THE VISCOUS BEHAVIOR OF HIGH Al_2O_3 CONTAINING BLAST FURNACE TYPE SLAGS

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ABSTRACT

The effect of alumina on the relationship between viscosity and structure of the CaO-SiO_2-Al_2O_3 ternary system and CaO-SiO_2-Al_2O_3-MgO quaternary system are investigated by employing viscometer using the rotating cylinder method and Fourier transform–infrared (FT-IR) spectra, respectively. In addition, the original Darken's excess stability function was introduced in order to understand the thermophysical phenomena and the role of alumina based on thermodynamics. Alumina behaves as an amphoteric oxide in the CaO-SiO_2-Al_2O_3-MgO melts, and this is not only experimentally confirmed but also thermodynamically proved by taking the Darken's excess stability function into account.

INTRODUCTION

The relationship between thermophysical properties and the structure of silicate melts is of importance to understand the microscopic origin of the thermodynamic properties not only in the metallurgical community but also in chemical geology. The viscosity, which determines the working temperature and process kinetics of the system, $CaO-SiO_2-Al_2O_3$ and $CaO-SiO_2-Al_2O_3-MgO$ melt, has been measured by many researchers.[1, 2, 3, 4] The structure of binary and ternary subsystems was investigated with various experimental techniques[5, 6, 7, 8, 9]. Also, we can find some reports on the measurement or optimization of thermodynamic activities of each component in this ternary and quaternary system at high temperatures [10, 11, 12, 13, 14]. Furthermore, there has been considerable interest in the amphoteric behavior of alumina, which acts as a network modifier or network former according to the composition of aluminosilicate melts [2, 3, 15, 16, 17, 18, 19].

Seetharaman *et al.* introduced the Gibbs free energy of mixing (ΔG^{mix}) to predict the activation energy for the viscous flow (ΔG^{*}) of ternary silicate melts in line with Richardson's consideration [20]. Thereafter, Aune *et al.* expected to link thermophysical and thermochemical properties by adopting Darken's excess stability concept, and they demonstrated that the second derivatives of the viscosities of binary silicate melts with respect to composition indicated maxima corresponding to the existence of stable compounds in these systems [21]. Recently, Lee investigated the relationship between the activity coefficient of silica and viscosity of silicate melts and glasses based on the quantitative estimation of the extent of disorder from solid-state ^{17}O 3QMAS NMR (triple quantum magicangle spinning nuclear magnetic resonance) and quasichemical approximation [22]. Although there are several studies on viscosities, structures, and thermodynamic properties of $CaO-SiO_2-Al_2O_3$ and $CaO-SiO_2-Al_2O_3-MgO$ slags, comprehensive explanations integrating all three factors together at a given system are still insufficient. We measured the viscosity and Fourier transform–infrared (FT-IR) transmitting spectra of $CaO-SiO_2-Al_2O_3$ (-MgO) melts and glasses [2] and revealed the amphoteric behavior of alumina based on the changes of activity coefficient of alumina and silica. In the present study, in line with previous works [3], the effect of alumina on the relationship between viscosity and structure of the $CaO-SiO_2-Al_2O_3$(-15 mole pct MgO) system is investigated by employing a viscometer using the rotating cylinder method and FT-IR spectra, respectively. In addition, the original Darken's excess stability function was introduced in order to understand the thermophysical phenomena and the role of alumina based on thermodynamics [23].

METHODOLOGY

The viscosities were measured by rotating cylinder method. The viscosity can be determined by the generated torque from the submerged spindle (Pt-10 mass pct Rh) in the oxide melt which is contained in the Pt-10 mass pct Rh crucible. The calibrated viscosities were calculated from the generated torque at constant speed by a viscometer (RVDV-II+, Brookfield, Middleboro, MA) set on the kanthal super electric furnace. Experimental methods, schematic diagram of the apparatus, and dimensions of spindle, crucible, and suspending wire are described in detail elsewhere [2]. The composition of the slags investigated in this study is listed in Table 1. In the measurement of FT-IR spectra, the oxide samples of composition listed in Table 1 were melted in a platinum crucible at 1773 K for 3 hours.

Table 1: Primary experimental composition of the oxide melts in the present study

sample	Content of oxide component (mol pct.)				Remarks
	CaO	SiO_2	Al_2O_3	MgO	
V1	43.0	34.9	7.5	14.5	Viscosity measurement of liquids at 1773 K
V2	42.3	34.3	8.7	14.7	
V3	41.5	33.7	9.9	14.8	
V4	40.4	32.8	11.9	15.0	
V5	39.0	31.5	12.8	15.5	
I1	50.2	46.9	2.9		FT-IR spectra measurement of quenched glasses
I2	48.7	45.4	5.9		
I3	47.0	43.9	9.1		
I4	45.3	42.3	12.4		
I5	43.5	40.6	15.9		
I6	56.5	40.6	2.9		
I7	54.8	39.3	5.9		
I8	52.9	38.0	9.1		
I9	51.0	36.6	12.4		
I10	49.0	35.2	15.9		
I11	46.9	33.6	19.5		
I12	43.0	34.9	7.5	14.5	
I13	40.2	33.9	11.2	14.7	
I14	38.5	32.7	13.8	14.8	

Subsequently, the oxide melts were directly poured onto the copper plate, which was cooled by flowing water. The samples were confirmed as a glass using an X-ray diffractometer (D8 Advance, Bruker AXS Inc., Madison, WI) and crushed to powders that are smaller than 100 μm. The FT-IR spectroscopy (Spectra 100, Perkin-Elmer inc., MA) was used, and the transmitting spectra were recorded in the 4000 to 400 cm^{-1} range using a spectrometer, equipped with a KBr (deuterated triglycine sulfate with potassium bromide windows) detector. The measurement procedure is described in detail elsewhere [8, 9].

RESULT AND DISCUSSION

$CaO-SiO_2-Al_2O_3$ Ternary System

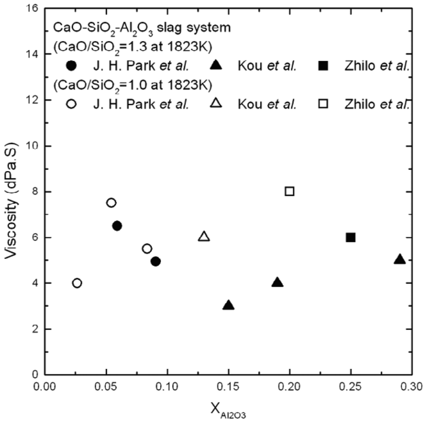


Figure 1: Viscosity of the $CaO-SiO_2-Al_2O_3$ ternary melt at 1823 K as a function of mole of Al_2O_3

The viscosities of $CaO-SiO_2-Al_2O_3$ slags at 1823 K are shown in Figure 1. There are two pronounced peaks of viscosity in low and high Al_2O_3 content ranges. The viscosity increase between 2.9 to 5.9 mol pct. and decrease up to 9.1 mole pct. at $CaO/SiO_2=1.0$. In case of $CaO/SiO_2=1.3$, the viscosity of slag decrease again at 30 mol pct. of alumina.

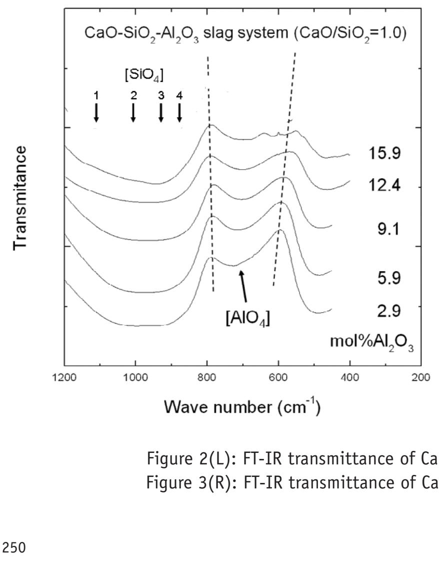
The structural role of Al_2O_3 in the aluminosilicate melts has frequently been investigated by spectroscopic studies based on the IR and Raman spectra [5, 6, 7, 8, 9]. The Al^{3+} ions would exist as a form of the $[AlO_4]$-tetrahedra incorporated into the $[SiO_4]$-tetrahedral units, when it behaves as a network former. Therefore, the macroscopic phenomena, i.e., viscosity of the $CaO-SiO_2-Al_2O_3$ slags observed in Figure 1, could be understood from the microscopic changes in slag structure by employing the FT-IR spectra analysis.

The FT-IR transmittance of the present system is shown in Figures 2 and 3 as a function of wave numbers and alumina concentration. In the $CaO-SiO_2-Al_2O_3$ ternary glass system, there are two IR band groups in the detecting range of this study, and these can be identified as follows. First, the broadband at about 1200 to 730 cm^{-1} corresponds to the stretching vibration of the Si-O bond in $[SiO_4]$-tetrahedral units with various non-bridging oxygen per silicon (NBO/Si),[2, 3, 8, 9] which are marked in Figure 2 as arrows. It is of interest that the relative intensity of the band for NBO/Si = 1 repeats increasing and decreasing as the viscosity changes in Figure 1. When $CaO/SiO_2=1.0$, the lower limit shift to higher wave numbers, but in case of $CaO/SiO_2=1.3$, it doesn't shift to anywhere before alumina reaches 12.4 mol pct. and after more addition of alumina up to 19.6 mol pct., it inclines toward lower wave numbers. This indicates an increase in bond length between bonded atoms that is a decrease in binding energy, and *vice versa*. This is based on the following Badger's rule (Equations 1, 2) [2, 3]

$$k^{-1/3} = a_{ij}(D_e - b_{ij}) \tag{1}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{or} \quad \tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \tag{2}$$

where k is the force constant for the vibration, D_e is the equilibrium bond length, and a_{ij} and b_{ij} are constants determined by the nature of the bonded atoms. Also,ν, $\tilde{\nu}$, μ, and c are, respectively, the frequency, wave number, reduced mass ($= m_1 \cdot m_2/(m_1 + m_2)$), m_1, and m_2 are the masses of the two nuclei in a diatomic molecules or ions), and the velocity of light (3×10^8 m/s).



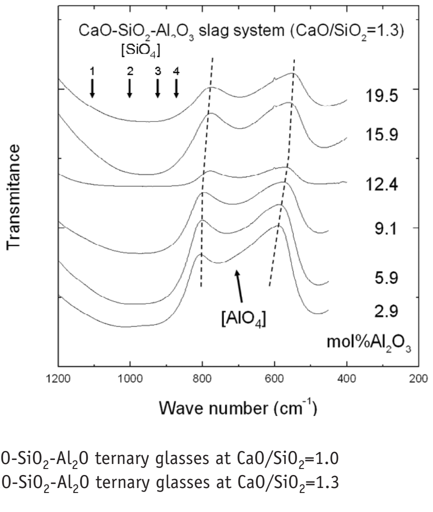


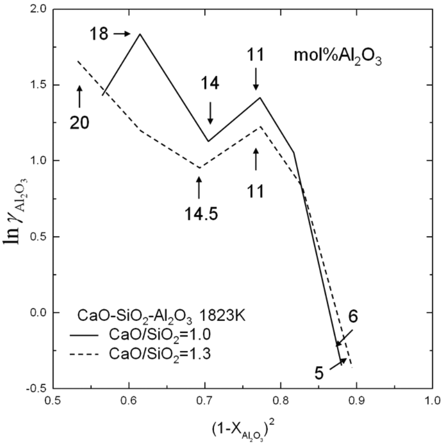
Figure 2(L): FT-IR transmittance of $CaO-SiO_2-Al_2O$ ternary glasses at $CaO/SiO_2=1.0$
Figure 3(R): FT-IR transmittance of $CaO-SiO_2-Al_2O$ ternary glasses at $CaO/SiO_2=1.3$

Second, the small band at about 800 to 550 cm^{-1}, of which the center is approximately 750 cm^{-1}, corresponds to $[AlO_4]$-tetrahedra [2, 3, 8, 9], *viz*. network forming units, and the center of this band incline toward low wave numbers (750 to 700 cm^{-1}) as increasing the concentration of alumina from 2.9 to 9.1 mole pct. and then does not show remarkable changes at alumina concentrations greater than 12.4. The width of this band is getting wider as increasing alumina concentration, especially, lower limit of this band shift to lower wave numbers (590 to 550 cm^{-1}).

Darken proposed that the thermodynamic behavior of solutions can be uniquely described by the second derivative of excess free energy with respect to the mole fraction of component, which is defined as an excess stability, as given in Equation 3 [23]

$$\psi_i^{xs} = -2RT\frac{d\ln\gamma_i}{d(1-X_i)^2} \tag{3}$$

where γ_i and X_i are the activity coefficient and the mole fraction of component *i*, respectively. The excess stability (ψ_i^{xs}), of course, is the property of the system rather than of a component in binary solution.[23] However, because we treat the $CaO\text{-}SiO_2\text{-}Al_2O_3$ ternary solution in the present study, the subscript i was used in Equation 3, and the *excess stability of alumina* could be defined. The activity coefficient of alumina, $\ln\gamma_{Al_2O_3}$ at 1823 K is calculated and described in Figure 4a. Here, the activity value at 1823 K was obtained from the measured data at 1873 K by Ohta and Suito based on the regular solution assumptions.[14] From the changes of $\gamma_{Al_2O_3}$, the excess stability of alumina can be deduced, as shown in Figure 4b, as a function of the concentration of alumina.



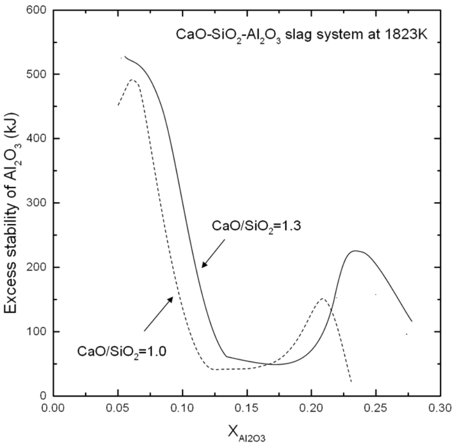


Figure 4a (L) : Dependence of activity coefficient of alumina in ternary melt at 1823 K
Figure 4b (R) : Changes of excess stability of alumina in ternary melt at 1823 K

It is particularly noteworthy that the peaks occurs at the composition of = 0.05 and 0.2 at CaO/SiO_2=1.0 and = 0.05 and 0.25 at CaO/SiO_2=1.3. Actually, It is well known that Darken's excess stability shows the critical peak at the phase boundary. In present slags system, the pahse boundary between wollastonite and gehlenite ($\gamma_{Al_2O_3}$= 0.05), gehlenite and corundum ($\gamma_{Al_2O_3}$ = 0.2 and 0.25) are close to the phase boundary which is shown in the pahse diagram [27]. The physical meanings of these peaks, however, should be studied more.

CaO-SiO2-Al2O3-MgO Quaternary System

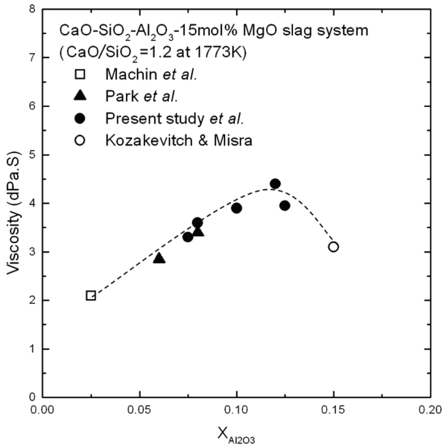


Figure 5: Viscosity of the CaO-SiO$_2$-Al$_2$O$_3$-MgO melt at 1773 K as a function of mole of Al$_2$O$_3$

The viscosity of CaO-SiO$_2$-Al$_2$O$_3$-MgO quaternary melt at 1773 K is shown in Figures 5 as a function of alumina concentration. The measured data available in the literature are compared through the wide composition range [25, 26]. The viscosity of the CaO-SiO$_2$-Al$_2$O$_3$ slags generally decreases by addition of 15 mol pct. of MgO because both of Mg^{2+} and O^{2-}ion act as network modifier such as CaO. The maximum value of viscosity is observed in the vicinity of 12 mole pct. of alumina, indicating that alumina behaves as a network forming element at less than about 12 mole pct by the incorporation of [AlO$_4$]-tetrahedral units into the silicate network with the charge compensation by Ca^{2+} cations. Alumina, however, decreases the network formability or degree of polymerization at higher than 12 mole pct. A different tendency from Figure 1 is shown in Figure 5. A High viscous region in 5.9 to 12.9 mol pct. of alumina is disappeared and the maximum peak is moved forward 12 mol pct. of alumina.

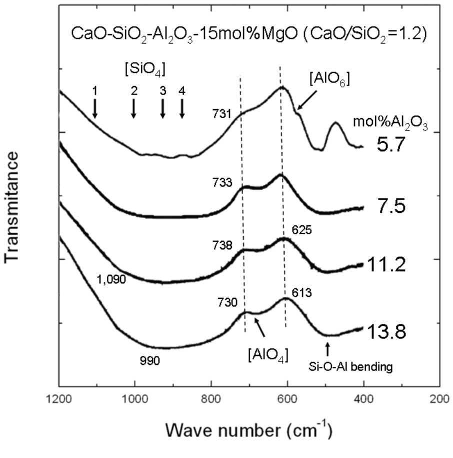


Figure 6: FT-IR transmittance of the CaO-SiO$_2$-Al$_2$O$_3$-15 mol pct. MgO glasses

The FT-IR transmittance of the present glass system is shown in Figure 6 as a function of wave numbers and alumina concentration and the previous result for the 5.7 mole pct

Al_2O_3 system is compared [8, 9]. As the $CaO-SiO_2-Al_2O_3$ ternary glass system, a remarkable peak is separated three kinds of group. One is $[SiO_4]$-tetrahedra broadband peak (about 1220 to 750 cm^{-1}), second is $[AlO_4]$-tetrahedra broadband peak (about 740 to 610 cm^{-1}) and the last is $[AlO_6]$-octahedra peak at about 590 cm^{-1}. The width of $[SiO_4]$-tetrahedra broadband is wider than that of the $CaO-SiO_2-Al_2O_3$ ternary system due to Mg^{2+} and O^{2-} from addition of MgO. The O^{2-} ion increase basicity of melt and the Mg^{2+} has charge compensation effect so that the network composed by $[SiO_4]$-tetrahedra would be modified more than in ternary system.

The intensity of $[AlO_4]$-tetrahedra increases by increasing the concentration of alumina from 5.7 to 7.5 mole pct. This band shifts to lower wave numbers (625 to 613 cm^{-1}) at alumina concentrations greater than about 11.2 mole pct.

The band for $[AlO_6]$-octahedra, network modifying units, at about 590 cm^{-1} disappears at alumina concentrations greater than 5.7 mole pct. [2, 3, 8, 9] Based on the preceding findings, we can propose that the degree of polymerization of silicate glasses increases by addition of alumina to about 11.2 mole pct due to the incorporation of alumina to the silicate tetrahedral network. The structure, however, becomes slightly modified, that is, an increase in bond length between silicon and oxygen, and aluminum and oxygen atoms in $[SiO_4]$- and $[AlO_4]$-tetrahedra by further addition of alumina. [2, 3] This tendency is well accorded with the behavior of viscosity changes.

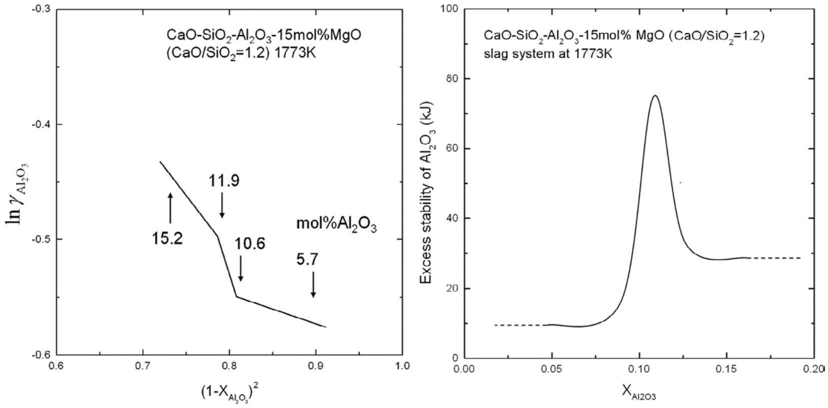


Figure 7a (L): Dependence of activity coefficient of alumina in quaternary melt at 1773 K
Figure 7b (R): Changes of excess stability of alumina in quaternary melt at 1773 K

Both of activity coefficient changes and Darken's excess stability are calculated in the same manner of ternary system and described in Figure 7a and 7b, respectively. The maximum peak is shown at 12 mole pct. of alumina and this shows good agreement with the viscosity changes in Figure 5. There is no specific compound at this composition such as ternary system, but at this composition, it could be found that the primary phase boundary between melilite and spinel in phase diagram. Qualitatively, this signifies that the structural and thermodynamic characteristics of the aluminosilicate melt abruptly changes at this composition, as given in Figures 1 through 7.

CONCLUSIONS

In summary, the results obtained in this study show that the alumina behaves as an amphoteric oxide in the both of $CaO-SiO_2-Al_2O_3$ ternary and $CaO-SiO_2-Al_2O_3-MgO$

quaternary melts, and this is not only experimentally confirmed by measuring viscosity and FT-IR spectra but also thermodynamically proved by taking the excess stability function into account. Further studies are needed to describe the thermophysical properties of aluminosilicate melts in terms of thermodynamic function by extending the present approach using the excess stability of the components to wider composition ranges and systems.

REFERENCES

Sukenaga, S., Saito, N., Kawakami, K. & Nakashima, K. (2006). *Viscosities of* CaO-SiO_2-Al_2O_3-(R_2O *or RO) Melts.* ISIJ Int., Vol. 46(3), pp. 375-384. [1]

Park, J. H. & Min D. J. (2004). *Effect of Fluorspar and Alumina on the Viscous Flow of Calcium Silicate Melts Containing MgO.* J. Non-Cryst. Solids, Vol. 337, pp. 150-156. [2]

Park, J. H., Min, D. J. & Song, H. S. (2004). *Amphoteric Behavior of Alumina in Viscous Flow and Structure of* CaO-SiO_2 (-MgO)-Al_2O_3 *Slags* Metall. Mater. Trans. B, Vol. 35B, pp. 269-275. [3]

Nakamoto, M., Tanaka, T., Lee, J. & Usui, T. (2004). *Evaluation of Viscosity of Molten* SiO_2-CaO-MgO-Al_2O_3 *Slags in Blast Furnace Operation.* ISIJ Int., Vol. 44(12), pp. 2115-2119. [4]

Mysen, B. O. & Toplis, M. J. (2007). *Structural Behavior of* Al^{3+} *in Peralkaline, Metaluminous, and Peraluminous Silicate Melts and Glasses at Ambient Pressure.* Am. Mineral., Vol. 92, pp. 933-946. [5]

Neuville, D. R., Cormier L., & Massiot, D. (2006). *Al Coordination and Speciation in Calcium Aluminosilicate Glasses: Effects of Composition Determined by* ^{27}Al *MQ-MAS NMR and Raman Spectroscopy.* Chem. Geol., Vol. 229, pp. 173-185. [6]

Malmberg, D., Björkvall, J., Malm, J. & Baath, L. (2005). *Preliminary Microwave Measurements on Liquid Slags*. Ironmaking Steelmaking, Vol. 32, pp. 61-67. [7]

Park, J. H., Min, D.J. & Song, H. S. (2002). *Structural Investigation of* $CaO–Al_2O_3$ *and* $CaO–Al_2O_3–CaF_2$ *Slags via Fourier Transform Infrared Spectra.* ISIJ Int., Vol. 42, pp. 38-43. [8]

Park, J. H., Min, D. J. & Song, H. S. (2002). *FT-IR Spectroscopic Study on Structure of* CaO-SiO_2 *and* CaO-SiO_2-CaF_2 *Slags*. ISIJ Int., Vol. 42, pp. 344-51. [9]

Beckett, J. R. (2002). *Role of Basicity and Tetrahedral Speciation in Controlling the Thermodynamic Properties of Silicate Liquids, Part 1: the System* CaO-MgO-Al_2O_3-SiO_2, Geochim. Cosmochim. Acta, Vol. 66, pp. 93-107. [10]

Turkdogan, E. T. (2001). *Critical Assessment of Activity Coefficients of Oxides in Molten Binary and Ternary Silicates.* Steel Res., Vol. 72, pp. 182-191. [11]

Björkvall, J., Sichen, D. & Seetharaman, S. (2001). *Thermodynamic Model Calculations in Multicomponent Liquid Silicate Systems.* Ironmaking Steelmaking, Vol. 28, pp. 250-57. [12]

Kume, K., Morita, K., Miki, T. & Sano, N. (2000). *Activity Measurement of* $CaO–SiO_2–AlO_{1.5}–MgO$ *Slags Equilibrated with Molten Silicon Alloys.* ISIJ Int., Vol. 40(6), pp. 561-566. [13]

Ohta, H. & Suito, H. (1998). *Activities of* SiO_2 *and* Al_2O_3 *and Activity Coefficients of* Fe_tO *and MnO in* CaO-SiO_2-Al_2O_3-MgO *Slags.* Metall. Mater. Trans. B, Vol. 29B, pp. 119-129. [14]

Lee, S. K. & Stebbins, J. F. (2006). *Disorder and the Extent of Polymerization in Calcium Silicate and Aluminosilicate Glasses: O-17 NMR Results and Quantum Chemical Molecular Orbital Calculations.* Geochim. Cosmochim. Acta, Vol. 70, pp. 4275-4286. [15]

Kang, Y. & Morita, K. (2006). *Thermal Conductivity of the* CaO-Al_2O_3- SiO_2 *System*. ISIJ Int. Vol. 46(3), pp. 420-426. [16]

Sasaki, Y. & Ishii, K. (2002). *Structures of Molten Silicate and Aluminosilicate Slag*. Tetsu-to-Hagane, Vol. 88(8), pp. 419-429. [17]

Yagi, T., Susa, M. & Nagata, K. (2001). *Ionic Character of Oxygen and its Local Structure in Silicate Glasses Containing Alumina*. Phys. Chem. Glasses, Vol. 42(4/5), pp. 287-291. [18]

Richet, P., Robie, R. A. & Hemingway, B. S. (1993). *Entropy and Structure of Silicate Glasses and Melts*. Geochim. Cosmochim. Acta, Vol. 57, pp. 2751-2766. [19]

Seetharaman, S., Sichen, D. & Ji, F. Z. (2000). *Estimation of Viscosities of Ternary Silicate Melts Using the Excess Gibbs Energy of Mixing*. Metall. Mater. Trans. B 31B, pp. 105–109. [20]

Aune, R. E., Hayashi, M. & Sridhar, S. (2005). *Thermodynamic Approach to Physical Properties of Silicate Melts*. Ironmaking Steelmaking, 2005, Vol. 32, pp. 141-150. [21]

Lee, S. K. (2005). *Microscopic Origins of Macroscopic Properties of Silicate Melts and Glasses at Ambient and High Pressure: Implications for Melt Generation and Dynamics*. Geochim. Cosmochim. Acta, Vol. 69, pp. 3695–3710. [22]

Darken, L. S. (1967). *Thermodynamics of Binary Metallic Solution*. Trans. TMS-AIME, Vol. 239, pp. 80-89. [23]

Park, J. H., Min, D. J. & Song, H. S. (2002). *The Effect of* CaF_2 *on the Viscosities and Structures of* CaO-SiO_2(-MgO)-CaF_2 *Slags*. Metall. Mater. Trans. B, Vol. 33B, pp. 723-729. [24]

Machin, J. S., Yee, T. B. & Hanna, D. L. (1952). *Viscosity Studies of the System* CaO-MgO-Al_2O_3-SiO_2*, III. 35, 45, and 50%* SiO_2. J. Am. Ceram. Soc., Vol. 35, pp. 322-325. [25]

Kozakevitch, P. (1954). *Viscosity of Blast-furnace Slags*. Rev. Metall., Vol. 57, pp. 149-160. [26]

Kowalski, M., Spencer, P. J. & Neuschutz, D. (1995). Slag Atlas, 2nd ed., Verlag Stahleisen GmbH, Dusseldorf, pp. 99-180. [27]

Zhilo, N. L, Dosov, O. B. & Pershina, R. F. (1987). *Effect of Barum Oxide on the Physicochemical Properties of Slag of The* CaO-Al_2O_3- SiO_2 *System,* Rasplavy, Vol. 1(1), pp. 86-91. [28]