction. The results were found to be in broad agreement with plant experience and observations.

KEY WORDS: tundish stopper; refractory wear; liquid inclusion; continuous casting.

1. Introduction

In tundish operation during continuous casting, nozzle clogging due to the deposit of solid inclusion is well known and has been the subject for extensive investigations.1–3) In comparison, little has been published on the wear of tundish stopper refractories, or submerged entry nozzles (SEN), due to interactions with liquid inclusion.

Tundish stopper tip erosion was experienced at the OneSteel Whyalla Steelworks billet caster during a transition period of equipment upgrade.4) In that transition time, new secondary steelmaking practices were developed as appropriate for a newly installed Ladle Metallurgy Furnace. In particular, the combination of free oxygen control with residual aluminium, and calcium treatment was used to engineer inclusion compositions to give stable casting operations. At that time, the effect of secondary treatment and hence inclusion composition on stopper tip performance became apparent. In some cases a severe wear of the MgO–C stopper tips used in the tundish was observed, resulting in short or unpredictable sequence length. Other stopper tip refractories were trialed. A laboratory test program was carried out to develop an understanding of the mechanisms of stopper tip wear as influenced by steel inclusion composition.

Three stopper tip refractories, Al₂O₃–C, ZrO₂–C and MgO–C, have been tested with inclusion slags (SiO₂–Al₂O₃–CaO–MnO–FeO) under argon at 1 570–1 610°C for 1–4 h using an in-situ gravimetric technique.5–7) The refractory performance, effect of the inclusion chemistry and the mechanisms for refractory wear were investigated.

2. Experimental

Inclusion compositions are dictated by various treatments used in secondary steelmaking operations.4) The inclusion compositions of interest to the present study are shown in Table 1. These compositions were determined from SEM/EDS analyses of inclusions observed in a low carbon, silicon killed steel grade made at OneSteel. Variations in ladle treatment practice and the resulting impact on inclusion composition is indicated. Slag 1 and Slag A correspond to a heavy calcium treatment practice, where the MnO content of the inclusion phase has been reduced to a small amount. Slag 1 corresponds to a lower free oxygen content, due to residual aluminium in steel, at the time just prior to calcium treatment. The net result is a higher Al₂O₃ content in the inclusion phase compared to Slag A. Slag B represents a light calcium treatment, where the CaO content is lower and the MnO content higher in comparison to Slag
1 and Slag A. Slag C is the average inclusion slags for a steel not treated with calcium.

Synthesized slags were prepared to match the inclusion compositions shown in Table 1 from laboratory grade chemicals, by weighing, mixing and melting in a muffle furnace in air at around 1 600°C. Three tundish stopper tips made of Al₂O₃–C, ZrO₂–C and MgO–C were tested. The chemical compositions are listed in Table 2 according to the datasheets supplied by the manufacturers.

An in-situ gravimetric technique was used to study the dynamic processes of refractory-slag interactions. The details of the technique have been described previously elsewhere.5-7) The experimental arrangement is schematically shown in Fig. 1. A cylindrical refractory sample was suspended from a balance and the “apparent” weight changed during the contact with the slag was logged to a computer.

The cylindrical refractory sample was inserted into a muffle furnace in air at around 1 600°C. Three tundish stopper tips made of Al₂O₃–C, ZrO₂–C and MgO–C were tested. The chemical compositions are listed in Table 2 according to the datasheets supplied by the manufacturers.

An in-situ gravimetric technique was used to study the dynamic processes of refractory-slag interactions. The details of the technique have been described previously elsewhere.5-7) The experimental arrangement is schematically shown in Fig. 1. A cylindrical refractory sample was suspended from a balance and the “apparent” weight was measured by the balance was logged at 5 readings per second to a PC during the test (1–4 h). At the conclusion of the test, the crucible was lowered slowly until the contact between the refractory and the slag was ceased and then returned to the pre-test position. The furnace was allowed to cool at 400°C/h from 1 570°C to 1 200°C and then at 200°C/h to room temperature. The refractory and the crucible were removed from the furnace. Samples were taken from the refractory and the slag, and prepared for chemical analysis using a calibrated XRF technique or SEM examinations.

3. Results

3.1. Weight Loss during Heating

The weight loss of carbon containing refractories at high temperature due to internal oxide–carbon reactions is well known and this has been studied previously using the thermal gravimetric technique.8,9) The information is readily available from the data obtained during the present in-situ gravimetric tests.

A blank experiment was conducted using an empty Mo crucible (no slag) and an Al₂O₃–C sample (dimension 20×28 mm, 22.7 g). The results are shown in Fig. 2. The weight loss during heating was slow initially, at a rate of about 0.3 g·m⁻²·min⁻¹ from room temperature to about 1 400°C. At temperatures above 1 400°C, the rate increased significantly to about 5 g·m⁻²·min⁻¹, due to the commencement of internal carbon-oxide reaction. At 1 570°C, the observed rates decreased progressively with the time and became negligibly low after about 2 hours (Fig. 2).

The weight loss during heating was also observed in all tests where slag was present. Figure 3(a) shows the results for Al₂O₃–C in all tests, in the form of the accumulated weight loss per unit surface area of the samples. In Fig. 3(b), the weight loss during heating prior to contacting Slag C was compared between different refractories. Similar results were obtained during the tests with Slag B.

The weight loss appeared to depend on the refractory type and each refractory behaved differently in different temperature ranges. At temperatures below 1 400°C, the Al₂O₃–C and the ZrO₂–C refractory showed less weight...
loss than the MgO–C refractory. At higher temperatures while the weight loss increased significantly for all refractories, the MgO–C and ZrO₂–C refractories showed a much higher rate of the weight loss than the Al₂O₃–C refractory (Fig. 3(b)).

The observed rates for the weight loss at test temperature estimated from the in-situ data measured during the 10–15 min holding time (prior to the contact with the slag) are summarized in Table 3. The ZrO₂–C refractory showed the highest rates and was closely followed by the MgO–C refractory. In comparison, the weight loss of the Al₂O₃–C refractory was less than one third of the rates for the other two refractories.

3.2. Effect of FeO

The effect of the FeO content in the slag was studied through the interactions of the Al₂O₃–C refractory with two slags: Slag 1 (43CaO–14SiO₂–38Al₂O₃–3.4FeO, wt%) and Slag A (43CaO–26SiO₂–30Al₂O₃–0.6MnO). The experimental arrangement used in the test with Slag 1 was slightly different from that described earlier, which was used in all other tests. The test with Slag 1 was conducted at 1 570°C for 4 h using a large Al₂O₃–C sample (Φ30×49 mm) and about 140 g slags contained in a Pt–10%Rh crucible (Φ70×35 mm) without graphite lid. The in-situ gravimetric data measured during the test with Slag 1, the sample after the test and a typical SEM image (back scatter electron image) of the hot face are shown in Fig. 4. The composition of the slag before and after the test

![Fig. 1. Schematic illustration of experimental set up.](image1)

![Fig. 2. Weight loss of Al₂O₃–C refractory during heating, and at 1 570°C, observed in the “blank” experiment (real time is used for the time scale).](image2)

![Fig. 3. The accumulated weight loss per surface area of the stopper tips during heating period (prior to slag contact): (a) all results for Al₂O₃–C and (b) comparison of different refractories being tested with Slag C.](image3)

![Fig. 4.](image4)

| Table 3. Observed rates (in g·m⁻²·min⁻¹) of the weight loss of the refractories at test temperatures prior to contact with slag. |
|---|---|---|---|
| Run No | Refractory type | Slag | Temp, °C | Rate |
| T1 | Al₂O₃–C | Slag 1 | 1570 | 4.57 |
| T2 | Al₂O₃–C | Slag B | 1570 | 3.86 |
| T6 | Al₂O₃–C | Slag C | 1570 | 4.17 |
| T5 | Al₂O₃–C | Slag A | 1610 | 4.23 |
| T3 | ZrO₂–C | Slag B | 1570 | 16.6 |
| T7 | ZrO₂–C | Slag C | 1570 | 16.5 |
| T4 | MgO–C | Slag B | 1570 | 14.6 |
| T8 | MgO–C | Slag C | 1570 | 13.5 |
is shown in Table 4.

The in-situ gravimetric data are plotted in Fig. 4(a) in the form of the change in the apparent weight as a function of contact time. The change in the apparent weight is calculated based on

\[ \Delta W = W - W_0 \]  

where \( W \) is the apparent weight and \( W_0 \) the weight of the free-hanging sample (plus the connecting shaft and Mo wire, Fig. 1) before the contact. The negative or positive values of \( \Delta W \) indicate weight “loss” or “gain”, respectively, in reference to the before-contact weight. The changes in the apparent weight correlate closely with slag–refractory interactions, which may include wetting and slag penetration (causing “weight gain”), and refractory dissolution or reactions releasing gas bubbles (causing “weight loss”).

The in-situ gravimetric data (Fig. 4(a)) showed vigorous reactions between the \( \text{Al}_2\text{O}_3\)–C refractory and the slag, apparently due to the oxidation of the carbon by the FeO in the slag namely,

\[ \text{(FeO)}_{\text{slag}} + \text{C(s)} = \text{Fe(l)} + \text{CO(g)} \]  

The reaction started as soon as the contact was made. The growing gas bubbles replaced the liquid slag below the sample and caused a continuous decrease in the “apparent” weight until the point when the bubble grew to a sufficiently large size and escaped. The bursting of the bubbles caused a “spike” on the in-situ gravimetric curve when the refractory–slag contact was re-established. The gas bubbles were seen escaping from around the bottom edge of the sample and varied in size from 5 to 10 mm diameter. The iron droplets were attached to the sample (Fig. 4(b)) retrieved after the test. The bursting bubbles enhanced flow and caused an accelerated wear at the bottom edge.

It is evident from the in-situ gravimetric curve that the reaction progressively slowed down and eventually almost stopped at the end of the 4 h test. The sample net weight loss after the test was about 3 g (without correction for metal droplets and slag film attached to the sample). The FeO concentration in the slag varied from 3.4% at the beginning to about 0.4% at the end of the experiment (Table 4). The slag composition also showed a slight increase in \( \text{Al}_2\text{O}_3 \) due to the refractory loss to the slag and a small decrease in \( \text{CaO} \). The SEM examination showed a slag layer (with some small iron droplets entrapped) at the surface, but little penetration into the carbon matrix inside the refractory (Fig. 4(c)). All in all, the wear of the refractory was predominantly due to vigorous carbon oxidation at the interface.

In comparison with Slag 1, Slag A contained no intentionally added FeO but only 0.6 wt% MnO. Because the slag had a high liquidus temperature close to 1600°C, the test was conducted at 1610°C for 1 h as the test temperature approached the maximum operating temperature (about 1650°C) for the furnace used. The test results are shown in Fig. 5.

The slag–refractory reactions, due to the oxidation of carbon by the MnO (similar to that by the FeO as shown in Eq. (2)):
(MnO)_{\text{slag}} + C(s) = Mn(l) + CO(g) ................ (3)

were more subdued at low level of MnO (0.6 wt%) compared with Slag 1. In the early stage, the reaction removed the carbon from the surface, resulting in a steady increase in the wetting of the refractory by the slag (Fig. 5(a)). After about 15 min, the escape of the gas bubbles seemed to become more difficult, probably due to a slag layer at the surface (Fig. 5(c)), which slowed down the reaction considerably as indicated by the lower frequency of bubble busting.

The net weight change of the sample and the variation of the slag composition after the test were both very small. Overall, the wear of the Al_{2}O_{3}–C by Slag A at 1 610°C was minimal compared with Slag 1, demonstrating the critical effect of FeO on the carbon reaction, and severe wear of the carbon containing stopper refractories.

3.3. Tests of Al_{2}O_{3}–C with Slag B and C

The Al_{2}O_{3}–C refractory was tested with Slag B (25CaO–35SiO_{2}–33Al_{2}O_{3}–6.6MnO_{x}) and Slag C (38SiO_{2}–29Al_{2}O_{3}–33MnO_{x}) at 1 570°C for 2 h. The results are shown in Figs. 6 and 7, respectively. The in-situ gravimetric data for the two tests showed similar patterns of slag–refractory reactions in the early stage, and the rate of gas bubble formation decreased significantly after a short period (about 3 min). In the late stage, more reactions were observed with Slag C (Fig. 7(a)) with a thinner slag layer at the surface. The sample weight loss and the changes in the slag compositions were relatively small. The overall impact of the attack of the Al_{2}O_{3}–C refractory by Slag C was only marginally greater than that by Slag B.

To check the reproducibility of the in-situ measurement, the crucible was lowered to break the slag–refractory contact during the test with Slag B (Fig. 6(a)). The contact was then re-established and, when the crucible was raised to the original position, the balance reading returned to previous values as marked on Fig. 6(a). Similar checks were also made in another test (see Fig. 10 later) and the results confirmed the in-situ gravimetric curves measured were “reproducible”.

3.4. Tests of ZrO_{2}–C with Slag B and C

The ZrO_{2}–C refractory was tested with Slag B and Slag C at 1 570°C for 2 h. The results are shown in Figs. 8 and 9, respectively. The reactions were obvious from the in-situ gravimetric data (Figs. 8(a) and 9(a)) and Slag C reacted more with the ZrO_{2}–C refractory due to higher MnO and a thin slag layer at the sample surface (Fig. 9(c)). The reactions with Slag B slowed considerably after 30 min (Fig. 8(a)) and then almost stopped, as a slag layer was formed at the surface (Fig. 8(c)). The variation in the slag composition was very small in both tests, and a slight increase in reaction with Slag C did not substantially increase the wear. Overall, the slag attack on the ZrO_{2}–C surface was not severe.

The performance of the ZrO_{2}–C refractory, however, was called into question by the underlying trend of the sample weight loss during both tests. In the test with Slag B, the continued weight loss after 30 min, when the reaction was almost stopped, was observed as shown in Fig. 8(a). The weight loss continued at a similar rate after the slag–refrac-
3.5. Tests of MgO–C with Slag B and C

The interactions of the MgO–C refractory with Slag B and Slag C were investigated at 1,570°C for 2 h. The results are shown in Figs. 10 and 11, respectively. The MgO–C sample was attacked severely by Slag C (Fig. 11(b)) due to enhanced reactions during the test as shown in Fig. 11(a). SEM examinations of the hot face (Fig. 11(c)) revealed not only metal droplets (metallic Mn with some Si) as the products of carbon reaction with MnO, but also the slag attack on the periclase grains. Similar chemical attack by Slag B also occurred (Fig. 10) but to a less extent because of lower MnO content. The reaction with Slag B subsided in the late stage (Fig. 10(a)) due to accretion formed at the surface (Figs. 10(b) and 10(c)).
A SEM image of the hot face region of the sample tested with Slag C (Fig. 12) showed the reactions between periclase grains with the Al$_2$O$_3$ in the slag to form MgO·Al$_2$O$_3$ spinel phases. The reaction caused cracking, probably due to a volume expansion.$^{10,11}$ The removal of the periclase grains exposed fresh carbon matrix for oxidation, and then further slag attack on newly exposed periclase grains. The two reactions worked in concert to cause progressive severe wear, as observed.

The sample weight loss (without correction for accretion and slag attached) during the tests was apparent (net loss about 2 g after the test with Slag B and 4 g with Slag C). The slag composition after the tests (Table 5) showed a substantial decrease in MnO due to carbon reactions and a significant increase in MgO due to the loss of refractory to the slag.

The in-situ data obtained in the two tests showed an underlying trend of gradual decline in the “apparent” weight, similar to the behavior observed with the ZrO$_2$–C refractory. This will be discussed further later.

### 4. Discussions

Molten steel flows at high speeds through the small gap between the tundish stopper and the entry port of SEN. Physical contact between the stopper and the liquid inclusions in the steel is highly likely or even unavoidable. Based on the results of the present investigation and plant experience, the wear of the stopper refractories is likely to be influenced by the chemical attack from liquid inclusions and the degradation of the stopper tip refractory due to internal carbon-oxide reactions. Possible reactions between the stopper refractory and liquid steel may also contribute to the stopper wear and this is, however, outside the focus of the present investigation.

The liquid inclusion could attack the stopper refractory via the oxidation of the carbon and chemical attack on the refractory grains. The FeO in the inclusion was found to have a detrimental effect on the oxidation of carbon and severe wear of the refractory as shown in Fig. 4. In comparison, the oxidation of carbon by MnO in the slag occurred at a much lower rate with a relatively much smaller impact. The difference in the reactivity of FeO and MnO with carbon is primarily due to a difference in the thermodynamic driving forces for the corresponding chemical reactions (Eqs. (2) and (3)).$^{12}$

For the weaker oxidant, MnO, the reaction with carbon seemed to have only a limited effect on the stopper wear, in absence of a substantial slag attack on refractory grains (such as in the case of the MgO–C). The reason may be due to the restrictions on reaction kinetics.

As schematically shown in Fig. 13, after the removal of the carbon matrix at the surface (which occurred readily in all tests), the exposed oxide grains, if not attacked and removed by the slag, will make the carbon matrix behind less accessible. Further carbon reaction is possible if (1) there is a sufficient stirring caused by vigorous reaction (such as that observed with carbon–FeO reactions), (2) strong wet-
ting of the grains by the slag, hence for the slag to reach carbon–grain interface, and (3) reaction through ferrying gas within the gas pocket (e.g. involving CO₂ as intermediate: \( \text{C} + \text{CO}_2 = 2\text{CO} \) at the carbon surface and \( \text{CO} + (\text{MnO}) = \text{CO}_2 + [\text{Mn}] \) at the slag surface with the net effect equivalent to the reaction shown by Eq. (3)). Although the latter two possibilities could not be categorically excluded, the experimental evidence from the present work seemed to suggest that the effect due to (2) and (3), if any, is limited, even with an MnO-rich inclusion slag (Slag C, Figs. 7 and 9).

The situation, however, is strikingly different if the slag attacks the exposed oxide grains and subsequently removes them from the surface, thereby exposing fresh carbon matrix for further reaction. This was clearly shown by the reactions of the MgO–C refractory with Slag C (Fig. 11), where the chemical attack by the slag was at its worst, as both carbon reaction and grain attack occurred simultaneously or alternately.

The weight loss due to internal carbon–oxide reactions at high temperatures is well known. The reactions between refractory oxides and graphite have been extensively studied previously or alternately. It is well known that the MgO–C reaction produces gaseous Mg and CO, hence causing significant weight loss. The reactions between Al₂O₃ and carbon might form aluminium carbide and possibly also some stable aluminium oxide carbides, with relatively less weight loss. The reaction of carbon with ZrO₂ has not been investigated previously. While the formation of zirconium carbide is one possible reason, the significant weight loss observed might also involve the SiC contained in the refractory.

Since internal carbon reactions occurred at the interfaces between the oxide grains and carbon matrix, it could cause extensive degradation of the refractory properties, such as loss of strength, which will inevitably have an adverse impact on the stopper performance. The ZrO₂–C refractory has shown a high rate of internal carbon–oxide reactions despite of reasonably good resistance to slag attack. The refractory performed poorly in the plant trials, suggesting that internal carbon oxidation is one of the important properties determining the stopper performance.

The MgO–C refractory also showed high weight loss due to internal carbon reaction. Combined with the slag attack on both the carbon matrix and the periclase grains, the refractory fared the worst among the three stopper refractories tested. In contrast, the Al₂O₃–C stopper showed a reasonably good resistance to the slag attack, a much lower rate of the internal carbon-oxide reaction, and was clearly the best performer. These observations were found to be in a broad agreement with plant experience and observations.

5. Conclusions

Three stopper tip refractories (Al₂O₃–C, ZrO₂–C and MgO–C) have been tested with inclusion slags (SiO₂–Al₂O₃–CaO–MnO–FeO) under argon at 1 570–1 610°C for 1–4 h using the in-situ gravimetric technique. The test results showed:

(1) The attack by liquid inclusions could in some cases cause severe wear of the carbon-containing stopper refractories, through oxidation of the carbon matrix and attack on the refractory grains. The FeO in the inclusion had a detrimental effect on the oxidation of carbon and severe wear.

(2) The oxidation of carbon by the MnO in the inclusion also occurred, but at a lower rate. The carbon–MnO reaction alone did not cause severe wear in the Al₂O₃–C and ZrO₂–C stoppers. Severe wear, however, occurred in the MgO–C stopper when the periclase grains were simultaneously attacked by the Al₂O₃ in the inclusion.

(3) The weight loss due to internal carbon–oxide reactions at steelmaking temperatures appeared to be an important issue. The ZrO₂–C and MgO–C stoppers showed a higher rate of weight loss while the Al₂O₃–C stopper showed a much lower rate of weight loss (about one third of those observed for the ZrO₂–C and MgO–C stoppers).

(4) The MgO–C stopper refractory performed poorly for an inclusion chemistry corresponding to nil calcium treatment. The Al₂O₃–C stopper performed well due to the less internal carbon reaction, and a good resistance to the MnO-containing inclusions.

(5) The in-situ gravimetric technique is an excellent technique for studying dynamic interactions between slags and carbon-containing refractories, and the mechanisms for refractory wear.

Acknowledgment

The financial support from OneSteel (formerly through BHP Whyalla and BHP Steel Research) and CSIRO Minerals is gratefully acknowledged. The authors wish to thank Tim Holt, Paul Whitehouse and Jari Peltonen of OneSteel Whyalla Steelworks and John Spink of BHP Refractory Technology for valuable discussions and contributions to the work.

REFERENCES

1. R. J. Fruehan: Metall. Trans. B, 28 (1997), 743.
2. Y. Fukuda, Y. Ueshima and S. Mizoguchi: ISIJ Int., 32 (1992), 164.
3. R. R. Maddalena, R. B. Rastogi and A. W. Cramb: Iron Steelmaker, (2000), Dec., 71.
4. C. Garlick, M. Griffiths, P. Whitehouse and C. Gore: The Sixth Int. Conf. on Molten Slags, Fluxes and Salts, Royal Institute of Technology and Helsinki University of Technology, Stockholm–Helsinki, CD ROM, (2000).
5. D. Xie, T. Tran and S. Jahanshahi: The Sixth Int. Conf. on Molten Slags, Fluxes and Salts, Royal Institute of Technology and Helsinki University of Technology, Stockholm–Helsinki, CD ROM, (2000).
6. D. Xie, T. Tran and S. Jahanshahi: High Temp. Mater. Proc., 20 (2001), 293.
7. D. Xie and T. Tran: Proceedings of 7th Unified Int. Technical Conf. on Refractories (UNITECR 2001), Vol. 3, ALAFAR, Rio de Janeiro, (2001), 1418.
8. B. Nagai, T. Matumura, S. Uto, T. Isobe and H. Ohsaki: Taskabutsu Overseas, 6 (1986), 51.
9. J. Scholle and T. Rymon-Lipinski: Proc. 1st. Eur. Oxygen Steelmaking Cong., VDEh., Düsseldorf, Germany, (1993), 301.
10. R. C. Rossi and R. M. Fulrath: J. Am. Ceram. Soc., 46 (1963), 145.
11. Z. Nakagawa, T. Inoh and N. Enomoto: Advances in Refractories for the Metallurgical Industries II, CIM, Montreal, Canada, (1996), 257.
12. D. R. Gaskell, Introduction to Metallurgical Thermodynamics, 2nd ed., McGraw-Hill, New York, (1981), 287.
13. K. L. Komarek, A. Coucoulas and N. Klinger: J. Electrochem. Soc., 110 (1963), 783.
14. W. E. Lee and S. Zhang: Int. Mater. Rev., 44 (1999), 77.
15. S. C. Carniglha: Am. Ceram. Soc. Bull., 52 (1973), 160.
16. J. Pierard, Du Sichen, P. Jonsson, S. Seetharaman and T. Landin: Ironmaking Steelmaking, 25 (1998), 374.