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Role of spinel composition in the slag resistance of Al_2O_3–spinel and Al_2O_3–MgO castables

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Abstract

The slag resistance of Al_2O_3–spinel, Al_2O_3–MgO and high-Al_2O_3 castables was tested using a gas-fired rotary slag test furnace and BOF slag ($CaO/SiO_2 = 3.8$, $Fe_2O_3 = 33.4$ wt.%). The spinels used in the test contained 73, 90 and 94 wt.% Al_2O_3. The XRD patterns showed that no spinels can be identified in the mixes consisting of 75 wt.% BOF slag +25 wt.% spinel and being fired up to 1400° or 1500 °C. The same mixes were used for a sessile drop test using a prefired Al_2O_3–spinel castable as a substrate. The experimental results indicated that the penetration decreases with the increasing MgO content in spinels. The role of spinel composition in the slag resistance of Al_2O_3–spinel and Al_2O_3–MgO castables is to dissolve itself in the penetrating slag and as a result to lessen the penetration.

Keywords: D. Spinel; D. MgO; Dissolution; Precipitation; Wetting; Slag resistance

1. Introduction

Both Al_2O_3–spinel and Al_2O_3–MgO castables have been widely used as steel ladle linings below the slag line because of increasing labor costs and the severe secondary steelmaking environment in the ladle. In Al_2O_3–spinel castables, spinels are added to the mixes as a grain phase, while in Al_2O_3–MgO castables MgO reacts with Al_2O_3 to form in situ spinel during service. Al_2O_3–MgO castables are replacing Al_2O_3–spinel castables because of their superior slag resistant properties and lower costs. However, Al_2O_3–spinel castables are still commonly used in the non-impact pad area of the steel ladle bottom.

The mechanism of suppressing slag penetration in Al_2O_3–spinel castables was summarized by Mori et al. [1] as follows: first, $CaO–FeO–SiO_2$ slag penetrates into the matrix and then the CaO in the slag reacts primarily with Al_2O_3 to form $CaO–Al_2O_3$ compounds such as CA_6, while the FeO forms a solid solution in the spinel. The slag composition moves to a SiO_2-rich composition as the penetration proceeds. This liquid phase becomes viscous and hence further penetration is suppressed.

Asano et al. [2,3] claimed that Al_2O_3-rich spinels have a higher concentration of cation vacancy, which traps FeO in the slag, and that the lattice defective MgO–Al_2O_3 spinels are responsible for suppressing the slag penetration on Al_2O_3–spinel castables.

Korgul et al. [4] microscopically observed that the spinel fines and grains in the castable take up MnO/FeO/Fe_2O_3 from the slag.

Nagai et al. [5] further found that the penetration is suppressed because of rises in both the melting point and the viscosity of the slag, based on a study of the phase diagram of $CaO–FeO–SiO_2$.

Fujii et al. [6] observed that fine grain spinels suppress the slag penetration of Al_2O_3–spinel castables, while coarse grain spinels raise the corrosion resistance; and further that peeling damage to the lining of steel ladles is lessened by using Al_2O_3-rich spinels.

The role of lattice defective spinels in the slag penetration resistance of Al_2O_3–spinel castables is diminished by the latest findings. Ko [7] found that Al_2O_3-rich spinels containing 94, 90 and 73 wt.% Al_2O_3 in the Al_2O_3–spinel castables fired at 1500 °C for 3 h release the excess alumina and convert to spinel containing 75 wt.% Al_2O_3. The purpose of the present work is to explore the role of spinel composition in the slag resistance of Al_2O_3–spinel and Al_2O_3–MgO castables.

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Table 1
Chemical analyses of the raw materials

Type	Composition (wt.%)								
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Na_2O	MgO	CaO	K_2O	B_2O_3
White fused Al_2O_3	99.7	0.016	0.013	0.004	0.15	–	–	–	–
Calcined Al_2O_3	99.7	0.02	0.01	–	0.27	–	–	–	–
Reactive Al_2O_3	99.7	0.02	0.01	–	0.26	–	–	–	–
94% Al_2O_3–spinel	94.1	0.05	0.05	–	–	5.41	0.29	–	–
90% Al_2O_3–spinel	89.04	0.11	0.03	0.04	0.21	10.51	0.15	–	–
73% Al_2O_3–spinel	72.78	0.28	0.18	0.04	0.28	26.39	0.36		–
MgO fines	0.27	2.80	0.13	–	–	95.48	0.95	–	0.37
MgO powders	0.32	2.68	0.20	–	–	95.28	1.10	–	0.42
Cement	80.0	0.08	0.08		–	0.08	17.20	–	–
Microsilica	0.70	96.0	0.30		0.30	0.50	0.30	0.6	–

2. Experimental procedures

2.1. Materials

The chemical analyses of the raw materials are shown in Table 1. The three Al_2O_3-rich spinels are commonly used in commercial Al_2O_3–spinel castables. The particle sizes of reactive and calcined Al_2O_3 are −10 and −15 μm, respectively. The particle sizes of MgO-fines and powders are −75 and −0.3 mm, respectively. Microsilica is a byproduct of the Norwegian metal industry.

High basicity (CaO/SiO_2) and high iron oxide content slags resulting in deep penetration and severe corrosion in refractories were reported [8,9]. Hence BOF slag containing 43.7 wt.% CaO, 11.5 wt.% SiO_2, 1.3 wt.% Al_2O_3, 33.4 wt.% Fe_2O_3, 3.2 wt.% MnO and 7.0 wt.% MgO was collected from the BOF shop. The slag ($CaO/SiO_2 = 3.8$, 33.4 wt.% Fe_2O_3) used for the present work was deemed similar to the slag ($CaO/SiO_2 = 3.6$, 33.7 wt.% Fe_2O_3) for the slag test of Al_2O_3–spinel castables by others [10].

The constitutents and compositions of castables are given in Table 2 and are similar to those of quality commercial castables.

The mix gradings of castables are as follows: 18 wt.%−30+10 mm, 2 wt.%−8+5 mm, 9 wt.%−5+3 mm, 22 wt.%−3+1 mm, 14 wt.%−1+0075 mm and <35 wt.%−0.075 mm. All the castables contained the same amounts of reactive and calcined Al_2O_3. Each type of Al_2O_3–spinel castable contained 10 wt.%−0.075 mm spinel and another 8.5 wt.%−1 mm spinel. Moreover, the total fines content of castables was controlled under 35 wt.%−0.075 mm to avoid serious spalling damage in the field.

The physical properties of the castables fired at 1500 °C for 3 h are listed in Table 3. As can be seen, porosity of the three Al_2O_3-spinel castables is around 24%, while that of Al_2O_3–MgO castables is around 22

Table 2
Constituents and chemical compositions of castables

Castable type	Constituent (wt.%)					Composition (wt.%)			
	Alumina	Spinel	Magnesia	Cement	Silica	Al_2O_3	MgO	CaO	SiO_2
73 wt.% Al_2O_3–spinel	71.5	18.5	0	10	0	93.4	4.9	1.7	0.02
90 wt.% Al_2O_3–spinel	71.5	18.5	0	10	0	96.4	1.9	1.7	0.02
94 wt.% Al_2O_3–spinel	71.5	18.5	0	10	0	97.3	1.0	1.7	0.02
High-Al_2O_3	90	0	0	10	0	98.3	0	1.7	0.02
5.5 wt.% MgO	85.75	0	5.5	8	0.75	92.65	5.2	1.4	0.75

Table 3
Physical properties of castables fired at 1500 °C for 3 h

Type	Bulk density (kg/cm^3)	Apparent porosity (%)	Cold crushing strength (MPa)	Cold modulus of rupture (MPa)	Reheat linear change (%)
73 wt.% Al_2O_3–spinel	2.90	24.0	63.5	15.1	−0.01
90 wt.% Al_2O_3–spinel	2.93	23.7	50.3	14.3	0.01
94 wt.% Al_2O_3–spinel	2.94	23.8	56.9	15.9	0.09
High-Al_2O_3	2.96	24.1	60.7	13.0	0.11
5.5 wt.% MgO	2.94	22.3	91.4	21.6	0.87

wt.% because of MgO fines and MgO powders containing a considerable amount of impurities such as B_2O_3, CaO and SiO_2, promoting the densification of castables.

2.2. Procedures

2.2.1. Specimen preparation

The specimen castables were cast with water (6.5 wt.% for Al_2O_3–spinel castables and 5.5 wt.% for Al_2O_3–MgO castables) using a refined byproduct from the wood industry (sodium lignosulfonate) as a deflocculant and with the aid of a vibrating table. Castables were cured in air at around 30 °C ambient temperature for 24 h and then dried at 110 °C for at least 16 h before firing. Specimens having the dimensions of 160×40×40 mm were cast to measure their physical properties. The physical properties of the castables fired at 1500 °C for 3 h were measured according to the Japanese Industrial Standard R2521–1995 [11]. Each property measurement was determined using three specimens.

2.2.2. Slag test

The slag resistance test was conducted using a gas-fired rotary slag test furnace [12]. The furnace was rotated at 2 rpm and fired rapidly to reach 1650 °C in 50 min. Eight hundred grams of block steel were charged into the furnace as soon as the furnace temperature reached 1200 °C. The steel started melting after 10 min and then 1000 g of lump slag were charged into the furnace. The slag and steel became molten in another 10 min. At the end of 60 min holding at 1650 °C, the slag was drained by tilting the furnace to a 60° position. One cycle consisted of adding 800 g of steel and 1000 g of slag to the rotary furnace and holding at 1650 °C for 60 min. A total of six consecutive cycles was required for one run for the combined test of slag attack and thermal shock [12]. However, the thermal shock test was excluded from the present work and hence four consecutive cycles were deemed sufficient for the slag test alone. After the completion of the test, the furnace was cooled naturally overnight. The specimens were removed from the furnace and cut longitudinally at the center. The crack pattern and slag penetration of the tested specimens were examined visually.

Corrosion in terms of percentage was calculated from the following equation:

$$\overline{X} = \frac{\sum_{i}^{n}(h - h_i)}{n\,h} \tag{1}$$

where $\overline{X}$ = corrosion (%)

h = mean thickness of the cut section of the specimen before the slag test (mm)

h_i = residual thickness of the cut section of the specimen after the slag test (mm)

n = number of longitudinal direction of the specimen

The penetration can be calculated from the same equation as above, except that the numerator should become $\sum_i^n$(residual thickness-unreacted thickness).

It should be noted that in the present work no thermal shock to simulate blowing compressed air into the rotary furnace was performed at the end of each cycle.

2.3. Slag-spinel melt test

Mixes consisting of 75 wt.% slag and 25 wt.% spinel to simulate porous refractories dissolved by a penetrating slag were prepared for the pyramid and the crucible tests. A trilateral pyramid of the slag–spinel mixes was prepared according to the Australian Standard 1038.15–1987 [13]. The vertical height of the pyramid was 12 mm and the width of the base 6 mm.

The "tiles" had a composition of 31.5 wt.% spinel, 37 wt.% alumina and 31.5 wt.% cement, similar to the matrix composition of a high-quality commercial Al_2O_3–spinel castable [7]. They had dimensions of 60×60×7mm and were formed by powder die pressing. The particle sizes of powders were −0.075 mm. They were fired at 1500 °C for 3 h prior to use. Porosity of the fired "tiles" was 36.5%.

Fifteen grams of the 75/25 slag and spinel mixtures were mixed for 1 min in a tungsten carbide vibrating mill for use in each pyramid test and crucible test.

Four pyramids were placed on one "tile" and fired to 1500 °C in an electric furnace at a heating rate of 10 °C min^{-1}, followed by overnight furnace cooling.

Four crucibles, each filled with 4.5 g of the prepared mix or slag, were fired to 1500 °C in an electric furnace at a heating rate of 10 °C min^{-1}, followed by overnight furnace cooling. The crucible (Leco product no. 528–018) having dimensions of outside diameter 21 mm, height 25 mm and depth 19 mm is normally used for the determination of the sulfur and carbon contents of steels.

3. Results and discussion

3.1. Effect of magnesia content in spinel on the slag resistance of castables

In a previous work [7] the author found that the alumina contents of the spinels containing 94, 90 and 73 wt.% Al_2O_3 in the Al_2O_3–spinel castables and the alumina content of the spinel in the Al_2O_3–MgO castables containing 5.5 wt.% MgO fired at 1500 °C for 3 h were all estimated to be around 75 wt.% Al_2O_3. Based on the XRD patterns it was concluded that a larger amount, as well as a smaller grain size of the in situ spinel in the matrix accounts for the better slag resistance of Al_2O_3–MgO castables, compared to Al_2O_3–spinel castables.

Table 2 shows that the magnesia contents of Al_2O_3–spinel castables using Al_2O_3-rich spinels containing 94, 90 and 73 wt.% Al_2O_3 are 1.0, 1.9 and 4.9 wt.%, respectively. Based on the above findings [7], the corresponding converted spinel contents in these castables at the hot end of the slag test furnace lining are expected to be of 4, 7.6 and 19.6 wt.%, respectively, while that in Al_2O_3–MgO castables of 20.8 wt.%.

The longitudinal sections of test specimens cut at the center are shown in Fig. 1. Fig. 2 indicates that both the penetration resistance and corrosion resistance of Al_2O_3–spinel castables increase with an increase in MgO or converted spinel content in the castables. The experimental results showed that the slag resistance of Al_2O_3–spinel castables depends mainly on the amount of converted spinel containing 75 wt.% Al_2O_3. As can be seen in Fig. 2, Al_2O_3–MgO castables have much better slag penetration and corrosion resistance, compared to Al_2O_3–spinel castables. That could be due to viscosity changes rather than other reasons.

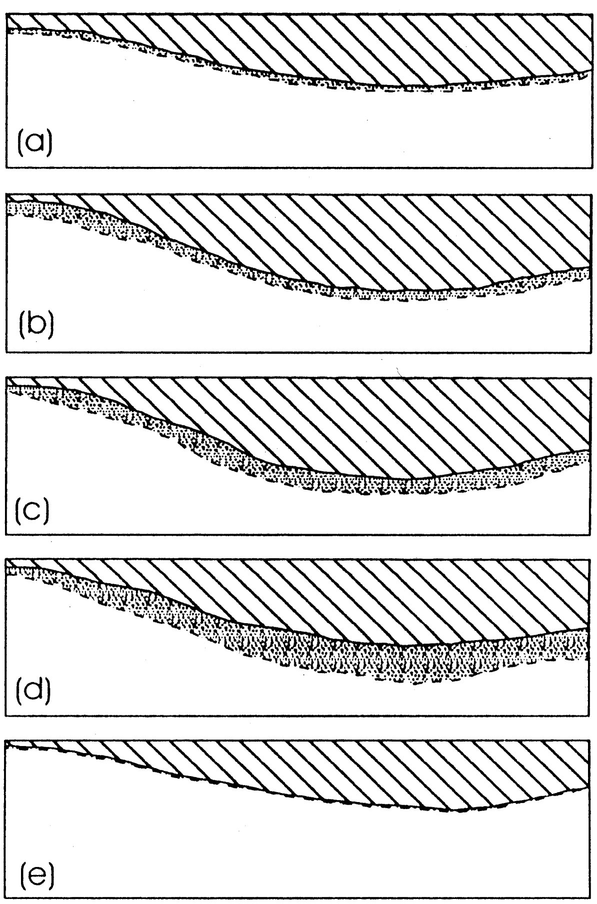

Fig. 1. Longitudinal sections of test specimens cut at center, (a) type 73 wt.% Al_2O_3 spinel, (b) type 90 wt.% Al_2O_3 spinel, (c) type 95 wt.% Al_2O_3 spinel, (d) type high-Al_2O_3, and (e) type 5.5 wt.% MgO.

3.2. Behavior of BOF slag–spinel melts

The X-ray diffraction (XRD) patterns of the mixes fired to 1400 or 1500 °C indicated that no spinels can be identified, while those with the addition of 5 wt.% spinel without being fired showed that spinels can readily be identified.

Numerous reports [14,15] indicated that slag penetration terminates at around 20 mm from the hot face of alumina–spinel castable linings. Moreover, Nagai et al. [15] estimated that the temperature at 20 mm from the hot face of the castable lining of a steel ladle is 1400–1500 °C. The spinel in the castable lining of a steel ladle is believed to dissolve itself in the penetrating slag.

In the present work the softening point of a mix is defined as the temperature at which the tip of a pyramid starts bending. The softening points of the mixes designated as a, b, c and d as shown in Table 4 were measured to be 1295, 1270 , 1272 and 1328 °C, respectively, using a Carbolite Ash Fusion Test Furnace (1600 °C) equipped with a telescope, suggesting that the dissolution of spinels in the slag starts below 1300 °C.

The morphologies of the melts (Table 4) on a Al_2O_3–spinel castable "tile" fired to 1500 °C are shown in Fig. 3. The "tile" was of the matrix composition of Al_2O_3–spinel castables. The spreading of the melts, in terms of the magnitude of a wetting area, decreases with the increasing MgO content in spinel, as indicated by Fig. 4.

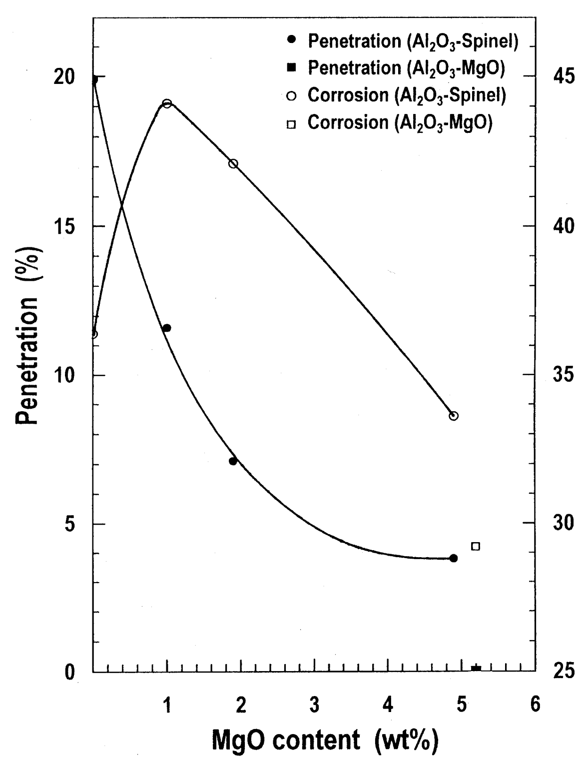

Fig. 2. Variation of penetration and corrosion of slag with the MgO content in various type castables.

Table 4
Type of BOF slag–spinel melts

Mix type	Constituent[a]	MgO content (wt.%)
a (73 wt.% Al_2O_3–spinel)	75 wt.% slag + 25 wt.% 73 wt.% Al_2O_3 spinel	6.6
b (90 wt.% Al_2O_3–spinel)	75 wt.% slag + 25 wt.% 90 wt.% Al_2O_3 spinel	2.6
c (94 wt.% Al_2O_3–spinel)	75 wt.% slag + 25 wt.% 95 wt.% Al_2O_3 spinel	1.4
d (BOF slag)	100 wt.% slag	0

[a] Grain size, 0.075 mm.

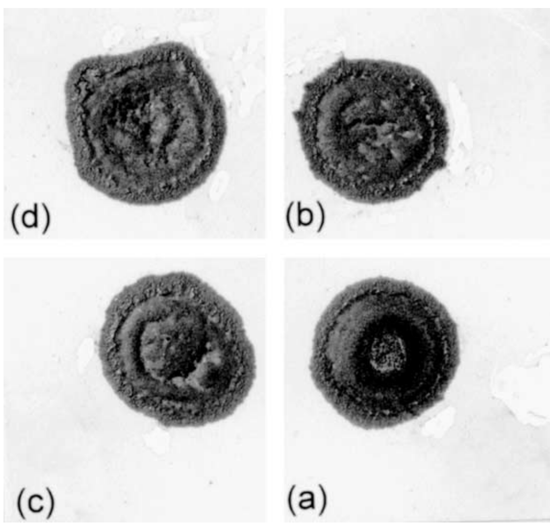

Fig. 3. Morphologies of 75 wt.% BOF slag +25 wt.% spinel mixes and BOF slag on a prefired Al_2O_3–spinel castable substrate fired to 1500 °C, (a) type 73 wt.% Al_2O_3 spinel, (b) type 90 wt.% Al_2O_3 spinel, (c) type 95 wt.% Al_2O_3 spinel, and (d) BOF slag (the spreadings were measured using an image analyzer, model number 2001, Leco Corp., St. Joseph, MI).

The contact angle is governed by interfacial energy as given by the Eq. [16]:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2)$$

where θ is the contact angle, γ_{SV} is the solid–vapor interfacial energy, γ_{SL} is the solid–liquid interfacial energy and γ_{LV} is the liquid–vapor interfacial energy. It can be seen that the wetting angle θ increases when the γ_{SL} increases, if the other two terms in equation (γ_{SV} and γ_{LV}) remain constant. Apparently, γ_{SL} increases with a decrease in spreading.

According to Kienow [17], penetration is governed by the following law:

$$h = \sqrt{\frac{(\gamma_{SV} - \gamma_{SL})\, rt}{2\eta}} \quad (3)$$

where h is the depth of penetration, r is the average pore radius, t is the time, η is the viscosity, γ_{SV} is the solid-vapor interfacial energy and γ_{SL} is the solid–liquid interfacial energy. Apparently, h decreases if γ_{SL} and η increases.Fig. 4 shows that the spreading of slag melts with the addition of 25 wt.% spinel decreases with the increasing MgO content in spinel. This may suggest that the castable-slag melt interfacial energy (γ_{SL}) increases with the increasing MgO content in castables. If the term γ_{SV}-γ_{SL} in the equation decreases with an increase in the MgO content in castables, then the penetration would be expected to decrease.

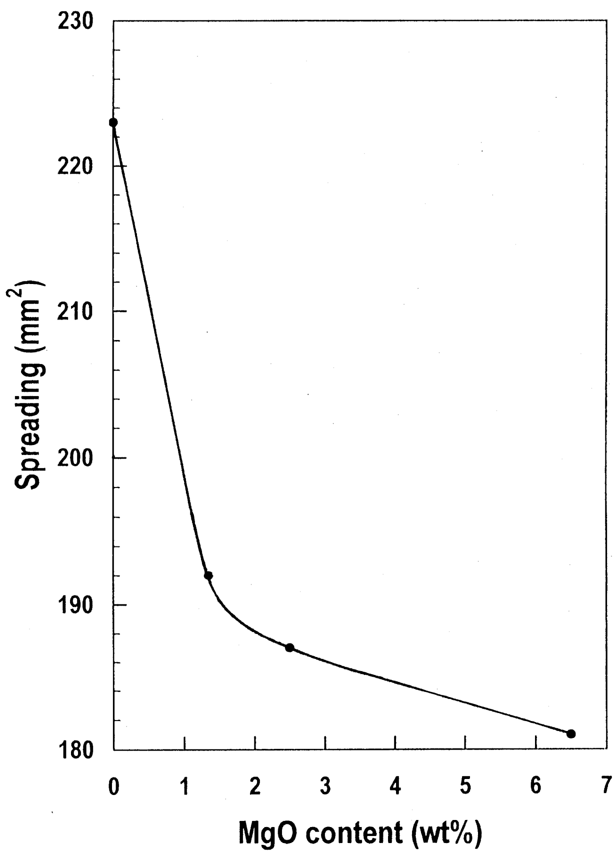

Fig. 4. Variation of spreading of 75 wt.% BOF slag +25 wt.% spinel melts and BOF slag melt with the MgO content in the melts.

SiO_2–FeO–CaO slag penetrates into the matrix and CaO in the slag reacts with Al_2O_3 to form CaO–Al_2O_3 compounds such as CA_6. The slag composition becomes SiO_2-rich. The influence of MgO content on the viscosity of SiO_2–FeO–CaO melts is shown in Fig. 5 [18]. As can be seen, the viscosity drastically increases when the precipion of MgO occurs and the higher the basicity of

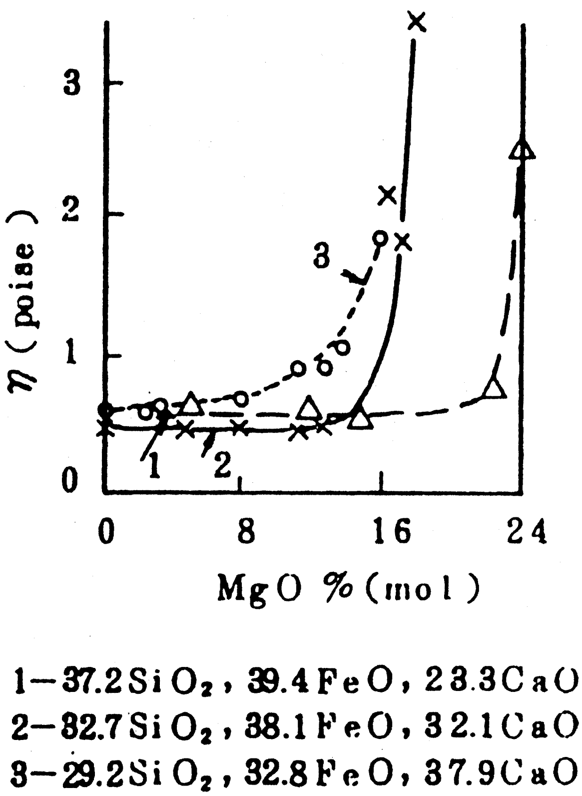

Fig. 5. Variation of viscosity of SiO_2–FeO–CaO melts with the MgO content (after Ref. [18]).

the melts, the lower the MgO content is required for the precipitation of MgO. It is believed that the dissolution of spinels and the precipation of MgO in the penetrating slag result in a drastic increase in the viscosity of the penetrating slag and hence the penetration is lessened.

4. Conclusions

1. The role of spinel composition in the slag resistance of Al_2O_3–spinel and Al_2O_3–MgO castables is to dissolve itself in the penetrating slag and as a result to lessen the penetration.
2. The experimental results indicated that the penetration decreases with increasing the MgO content in spinels.
3. The XRD patterns showed that no spinels can be identified in melts consisting of 75 wt.% BOF slag and 25 wt.% spinel and being fired up to 1400 or 1500 °C, while in mixes consisting of 95 wt.% BOF slag and 5 wt.% spinel without being fired spinels can be readily identified.
4. The softening point of the mixes consisting of 75 wt.% BOF slag and 25 wt.% spinel was in the temperature range 1295–1270 °C, compared to 1328 °C for the BOF slag, suggesting that the dissolution of spinels in the BOF slag can take place below 1300 °C. It is believed that the dissolution of spinels and the precipitation of MgO in the penetrating slag result in a drastic increase in the viscosity of the penetrating slag and hence the penetration is lessened.

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