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The viscosities and structures of calcium silicate slags containing MgO, CaF_2, and $A1_2O_3$

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The viscosities and the infrared spectra of the $CaO-SiO_2-MgO-CaF_2$ (or Al_2O_3) slags were measured to enhance our understanding of the interrelationship among the thermophysical property, microscopic structure, and chemical thermodynamics of molten slags. The structural role of CaF_2 and Al_2O_3 in the calcium silicate melts can be explained by a change of the degree of polymerization (DOP). The effect of CaF_2 on the viscous flow of molten slags is based on a decrease in the DOP by F^- as well as by O^{2-} ions and this was confirmed by the infrared (IR) spectra of the quenched slags. The effect of Al_2O_3 on viscosity increase can be understood from an increase in the DOP by the incorporation of the $[AlO_4]$-tetrahedra into the $[SiO_4]$-tetrahedral units and this was also confirmed by the IR spectra. An amphoteric behaviour of Al_2O_3 in the aluminosilicate melts could be correlated to the effect of ionic species of alumina, that is $[AlO_4]$-tetrahedra and $[AlO_6]$-octahedra, on the stability of silicate polyanions by taking the activity coefficients of slag components into account.

Keywords: viscosity; infrared spectra; degree of polymerization; amphoteric behaviour; stability; activity coefficient

Introduction

The physico-chemical properties of slags have drawn our attention during several decades in iron and steelmaking processes. Thus, there have been the popular phrases ‘A good steelmaker is a good slagmaker’ or ‘Take care of the slag and the metal will take care of itself’ in the metallurgical community.[1] Some groups in academia have investigated the properties of slags. Some metallurgists have studied the thermochemical properties likely capacities, activities, and phase equilibria, etc; others have measured the thermophysical properties such as viscosities and conductivities, etc. On the other hand, the ceramists and the geologists, as well as some metallurgists, have studied the structures of the (alumino-) silicates using various experimental techniques. However, because the macroscopic phenomena related to slags result from the microstructural changes, there have been, recently, some trials to reveal the mutual consistency between the physico-chemical properties and the structures of molten slags.[2-6]

In the present work, simple trials to interlink the slag properties among the thermophysical and chemical properties and the structures have been carried out. Thus, the viscosities and the infrared (IR) spectra of the $CaO-SiO_2-MgO-CaF_2$ (or Al_2O_3) slags were measured and the relationship between the structures and the activity coefficients of components in the slags was also discussed.

Experimental

Viscosity measurement

All of the slag samples were prepared using reagent-grade chemicals. The master slags were used for the premelting of slags, and then each component was added into the premelted slags to control the exact composition in each run. The premelting was carried out by using a graphite crucible under an Ar atmosphere in a super kanthal electric furnace.

The rotating cylinder method was used in the present study and a schematic diagram of the experimental apparatus is shown in Figure 1. A rotating viscometer (Brookfield, model RVDV-II+, Middleboro, MA) set on the super kanthal electric furnace was connected with a computer to record the value of the torque from the rotation of the spindle. The temperature was measured using an R-type (Pt/Pt-13%Rh) thermocouple in an alumina sheath placed in contact with the base of the crucible. The experimental temperature range was about 1473 to 1823 K.

The measurements of viscosity in the present study were made using a Pt-10%Rh spindle, crucibles and suspending wire. The experiment was started by placing the crucible, containing premelted slag and added powder mixture to control each composition, inside the reaction chamber at 1823 K. Then the spindle, rotating at a speed of 100 rpm, was lowered into the slag. The tip of the bob was placed

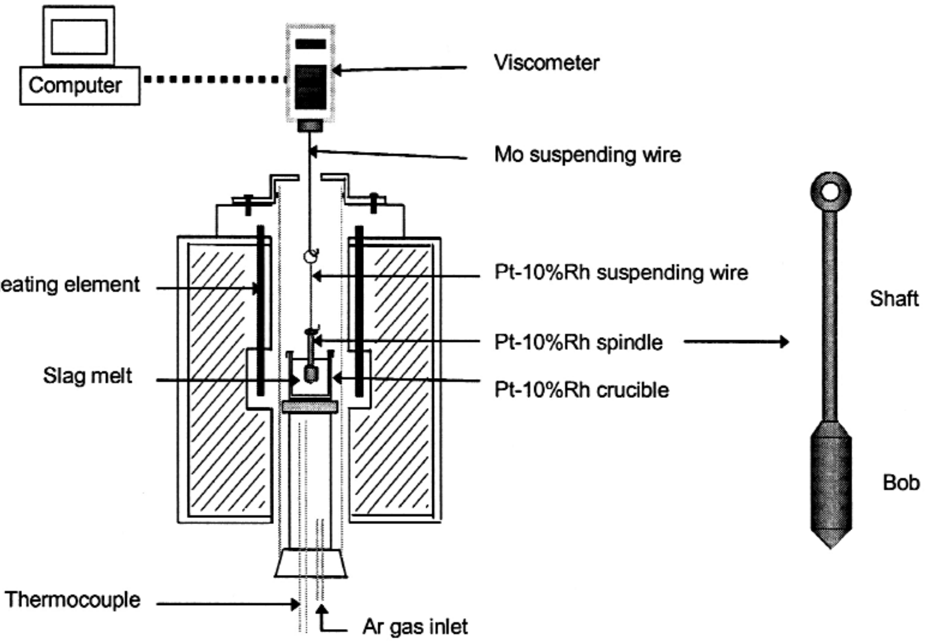


Figure 1. Experimental apparatus for the measurement of slag viscosity

about 7 mm above the base of the crucible and about 7 mm of the shaft was immersed in the melt. All of the measurements were performed during cooling cycles. The equilibration time was approximately 30 minutes at each temperature. Standard oil samples with viscosity of 0.0485, 0.096, 0.485, 0.975, and 5.04 Pa•s (0.485, 0.96, 4.85, 9.75, and 50.4 poise) were used to calibrate the spindle. Finally, some slag samples were reheated to about 1773 to 1823 K after viscosity measurements, and then water quenched to measure the IR spectra of the slags.

Infrared spectra measurement

The structure of the investigated slags was analysed by fourier transform infrared (FT-IR) spectroscopy (Nicolet, Avatar 360).[6-7] FT-IR transmitting spectra were recorded in the 4000–400 cm^{-1} range using a spectrometer, equipped with a KBr (deuterated triglycine sulfate with potassium bromide windows) detector. A spectral resolution of 2 cm^{-1} was chosen. Each sample of 2.0 mg was mixed with 200 mg of KBr in an agate mortar, and then pressed into pellets of 13 mm diameter. The spectrum for each sample represents an average of 20 scans, which were normalized to the spectrum of the blank KBr pellet.

Results and discussion

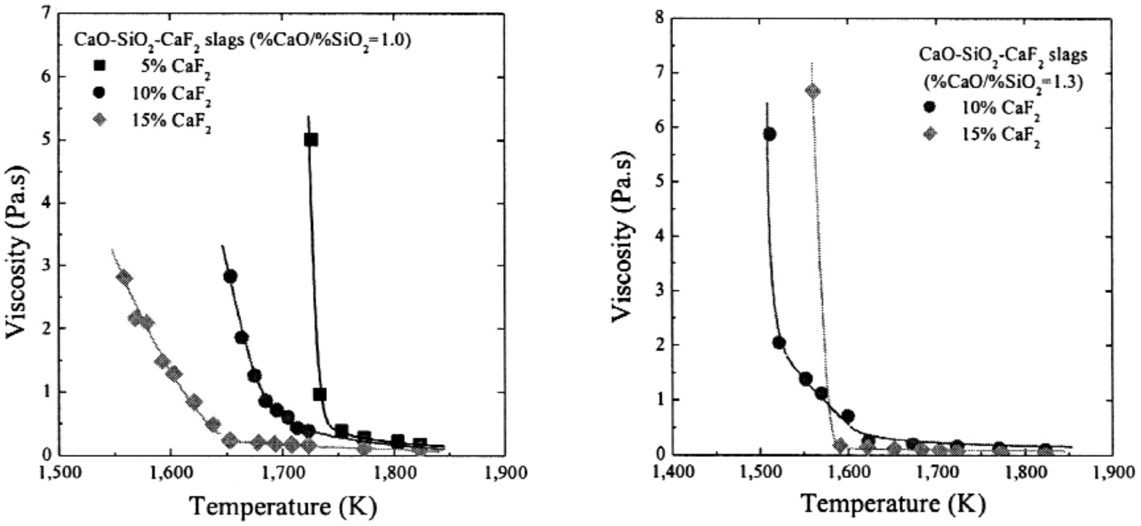
Viscosity of calcium-fluoro-silicate melts

The dependence of slag viscosity on temperature at different CaF_2 contents is shown in Figure 2 for the values of B (≡(per cent CaO)/(per cent SiO_2))=1.0 and 1.3, respectively. The critical temperature (T_{CR}) of the slags (B=1.0) decreases from about 1753 to 1643 K with increasing CaF_2 content from 5 to 15 mass per cent. This tendency can easily be expected from the phase diagram shown in Figure 3.[8] It is of interest that the T_{CR} is from 10 to 30 K lower than that of the liquidus temperature (T_{LQ}) read from the phase diagram. These results indicate that some extent of undercooling as a driving force is needed for the precipitation of solid particles in the melt. The primary solid phase precipitated from the slags with B=1.0 is pseudowollastonite ($CaSiO_3$).

The T_{CR} of the CaO-SiO_2-15 per cent CaF_2 (B=1.3) system (Figure 2 (b)) is also about 30 K lower than the T_{LQ}. However, the viscosity-increasing rate of the 10 per cent CaF_2 containing system is less than that of the 15 per cent CaF_2 system at temperatures lower than about 1623 K, which is somewhat different from the results shown in Figure 2 (a). The slag composition with 15 per cent CaF_2 is within the primary field of crystallization of cuspidine ($Ca_4Si_2O_7F_2$), while the composition with 10 per cent CaF_2 is near that of the ternary eutectic reaction 'liquid slag pseudowollastonite + larnite (Ca_2SiO_4) + cuspidine' (Figure 3). Hence, the partial crystallization of some of these phases with decreasing temperature could change the composition of liquid slag, which would gradually increase viscosity at temperatures from 1623 to 1523 K (transition region).

Hence, it can be concluded that the CaF_2 significantly affects the critical temperature of the CaO-SiO_2-CaF_2 slags; that is, the greater the content of CaF_2, the lower the T_{CR} of the slags. Also, the activation energy for the viscous flow of slags decreases with increasing CaF_2 content. This will be discussed later in detail.

The viscosity of the CaO-SiO_2-10 per cent MgO-CaF_2 slags is shown as a function of temperature in Figure 4 for the values of B=1.0 and 1.3, respectively. The critical temperature of the CaO-SiO_2-10 per cent MgO-5 per cent CaF_2 (B=1.0) system is about 1543 K as shown in Figure 4 (a). The addition of CaF_2 to greater than 10 mass per cent retards the precipitation of a solid phase in the melt. Although the phase diagram of the CaO-SiO_2-MgO-CaF_2 quaternary system is not available, it is suggested that the Newtonian flow region would be wider, i.e., deeper as the content of CaF_2 increases in the present system. The more basic slags (B=1.3) exhibit a definite T_{CR} at about 1723 and 1673 K at CaF_2 content of 10 and 15 mass per cent, respectively (Figure 5 (b)).



(a)

(b)

Figure 2. Viscosities of CaO-SiO$_2$-CaF$_2$ slags as a function of temperature and CaF$_2$ content

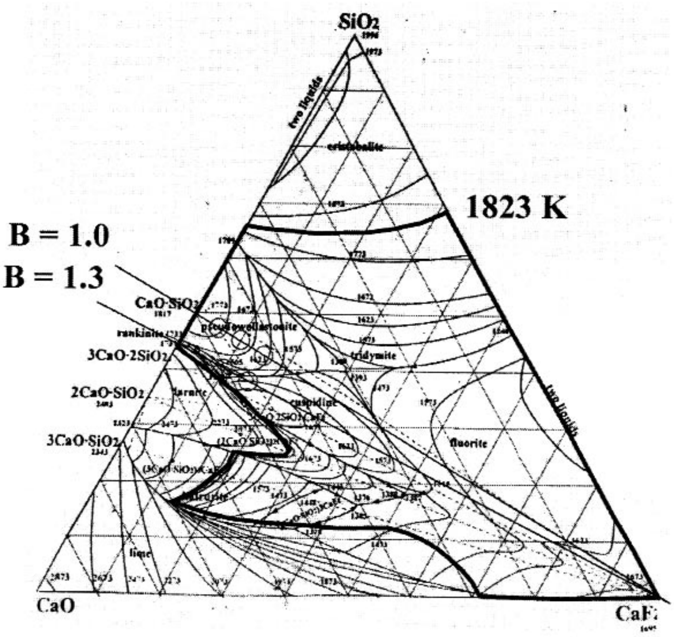


Figure 3. Phase diagram of CaO-SiO$_2$-CaF$_2$ slags (open circles: experimental composition)[8]

Viscosity of calcium-alumino-silicate melts

The dependence of slag viscosity on temperature at different Al_2O_3 contents is shown in Figure 5 for the values of B=1.0 and 1.3, respectively. The values reported by Machin *et al.* and Kozakevitch and Misra are also presented in each system for comparison.[9,10] The viscosity of the slags (B=1.0) increases with increasing Al_2O_3 content up to 10 mass per cent, followed by a decrease on the basis of the combined results of the present work and Machin *et al.*[9] This indicates that the Al_2O_3 would behave as an amphoteric oxide with its content in the present systems. This will be discussed later in detail.

The critical temperature of the CaO-SiO$_2$-10 per cent MgO-Al$_2$O$_3$ (B=1.0) system exhibits a minimum value at 10 per cent Al_2O_3, which is similar result to that of the T_{LQ} read from the phase diagram as shown in Figure 6.[11] This tendency would be originated from the mineralogical characteristics of the melilite (solid solution between gehlenite ($Ca_2Al_2SiO_7$) and akermanite ($Ca_2MgSi_2O_7$)), which has uneven melting points with its composition (Figure 6). The T_{CR} is from 60 to 100 K lower than the T_{LQ}. The T_{CR} of the more basic slags (B=1.3) is observed at about 1733 and 1683 K, which is also from 20 to 50 K lower than the T_{LQ} in the composition of 10 and 15 per cent Al_2O_3, respectively (Figure 5 (b)). The extent of undercooling for the crystallization of the slags with B=1.0 is greater than that of the more basic slags. The primary crystallized phases from the melts with B=1.0 and B=1.3 are melilite and merwinite, respectively. Hence, it can be proposed that the thermodynamic driving force for the crystallization of melilite would be larger than that of merwinite in the MgO containing slags.

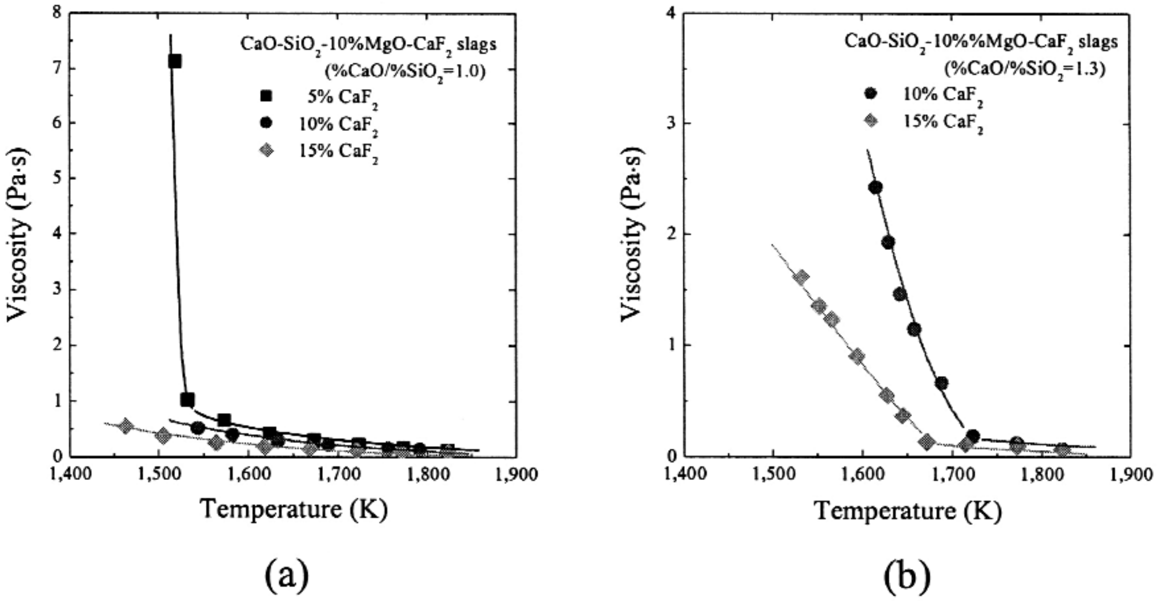
Structure and activation energy for viscous flow

The viscosity of the slags is strongly dependent on the degree of polymerization (DOP), which is a function of temperature and composition. The relationship between them has generally been discussed by taking the activation energy for the viscous flow into account.[12] The activation energy for the viscous flow of the silicate melts is obtained from the following (Arrhenius) equation:

$$\eta = \eta_o exp\left[\frac{E}{RT}\right] \qquad [1]$$

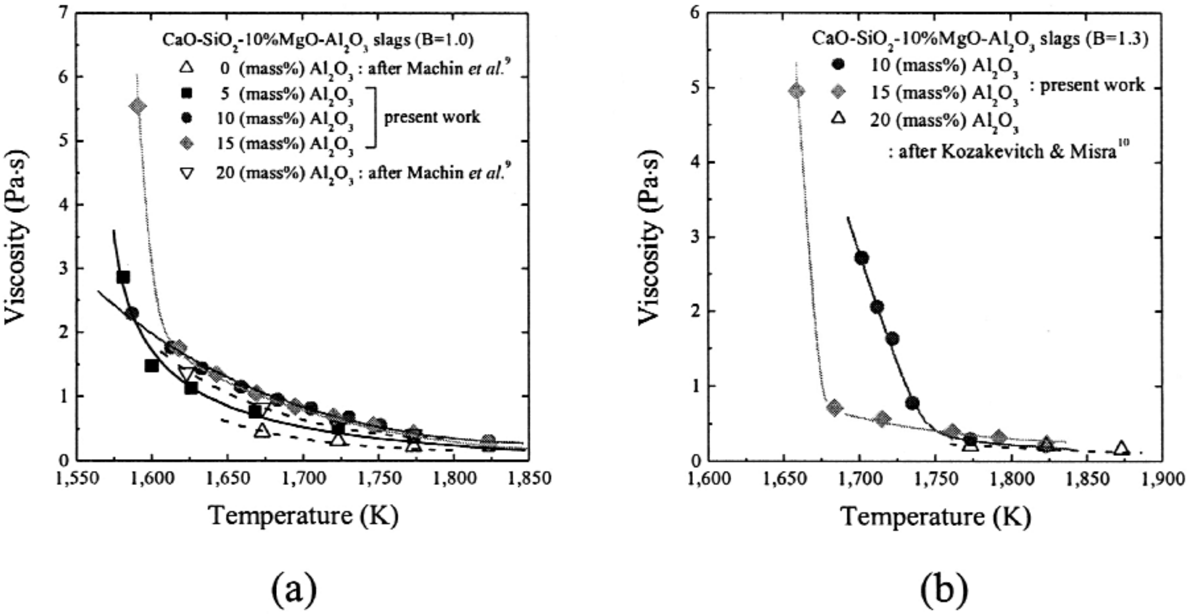
where η, η_o, E, R, and T are the viscosity, a constant, an activation energy, a gas constant, and an absolute temperature, respectively.

The Arrhenius plot for the CaO-SiO$_2$-10 per cent MgO-CaF$_2$ (or Al_2O_3) (B=1.0) system is shown in Figure 7 at different contents of CaF_2 and Al_2O_3, respectively. Here, the viscosities of the partially crystallized melts are excluded, that is, the viscosities of the melts that exhibit a



(a) (b)

Figure 4. Viscosities of CaO-SiO$_2$-10%MgO-CaF$_2$ slags as a function of temperature



(a) (b)

Figure 5. Viscosities of CaO-SiO$_2$-10%MgO-Al$_2$O$_3$ slags as a function of temperature

Newtonian flow are taken into account. The viscosity, ln η of the slags linearly increases with increasing 1/T. The slope of the lines decreases by increasing the content of CaF$_2$ in the CaO-SiO$_2$-10 per cent MgO-CaF$_2$ system, indicating that the DOP of the silicate melts decreases by addition of CaF$_2$ due to the depolymerization reaction of silicate network by F$^-$ ions, for example, as follows:

$$\left[Si_3O_9\right]^{6-}(ring)+2F^-=\left[Si_2O_6F\right]^{5-}(chain)+\left[SiO_3F\right]^{3-}(monomer) \quad [2a]$$

$$\left[Si_2O_6F\right]^{5-}(chain)+\left[SiO_3F\right]^{3-}(monomer)+2F^-=2\left[SiO_3F\right]^{3-}(monomer)+\left[SiO_2F_2\right]^{2-}(monomer)+O^{2-} \quad [2b]$$

Hence, the ring structure with NBO/Si=2 (NBO/Si: non-bridging oxygen per silicon) could not only be broken down to simple tetrahedra containing fluorine (NBO/Si=2 and 3) but could also release free oxygen ions, which contribute to a decrease in the DOP of the residual silicate polyanions.7

On the other hand, the Al$_2$O$_3$ increases the activation energy of the CaO-SiO$_2$-10 per cent MgO-Al$_2$O$_3$ slags from about 46.5 to 50.5 kcal/mol. This means that the incorporation of the [AlO$_4$]-tetrahedra into the silicate network increases the DOP of the melts. The following reaction can be taken into account, for example.

$$2\left[Si_2O_7\right]^{6-}(dimer)+Ca^{2+}+2Al_2O_3=2\left[Si_2AlO_{10}\right]^{9-}(trimer)+Ca^{2+}+2Al^{3+} \quad [3]$$

Thus, the increase in the length of silicate polyanions probably increases the activation energy for the viscous flow of the aluminosilicate melts.

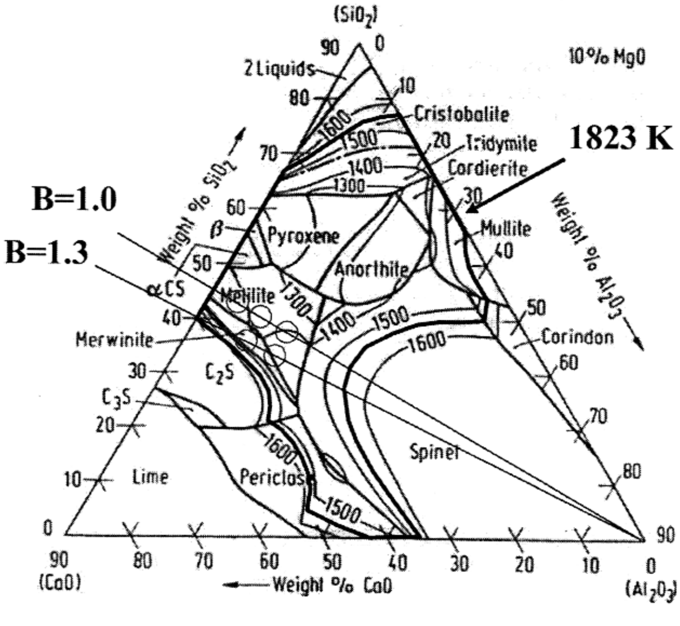


Figure 6. Phase diagram of $CaO-SiO_2-10MgO-Al_2O_3$ slags (O: experimental composition)[11]

The activation energy for the viscous flow of the silicate melts is strongly dependent on the DOP, which is affected by the composition of the slags. The activation energy of the melts investigated in the present study is shown in Figure 8 as a function of compositions with the results of Mackenzie for the binary silicate melts.[12-13] The activation energies of the $CaO-SiO_2$-10 per cent $MgO-CaF_2$ slags are on the extended curve for the binary alkaline-earth silicates, while those of the $CaO-SiO_2$-10 per cent $MgO-Al_2O_3$ slags are slightly above this curve. Richardson discussed that as the silicate groups become smaller, the number of associated negative charges becomes less; thus the number of ionic bonds, which have to be broken or distorted to enable the group to move, becomes fewer, so one would expect the values of 'E' to decreases.[12] Based on his remarks, it is confirmed that the CaF_2 decreases the DOP of the melts, while the Al_2O_3 increases the DOP of the present slags by the mechanisms proposed above.

Structure and viscosity of molten slags

The effect of CaF_2 and MgO addition on the viscosity of the calcium silicate melts at 1823 K is shown in Figure 9 as a function of the content of each additive. The viscosities of the $CaO-SiO_2$ binary and $CaO-SiO_2-MgO$ ternary slags have been taken from the literature.[14-15]

The viscosity of the $CaO-SiO_2-CaF_2$ (B=1.0) system decreases from about 0.3 to 0.1 Pa•s with increasing CaF_2 content up to 15 mass per cent. Also, the viscosity of the slag with B=1.3 decreases from about 0.2 to 0.05 Pa•s as the content of CaF_2 increases. Thus, the effect of CaF_2 on the viscous flow of molten slags can be understood based on Equation [2]. These macroscopic phenomena, such as viscosity, could originate from the variation of the microscopic structure of slags as follows.

Figure 10 exhibits the infrared spectra of the $CaO-SiO_2-CaF_2$ (B=1.0) slags as a function of wave number at different CaF_2 contents. The relative intensity of the IR bands for $[SiO_4]$-tetrahedra with NBO/Si=1+2 (1090 and 990 cm^{-1} bands) decreases as the content of CaF^2 increases, while that of the IR bands for $[SiO_4]$-tetrahedra with NBO/Si=3+4 (930 and 850 cm^{-1} bands) increases with increasing CaF_2 content.[7] Also, the center of gravity of the $[SiO_4]$-tetrahedral bands at about 1160–780 cm^{-1} shifts from about 990 to 930 cm^{-1} as the composition of slags varies from the $CaO-SiO_2$ binary to the $CaO-SiO_2$-15 per cent CaF_2 ternary system. Therefore, it is concluded that the viscous behaviour of the silicate melts observed in Figure 9 is caused by a continuous decrease in the DOP of silicate units by CaF_2 addition.

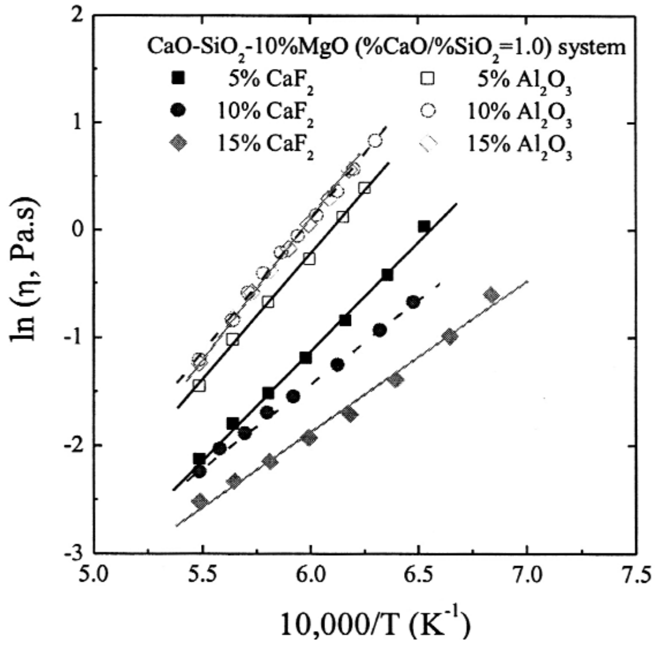


Figure 7. Arrhenius plot for $CaO-SiO_2-10MgO-CaF_2$ (or Al_2O_3) slags at Newtonian flow region

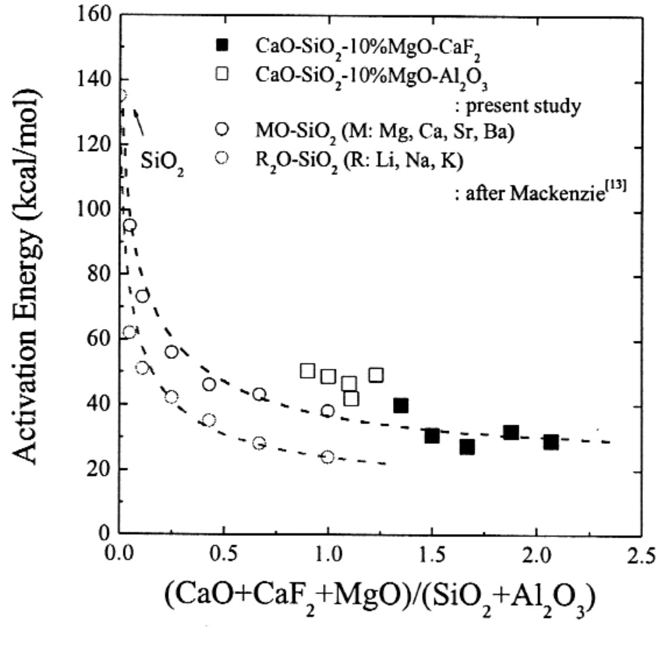


Figure 8. Apparent activation energies for the viscous flow of molten slags

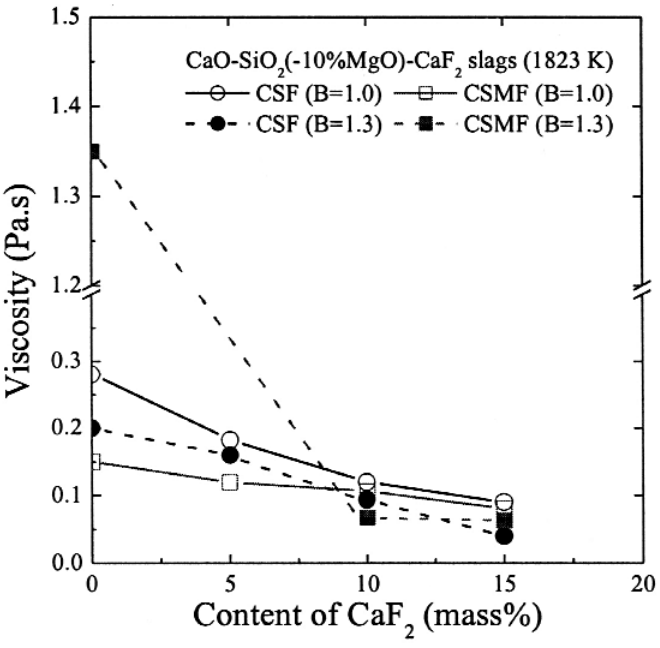


Figure 9. Viscosities of the CaO-SiO$_2$ (-10%MgO)-CaF$_2$ slags as a function of CaF$_2$ content

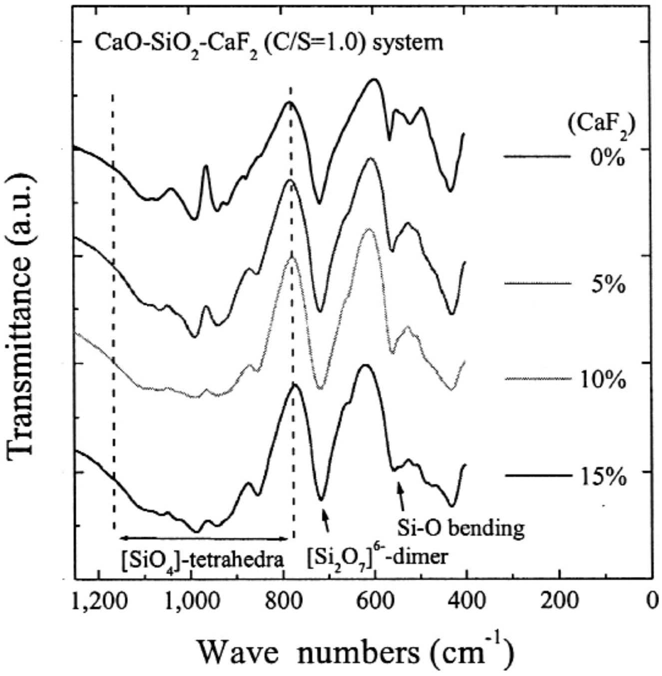


Figure 10. IR transmittance of the CaO-SiO$_2$-CaF$_2$ (B=1.0) slags as a function of wave numbers

The effect of Al$_2$O$_3$ and MgO addition on the viscosity of the calcium silicate melts at 1823 K is shown in Figure 11 as a function of the content of each additive. The viscosity of the CaO-SiO$_2$-Al$_2$O$_3$ (B=1.0) system increases from about 0.3 to 0.8 Pa•s with increasing Al$_2$O$_3$ content up to about 10 mass per cent, followed by a slight decrease.**16** The viscosity of the slag with B=1.3 exhibits a similar tendency. These complex results can be understood from the amphoteric characteristics of Al$_2$O$_3$ in the aluminosilicate melts. The structural role of Al$_2$O$_3$ in the aluminosilicate melts has frequently been investigated by spectroscopic studies based on the IR and Raman spectra.**17-18** The Al^{3+} ions would exist as a form of the [AlO$_4$]-tetrahedra incorporated into the [SiO$_4$]-tetrahedral units, when it behaves as a network former. However, the Al^{3+} ions would form the [AlO$_6$]-octahedra for the network-modifying role. Therefore, the macroscopic phenomena, i.e., viscosity of the CaO-SiO$_2$-Al$_2$O$_3$ slags observed in Figure 11 could be understood from the microscopic changes in slag structure as follows.

The IR transmittance of the CaO-SiO$_2$-Al$_2$O$_3$ (B=1.3) slags is shown in Figure 12 as a function of wave numbers at different Al$_2$O$_3$ contents. The IR bands for the [SiO$_4$]-tetrahedra merge into the broad and strong band by addition of Al$_2$O$_3$ about 10 mass per cent to the CaO-SiO$_2$ binary system. The broadening of IR bands for the [SiO$_4$]-tetrahedra has been known to occur from the random networking of the [SiO$_4$]-tetrahedra with various NBO/Si in the melts, indicating an increase in the DOP of silicates to some extent.**19-21** These structural variations of silicate melts with Al$_2$O$_3$ addition could explain the role of alumina as a network former in the viscous flow of the slags (Equation [3]).

The excess addition of Al$_2$O$_3$ greater than 10 mass per cent results in the extension of the lower limit of IR bands for the [SiO$_4$]-tetrahedra from about 760 to 720 cm^{-1}, representing a decrease in the DOP of silicates. That is, the relative intensity of the bands at higher wave number decreases and that of the bands at lower wave number within the [SiO$_4$]-tetrahedral range increases by increasing the content of Al$_2$O$_3$ from 10 to 15 mass per cent. Thus, the centre of gravity of the bands shifts from about 960 to 800 cm^{-1}, indicating the increase in the relative fraction of the [SiO$_4$]-tetrahedra with NBO/Si=4 (orthosilicates) units in the slags. Also, a new [AlO$_6$]-octahedral band appears (570 cm^{-1}) at 15 per cent Al$_2$O$_3$ content. Therefore, the viscosity of the CaO-SiO$_2$-Al$_2$O$_3$ slags observed in Figure 11 would be strongly dependent on the structural role of Al$_2$O$_3$ in the

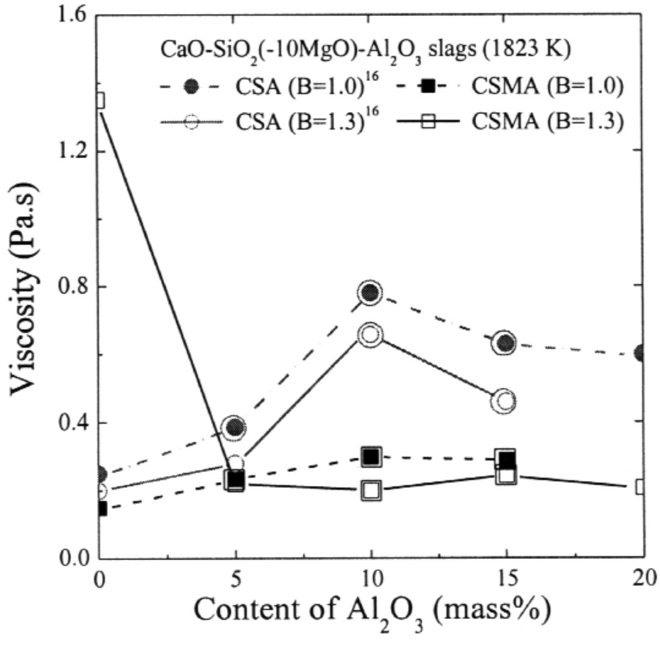


Figure 11. Viscosities of the CaO-SiO$_2$ (-10%MgO)-Al$_2$O$_3$ slags as a function of Al$_2$O$_3$ content (double marks: by some of the present authors)

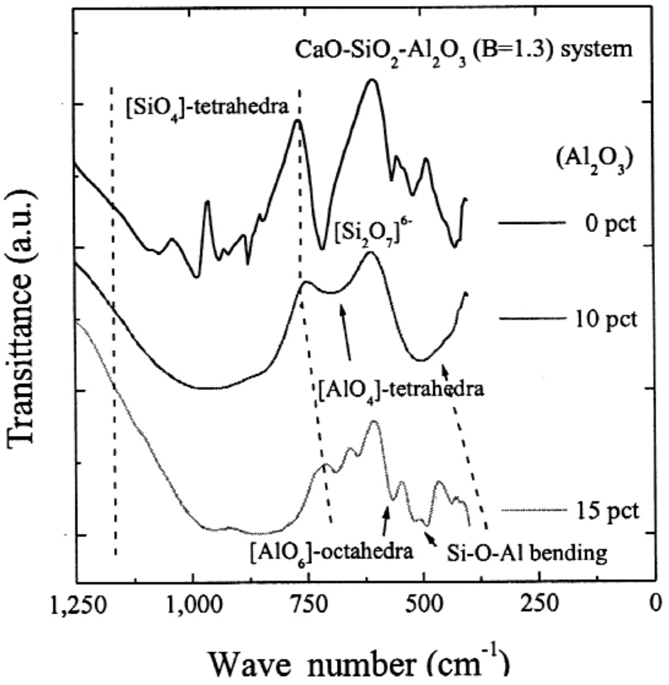


Figure 12. IR transmittance of CaO-SiO$_2$-Al$_2$O$_3$ (B=1.3) slags as a function of wave number[16]

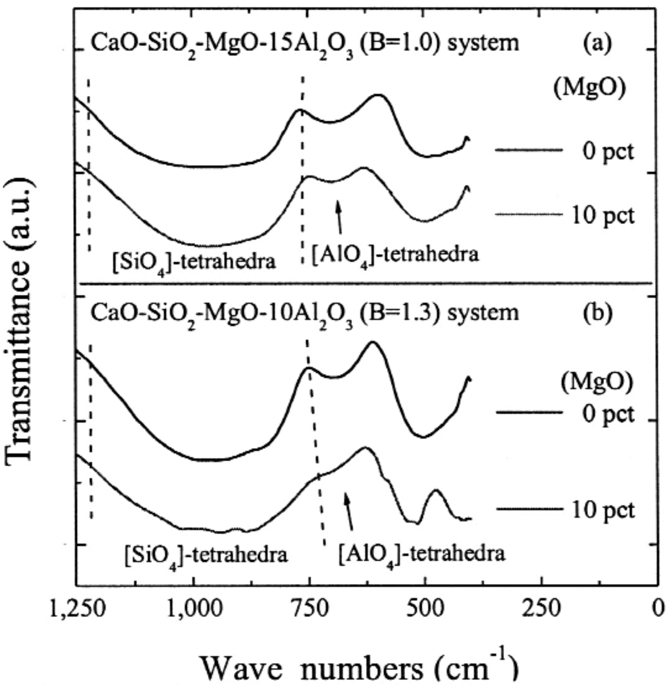


Figure 13. Effect of MgO on IR spectra of CaO-SiO$_2$-Al$_2$O$_3$ slags as a function of wave number

slags. The addition of Al_2O_3 greater than about 10 mass per cent in the aluminosilicate melts decreases the viscosity because of an increase in the relative fraction of the [AlO_6]-octahedral units.

The effect of MgO on the viscosity of the aluminosilicate melts is also observed in Figure 11. The viscosity of the CaO-SiO_2-Al_2O_3 slags generally decreases by 10 per cent MgO addition and the MgO effect on the viscosity is significant as the content of Al_2O_3 increases. This means that the modification reaction of silicate melts with high DOP is more effective than that of the systems with low DOP by contribution of Mg^{2+} as well as Ca^{2+} ions to the depolymerization of the silicate network. Hence, the relative fraction of the polymerized units, which are able to accommodate the [AlO_4]-tetrahedra, in the slags containing MgO would be less than that in the slags without MgO. This probably results in a decrease in the relative fraction of the [AlO_4]-tetrahedra incorporated into the [SiO_4]-tetrahedral units in the slags containing MgO and could be confirmed by the FT-IR spectra analysis as follows.

Figure 13 exhibits the FT-IR spectra of (a) the CaO-SiO_2 (-MgO)-15 per cent Al_2O_3 (B=1.0) and (b) the CaO-SiO_2 (-MgO)-10 per cent Al_2O_3 (B=1.3) systems as a function of wave numbers. In Figure 13(a), the IR bands for the [SiO_4]- and [AlO_4]-tetrahedral units are observed at about 1220–760 and 700 cm^{-1}, respectively. The relative intensity of the IR band for the [AlO_4]-tetrahedral units in the 10 per cent MgO-containing slags is less than that in the non-MgO slags. Thus, it is suggested that the addition of 10 per cent MgO into the CaO-SiO_2-15 per cent Al_2O_3 (B=1.0) system would decrease the relative fraction of the [AlO_4]-tetrahedral units. Consequently, the DOP of the silicate melts would be decreased.

Although the IR bands for the [SiO_4]-tetrahedra are shown at about 1220–750 cm^{-1} in the CaO-SiO_2-10 per cent Al_2O_3 (B=1.3) system, the lower limit of the bands extends to about 730 cm^{-1} by MgO addition (Figure 13 (b)). The shift of the band to lower wave numbers indicates an increase in the relative fraction of the [SiO_4]-tetrahedra with NBO/Si=3+4 units. The relative intensity of the [AlO_4]-tetrahedra at about 690 cm^{-1} drastically decreases by MgO addition. Actually, the viscosity of the CaO-SiO_2-15 per cent Al_2O_3 (B=1.0) system decreases from about 0.6 to 0.3 Pa•s (i.e., approximately 1/2 level), while that of the CaO-SiO_2-10 per cent Al_2O_3 (B=1.3) system decreases from about 0.7 to 0.2 Pa•s (i.e., about 1/4 level) by 10 per cent MgO addition as shown in Figure 11. Therefore, the addition of 10 per cent MgO decreases the DOP of the CaO-SiO_2-Al_2O_3 slags regardless of the ratio CaO/SiO_2, which would be originated from a decrease in the relative fraction of the [AlO_4]-tetrahedral units incorporated into the silicate network.

Thermodynamic activity coefficients and structure of molten slags

An amphoteric behaviour of Al_2O_3 in the aluminosilicate melts has been discussed in a previous section based on the structural analysis by combining the measured results of viscosity and FT-IR spectra. In this section, the interaction between Al_2O_3 and SiO_2, and the effect of MgO addition on the stability of each component will be discussed by taking the activity coefficient of each oxide into account.

Figure 14 exhibits the activity coefficients of SiO_2 and Al_2O_3 in the CaO-SiO_2(-MgO)-Al_2O_3 slags at 1823 K.[22] The activity coefficient of SiO_2 (γ_{SiO_2}) in the CaO-SiO_2-Al_2O_3 slags significantly decreases with increasing Al_2O_3 content up to 10 mass per cent, followed by a slight decrease, while the activity coefficient of Al_2O_3 ($\gamma_{Al_2O_3}$) exhibits a minimum value at 10 per cent Al_2O_3. Therefore, it is suggested that the incorporation of the [AlO_4]-tetrahedra into the [SiO_4]-tetrahedral units could increase the stability of the silicate polyanions ($Si[Al]_xO_y^{n-}$), if the 1/2 Ca^{2+} ions are located near the [AlO_4]-tetrahedral units for the electronic charge balance.[12,23] In the composition

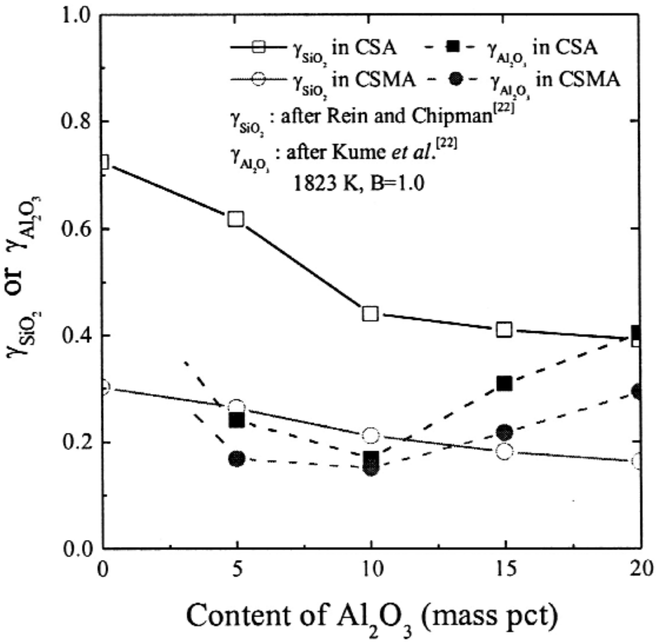


Figure 14. Activity coefficient of SiO_2 and Al_2O_3 in CaO-SiO_2 (-MgO)-Al_2O_3 slags at 1823 K

greater than 10 per cent Al_2O_3, the relative fraction of the [AlO_6]-octahedra, which is not incorporated into the silicate network, increases as shown in the previous section. Hence, the $\gamma_{Al_2O_3}$ increases by increasing the content of Al_2O_3 in this region.

The addition of 10 per cent MgO into the CaO-SiO_2-Al_2O_3 slags decreases both γ_{SiO_2} and $\gamma_{Al_2O_3}$. In the slags containing MgO, the activity coefficients of SiO_2 and Al_2O_3 similarly change to those in the CaO-SiO_2-Al_2O_3 ternary system. However, the slope of each line is less than that in ternary slags; that is, the effect of Al_2O_3 on the stability of the silicate network in the quaternary system is less than that in ternary system. This is in good agreement with the experimental results of the viscosity of each system shown in Figure 11.

In summary, it can be suggested that the macroscopic thermophysical phenomena of molten slags could be originated from the changes in the microscopic structure. Furthermore, the thermophysical property such as viscosity could also be understood based on thermodynamic fundamentals.

Conclusions

The viscosities and the infrared spectra of the CaO-SiO_2-MgO-CaF_2 (or Al_2O_3) slags were measured to enhance our understanding of the interrelationship among the thermophysical property, microscopic structure, and chemical thermodynamics of molten slags. The following conclusions were obtained.

1. The structural role of CaF_2 in the calcium silicate melts could be explained by a decrease in the DOP and vice versa for the case of Al_2O_3 from the measurements of viscosity.
2. The observation of infrared spectra of the slags qualitatively proved that the effect of CaF_2, Al_2O_3, and MgO on the viscosities of the calcium silicate melts.
3. An amphoteric behaviour of Al_2O_3 in the aluminosilicate melts could be correlated to the effect of ionic species of alumina, that is [AlO_4]-tetrahedra and [AlO_6]-octahedra, on the stability of silicate polyanions by taking the activity coefficients of slag components into account.

References

1. DEO, B. and BOOM, R. *Fundamentals of Steelmaking Metallurgy*, Prentice Hall International, New York, 1993, pp. 161–188.
2. SEETHARAMAN, S., SICHEN DU, and JI, F.Z. *Metall. Mater. Trans. B*, vol. 31B, 2000, pp. 105–110.
3. SEETHARAMAN, S., SRIDHAR, S., SICHEN DU, and MILLS, K.C. *Metall. Mater. Trans. B*, vol. 31B, 2000, pp. 111–119.
4. HAYASHI, M., AUNE, R.E., FREDRIKSSON, P., SICHEN, DU, and SEETHARAMAN, S. *ISSTech 2003 Conf. Proc.*, Indianapolis, April 27–30, 2003, ISS, Warendale, PA, vol. 1, pp. 309–319.
5. PARK, J.H., MIN, D.J., and SONG, H.S. *Metall. Mater. Trans. B*, vol. 33B, 2002, pp. 723–729.
6. PARK, J.H., MIN, D.J., and SONG, H.S. *Iron Steel Inst. Jpn. Int.*, vol. 42, 2002, pp. 38–43.
7. PARK, J.H., MIN, D.J., and SONG, H.S. *Iron Steel Inst. Jpn. Int.*, vol. 42, 2002, pp. 344–351.
8. WATANABE, T., FUKUYAMA, H., and NAGATA, K. *Proc. ICS 2001*, Wales, April 10–11, 2001, IoM, London, pp. 613–622.
9. MACHIN, J.S., YEE, T.B., and HANNA, D.L. J. *Am. Ceram. Soc.*, vol. 35, 1952, pp. 322–325.
10. KOZAKEVITCH, P. and MISRA, N. *Rev. Metall.*, vol. 63, 1966, pp. 471–476.
11. KOWALSKI, M., SPENCER, P.J., and NEUSCHUTZ, D. *Slag Atlas, 2^{nd}* edn., Verlag Stahleisen GmbH, Dusseldorf, 1995, pp. 99–180.
12. RICHARDSON, F.D. *Physical Chemistry of Melts in Metallurgy*, Academic Press, London, vol. 1, 1974, pp. 92–106.
13. MACKENZIE, J.D. *Adv. Inorg. Chem. Radiochem.*, vol. 4, 1962, p. 293.
14. MILLS, K.C. *Slag Atlas*, 2nd edn., Verlag Stahleisen GmbH, Dusseldorf, 1995, pp. 349–402.
15. IIDA, T. and SHIRAISHI, Y. *Handbook of Physico-chemical Properties at High Temperatures*, ISIJ, Tokyo, 1988.
16. PARK, J.H., MIN, D.J., and SONG, H.S. *Metall. Mater. Trans. B*, vol. 35B, 2004, in print
17. MYSEN, B.O., VIRGO, D., and KUSHIRO, I. *Am. Mineral.*, vol. 66, 1981, pp. 678–701.
18. IGUCHI, Y., YONEZAWA, K., FUNAOKA, Y., BAN-YA, S., and NISHINA, Y. *Proc. 3^{rd} Int. Conf. Molten Slags and Fluxes*, Glasgow, June 27–29, 1988, IoM, London, 1989, pp. 169–171.
19. TSUNAWAKI, T., IWAMOTO, N., HATTORI, T., and MITSUISHI, A. *J. Non-Cryst. Solids*, vol. 44, 1981, pp. 369–378.
20. MCMILLAN, P. *Am. Mineral.*, vol. 69, 1984, pp. 645–659.
21. LUTH, R.W. *Am. Mineral.*, vol. 73, 1988, pp. 297–305.
22. KUME, K., MORITA, K., MIKI, T., and SANO, N. *Iron Steel Inst. Jpn. Int.*, vol. 40, 2000, pp. 561–566.
23. DUAN, R.G., LIANG, K.M., and GU, S.R. *Mater. Trans., JIM*, vol. 39, 1998, pp. 1162–63.