Viscous Behavior of Alumina Rich Calcium-Silicate Based Mold Fluxes and Its Correlation to the Melt Structure

Gi-Hyun KIM, Chang-Soo KIM, Il SOHN
2) Materials Science and Engineering, University of Wisconsin-Milwaukee, 3202 North Maryland Avenue Milwaukee, WI 53202, USA.

(Received on July 11, 2012; accepted on September 25, 2012)

The substitutional effect of SiO2 with Al2O3 content on the viscosity in the calcium-silicate melt-based system containing 12 mass% Na2O and 5 mass% Li2O was studied. Additions of Al2O3 increased the viscosity and higher Al2O3 concentrations modified the dominant silicate network into complex alumino-silicates with the aluminate structure becoming particularly prevalent at an Al2O3 content of 20 mass% and higher. FTIR (Fourier transform infrared) and Raman analysis showed increased amounts of symmetric Al–O0 and Si–O–Al stretching vibrations with higher Al2O3. Compared to the effect of Al2O3, structural changes and the viscosity with higher CaO/(SiO2+Al2O3) were not as significant. However, the symmetric Al–O0 stretching and the Si–O–Al in the [AlO4]5–-tetrahedral units seems to decrease with increased apparent basicity. The apparent activation energy for viscous flow increased with higher Al2O3 due to the increased polymerization of the melt and varied from 129 to 156 kJ/mol.

KEY WORDS: Al2O3; CaO/(SiO2+Al2O3); viscosity; FTIR; Raman; alumino-silicate structures.

1. Introduction

As global energy consumption continue to define new peaks and consumer appetite for goods increase in the developing countries, research in energy conservation and efficiency has driven development on ultra-lightweight steel products. Steels robust mechanical behavior and low costs makes it an attractive material for structural applications including construction, consumer appliances, transportation, and various support vessels. In particular, automotive applications of steels have been at the forefront of steel research. To decrease the weight to strength ratio of steels while maintaining the cost-advantage of steels, there have been enormous efforts in developing steel products containing significant amounts of Al and Mn to enhance not only the strength and formability of steels, but to decrease the overall weight.1,2) Although many of the alloying compositions of these new grades of steel are well-known and proven industrial processing exists, there are still significant issues in the continuous casting of high Al-containing steels due to the reaction of the steels with the silica-based mold fluxes and the subsequent decrease in the physical properties of the molten fluxes.3,4) Thermodynamic driving forces of reducing SiO2 with Al that comprise the majority of the mold flux result in significant chemistry changes of the initial calcium-silicate flux to a calcium-aluminate flux. According to previously published results by the authors,4) the substitution of SiO2 with Al2O3 in the flux chemistry can result in significant increase in the viscosity reducing lubrication between the partially solidified shell and the copper mold and if severe ultimately result in a caster breakout. Thus, understanding and controlling the viscous behavior of the molten flux as a function of the chemical composition can provide fundamental data to design optimum fluxes for high Al-containing steels.

Recent studies on the viscous behavior of mold flux based slag systems and the structural relationship with viscosity has been performed by the present authors and several others.3–7) The general consensus of these studies indicate that highly structured complex silicate, alumino-silicate, and aluminate structures are prevalent at high viscosity and decreasing the viscosity is essentially related to de-polymerizing the bridged-oxygen (O5) network bonds. It has been shown that these complex silicate and aluminate structures provide the bulk of the viscous forces of the molten slag. Using various spectroscopic techniques such as FTIR (Fourier transform infrared), Raman, XPS (X-ray photoelectron spectroscopy), and NMR (nuclear magnetic resonance), the structural units of the molten slag can be elucidated. Deconvolution of the various spectra provides a semi-quantitative analysis of the various structural species and the complexity of the structure as various chemical constituents in the slag changes. When both silicate and aluminate structures are present, certain chemical species such as alkali oxides of Na2O or Li2O can interact at preferred sites of aluminates than silicates due to its mono-valency, described as the ionic compensation effect.8,9) Di-valent alkali earth oxides such as CaO and MgO tend to affect both the silicate and aluminate structures, but may also have a preference depending upon the electronegative state of the dominant network structures.10,11)

In this study, the effect of SiO2 substitution with Al2O3 on
the viscosity in the CaO–SiO₂–Al₂O₃–Na₂O–Li₂O slag system at fixed CaO/(SiO₂+Al₂O₃) mass ratio of 0.8 with 12 mass% Na₂O and 5 mass% Li₂O was investigated. In addition, the effect of CaO/(SiO₂+Al₂O₃) on the viscosity at a fixed Al₂O₃ of 30 mass% and Li₂O of 5 mass% was also studied. The slag structure and its relationship with the viscosity is also presented by using a combination of FTIR and Raman spectroscopy on as-quenched melts from 1773 K.

2. Materials and Procedures

2.1. Sample Preparation and Experimental Method

According to published work on silica-based mold flux compositions for high Al-containing steels, the typical chemical composition can be approximated as shown in Table 1. Considering the major constituents of the mold flux is calcium-silicate based with Na₂O, CaF₂, and Li₂O, which can react with the Al in the steels to form calcium-aluminate based fluxes, the present work focuses on the substitutional effect of SiO₂ with Al₂O₃ at a fixed extended basicity of CaO/(SiO₂+Al₂O₃) mass ratio at 0.8. Reagent grade chemicals of CaO, SiO₂, Al₂O₃, Na₂CO₃, and Li₂O were used to prepare the samples. Furthermore, since the role of CaF₂ is to create cuspidine (3CaO·2SiO₂·CaF₂) phases for scattering the radiative heat across the mold flux film and lower the total heat transfer from the partially solidified shell, low amounts of SiO₂ will inhibit the formation of cuspidine and CaF₂ is likely to become unnecessary. Thus, the present study focuses on the fluorine free high alumina containing CaO–SiO₂–Al₂O₃–Na₂O–Li₂O slag system. The CaO/(SiO₂+Al₂O₃) was varied between 0.8 to 1.2.

The chemical constituents were placed in a Pt-10 mass% Rh crucible and pre-melted at 1773 K with an Ar flow of 0.4 lpm for approximately 5 h to calcinate the carbonates and obtain homogeneous master slags for subsequent viscosity measurements. The post-experimental chemical composition of the melts was analyzed using XRF (X-ray fluorescence) spectroscopy (S4 Explorer; Bruker AXS GmbH, Karlsruhe, Germany) and ICP-OES (induction coupled plasma-optical emission spectroscopy; 700 Series, Agilent Technologies, Santa Clara CA, USA) was especially used to determine the LiO₂ content in the slag, as shown in Table 2.

100 g of the master slag sample was placed in a beaker-type Pt-10 mass% Rh crucible and inserted into the hot zone of a vertical resistance furnace held at 1273 K under an Ar atmosphere of 0.4 lpm. The temperature was increased to 1773 K and held for 1 h to obtain thermal equilibrium of the melt. The viscosity was then measured using a standard rotating Pt-10 mass% Rh spindle connected to a Brookfield rheometer (model LVDV-II+; Brookfield Engineering Laboratories, Middleboro, MA). The rheometer was calibrated with several reference silicone oils (0.485, 0.96, 4.85, 9.75, and 50.4 dPa·s) at room temperature (293 K) before each experiment. A schematic of the experimental apparatus is provided in Fig. 1. To determine the temperature dependency of the slags, the temperature of the furnace was decreased in 25 K increments at a rate of 5 K/min and each measurement at the target temperature was taken after holding for 25 min to ensure thermal equilibrium of the sample was obtained. All viscosity measurements were taken well above the break temperature of the slag, where the slag exists in the fully liquid region.

2.2. FTIR and Raman Spectroscopy

To identify the slag structure at high temperatures and the compositional effects on the structure, the melts were
removed from the furnace at 1 773 K and quenched in liquid N₂. The amorphous glassy slags were analyzed using FTIR spectroscopy (Spectra100; Perkin-Elmer, Shelton, CT) and Raman spectroscopy (RD-PSH300; Photo Design, Japan). Separate preliminary experiments of the as-quenched slag samples showed XRD patterns with no characteristic peaks indicating the samples to be amorphous. The wavenumber range of the FTIR transmission spectra were between 4 000 to 400 cm⁻¹.

Using a 514 nm laser, the Raman spectra was fitted using a non-parametric baseline fitting routine and deconvoluted using the PeakFit V4 (AISN software Inc., U.K.) program. The results of the FTIR and Raman complement one another since the cation-anion bondings maybe IR active, Raman active, or both depending on the composition of the slag as obtained in previous published works.³⁻⁵

3. Results and Discussion

3.1. Substitutional Effect of SiO₂ with Al₂O₃ on the Viscous Behavior

Considering the mold flux chemistry changes from a silica rich to an alumina rich composition for high Al-containing steels, viscosity of the CaO–SiO₂–Al₂O₃–12 mass% Na₂O–5 mass% Li₂O slag system were measured as SiO₂ is substituted with Al₂O₃ at a fixed CaO/(SiO₂+Al₂O₃) of 0.8. Figure 2 shows higher concentrations of Al₂O₃ results in higher viscosity and was more pronounced at lower temperatures. In the present slag system containing highly basic oxides of more than 50 mass% including CaO, 12 mass% Na₂O, and 5 mass% Li₂O, the amphoteric oxide of Al₂O₃ is likely to behave as a network forming acidic oxide similar to SiO₂. Thus, Al₂O₃ additions polymerize the slag structure subsequently increasing the viscosity, which has also been observed in simpler ternary CaO–SiO₂–Al₂O₃ systems by Machin et al.¹⁵ and others.¹⁶,¹⁷ According to previous work on Li₂O-free high aluminate slags containing 12 mass% CaF₂,⁴ this increase in the viscosity was due to the increase in the larger aluminosilicate and complex aluminate structural units available as the Al₂O₃ concentrations increased. It was also observed that a critical concentration of 20 mass% Al₂O₃ changes the dominant network structural units from a silicate to an aluminate.

The effect of Al₂O₃ additions and polymerization of the network structures is particularly prevalent at lower temperatures, where the thermal energy for the dissociation of bonds is not as large compared to higher temperatures and thus larger complex structural units can exist near the liquidus temperature of the melt. The effect of the amount of superheat on the slag structure in the fully liquid region has previously been presented by Kim and Sohn⁵ using structural data obtained from FTIR analysis. At temperatures of 1 598 K and below, there seems to be an inflexion point at approximately 20 mass% Al₂O₃, similar to the results obtained in the CaO–SiO₂–12 mass% Na₂O–12 mass% CaF₂ slag system.⁴ The slope of the viscosity increments with Al₂O₃ is significantly higher. This inflexion point seems to correlate to the transition of a [SiO₄]⁴⁻ silicate dominant network structure to an [Al₂O₆]⁴⁻ aluminate dominant network structure, which was later indirectly verified from Raman analysis of the slag structure.

3.2. Effect of CaO/(SiO₂+Al₂O₃) on Viscous Behavior

Figure 3 shows the effect of the extended basicity ((CaO)/(SiO₂+Al₂O₃)) on the viscosity at various temperatures from 1 773 K to 1 623 K in the present slag system. Higher CaO/(SiO₂+Al₂O₃) resulted in lower viscosity due to the availability of free oxygen ions (O²⁻) with higher CaO content and its subsequent interaction with the bridged oxygen (O₀) within the complex silicate and aluminate structures depolymerizing the slag and lowering the viscosity. The decreasing trend was comparable to the CaF₂ containing flux at 1 773 K.⁴ Although the slag at an extended basicity of 1.2 at 1 773 K was fully liquid, partially solid phases were observed at temperatures from 1 748 K and below. However, measurements in the fully liquid region for temperatures 1 748 K and below generally showed similar decreasing trends when the extended basicity was increased from 0.8 to 1.0. Other slag systems including ironmaking type slags with 17 mass% Al₂O₃, 10 mass% MgO, and 5 mass% TiO₂ also showed a decrease in the viscosity with higher basicity.¹⁸ Subtle differences on the extent of the decrease in the viscosity with CaO/(SiO₂+Al₂O₃) can exist depending upon the amount of existing complex silicate and
aluminate structures within the slag, but the overall trend seems to indicate a depolymerizing effect with higher CaO/(SiO$_2$+Al$_2$O$_3$).

### 3.3. Structural Analysis of Slags Using FTIR and Raman Spectroscopy

Using FTIR and Raman spectroscopy, the characteristic vibration frequencies of silicate and aluminate structures can be identified. Depending on the network structure of the slag, the various symmetric and asymmetric stretching vibrations and bending vibrations can be IR and/or Raman active. NBO/Si in the [SiO$_4$]$^4-$tetrahedral symmetric stretching region existing between 1 200 to 800 cm$^{-1}$ is the non-bridged oxygen per silicon atom within the unit structure of particular interest with silica containing melts. As the unit structures polymerize into more complex networks, the NBO/Si decreases. Thus, a slag structure having an increase of NBO/Si=1 or NBO/Si=2 and a decrease of the NBO/Si=3 or NBO/Si=4 with additions of acidic oxide components such as SiO$_2$ or Al$_2$O$_3$ suggests polymerization occurring within the slag structure, which subsequently result in higher viscosities.

The strong peaks of [AlO$_4$]$^5-$symmetric and -asymmetric stretching vibrations suggest highly polymerized structures of complex aluminates within the slag melts. In addition, the Al–O and Al–O found in the Raman spectra are typically observed for high alumina containing slags, where the [AlO$_4$]$^5-$tetrahedral stretching is highly polymerized resulting in increased viscosity.

Figure 4 shows the effect of Al$_2$O$_3$ on the slag structure using FTIR analysis of as-quenched CaO-SiO$_2$-Al$_2$O$_3$-Na$_2$O-Li$_2$O slag samples at fixed CaO/(SiO$_2$+Al$_2$O$_3$) of 0.8. The characteristic transmittance troughs for the FTIR spectra of the various structural units were determined from established literature shown in Table 3. It is clearly evident that with higher Al$_2$O$_3$ concentrations the [SiO$_4$]$^4-$tetrahedral symmetric stretching vibration troughs existing between 1 200–800 cm$^{-1}$ becomes less pronounced and the [AlO$_4$]$^5-$symmetric stretching bands near 780 cm$^{-1}$ become highly pronounced. At Al$_2$O$_3$ additions of 30 mass%, the silicate structure almost disappears and a separate [AlO$_4$]$^5-$symmetric stretching trough becomes deeper and broader. This indicates that the dominant slag structure is changed from a silicate to the aluminate structure near 30 mass% Al$_2$O$_3$ and likely at intermediate concentrations of Al$_2$O$_3$ of 10 and 20 mass%, the silicate and alumino-silicate structure is dominant. The Si–O–Si rocking bands near 500 cm$^{-1}$ also becomes less pronounced with higher Al$_2$O$_3$ due to a decrease in the absolute amount of SiO$_2$ in the slag. It should be noted that the characteristic vibrations for the Si–O–Si rocking bands are more IR than Raman active and the Si–O–Si rocking bands in the Raman spectra is not pronounced. For the present slag system, the trough near 500 cm$^{-1}$ of the FTIR spectra can be qualitatively identified by either the Si–

![Figure 4](image_url)

**Figure 4.** FTIR spectra of as-quenched samples with varying Al$_2$O$_3$ concentration in the CaO–SiO$_2$–Al$_2$O$_3$–12 mass% Na$_2$O–5 mass% Li$_2$O system at CaO/(SiO$_2$+Al$_2$O$_3$)=0.8.

![Figure 5](image_url)

**Figure 5.** FTIR spectra of as-quenched samples with varying CaO/(SiO$_2$+Al$_2$O$_3$) in the CaO–SiO$_2$–30 mass% Al$_2$O$_3$–12 mass% Na$_2$O–5 mass% Li$_2$O system.

<table>
<thead>
<tr>
<th>'x' mass% Al$_2$O$_3$</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>30</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basicity C/(S+A)</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>Raman shift (cm$^{-1}$)</td>
<td>536</td>
<td>539</td>
<td>543</td>
<td>544</td>
<td>544</td>
</tr>
<tr>
<td>-</td>
<td>684</td>
<td>665</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>791</td>
<td>778</td>
<td>770</td>
<td>772</td>
<td>-</td>
</tr>
<tr>
<td>839</td>
<td>837</td>
<td>837</td>
<td>835</td>
<td>837</td>
<td>837</td>
</tr>
<tr>
<td>884</td>
<td>867</td>
<td>872</td>
<td>863</td>
<td>869</td>
<td>-</td>
</tr>
<tr>
<td>939</td>
<td>899</td>
<td>910</td>
<td>912</td>
<td>938</td>
<td>938</td>
</tr>
<tr>
<td>1014</td>
<td>964</td>
<td>956</td>
<td>968</td>
<td>983</td>
<td>983</td>
</tr>
<tr>
<td>-</td>
<td>1080</td>
<td>1083</td>
<td>1082</td>
<td>1079</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 3.** Peak analysis of Raman in the CaO–SiO$_2$–Al$_2$O$_3$–12 mass% Na$_2$O–5 mass% Li$_2$O system at 1 773 K using established references.

<table>
<thead>
<tr>
<th>Raman bands</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bending Si–O$^8$ vibration of [SiO$_4$]$^4-$ (NBO/Si=2)</td>
<td>24–25</td>
</tr>
<tr>
<td>Symmetric stretching Al–O$^8$ vibration of [AlO$_4$]$^5-$</td>
<td>28–29</td>
</tr>
<tr>
<td>Stretching Si–O–Al vibration</td>
<td>29–30</td>
</tr>
<tr>
<td>Symmetric stretching Si–O$^8$ of [SiO$_4$]$^4-$ (NBO/Si=4)</td>
<td>24–25</td>
</tr>
<tr>
<td>Symmetric stretching Si–O$^8$ of [SiO$_4$]$^4-$ (NBO/Si=3)</td>
<td>24–26</td>
</tr>
<tr>
<td>Symmetric stretching Si–O$^8$ of [SiO$_4$]$^4-$ (NBO/Si=2)</td>
<td>19, 23–26</td>
</tr>
<tr>
<td>Symmetric stretching Si–O$^8$ of [SiO$_4$]$^4-$ (NBO/Si=1)</td>
<td>19, 23, 27</td>
</tr>
</tbody>
</table>
O–Si rocking or the Si–O–Al bending vibrations.\textsuperscript{9,10} However, considering the depth of the trough of the FTIR spectra near 500 cm\(^{-1}\) decreases with higher Al\(_2\)O\(_3\) and the peak of the Si–O–Al stretching in the Raman spectra increases with higher Al\(_2\)O\(_3\) later described in Fig. 7, it is reasonable to assume that the FTIR trough near 500 cm\(^{-1}\), which becomes less pronounced with higher Al\(_2\)O\(_3\), is the Si–O–Si rocking bands as the overall amount of SiO\(_2\) in the slag is decreased.

The effect of CaO/(SiO\(_2\)+Al\(_2\)O\(_3\)) on the FTIR analysis of as-quenched slag samples is presented in Fig. 5. An increase in the CaO/(SiO\(_2\)+Al\(_2\)O\(_3\)) seems to decrease the depth of the [SiO\(_4\)]\(^4–\)-tetrahedral symmetric stretching troughs and the [AlO\(_4\)]\(^5–\)-symmetric stretching trough also becomes less pronounced. A similar decrease in the [AlO\(_4\)]\(^5–\)-asymmetric stretching troughs with higher CaO/(SiO\(_2\)+Al\(_2\)O\(_3\)) is also observed. The depth of the Si–O–Si rocking bands decreases with higher CaO/(SiO\(_2\)+Al\(_2\)O\(_3\)). This decrease in the transmittance trough of the network forming silicate and aluminate structures suggest a depolymerization of the slag structure with higher CaO/(SiO\(_2\)+Al\(_2\)O\(_3\)), which can result in lower viscosity as observed from Fig. 3.

The deconvolution of the Raman spectra at various Al\(_2\)O\(_3\) concentrations for specific vibrations of silicate and aluminate structural units is shown in Fig. 6(a). The individual deconvoluted peaks from the overall Raman spectra are typically fitted until an R\(^2\) value greater than 99.9\% is obtained. The characteristic peaks for the Raman spectra of the various structural units were determined from established literature provided in Table 3. The integrated area of the individual deconvoluted peaks provides a semi-quantitative evaluation of the amount of the characteristic structural units available in the melt. The ratio of the integrated area of an individual characteristic structural unit over the sum of the integrated area of all the characteristic structural units provides the fraction of structural units present in the melt. The Raman spectra and its deconvoluted peaks at various CaO/(SiO\(_2\)+Al\(_2\)O\(_3\)) is presented in Fig. 6(b). Similar structural units are used to deconvolute the spectra.

From the integration of the deconvoluted spectra of the various structural unit species, the fraction of the silicate and aluminate structural units as a function of Al\(_2\)O\(_3\) content is presented in Fig. 7. The substitution of SiO\(_2\) with Al\(_2\)O\(_3\) at a fixed CaO/(SiO\(_2\)+Al\(_2\)O\(_3\)) of 0.8 indicates significant decrease in the dominant silicate structural units from NBO/Si=2 to NBO/Si=4 and negligible amounts of NBO/Si=1, which is a direct result of the decrease in the absolute amount of SiO\(_2\) as Al\(_2\)O\(_3\) increases. Contrary to the silicate structural units, the aluminate structural unit of Al–O\(^0\), Al–O\(^–\), and Si–O–Al increase with higher Al\(_2\)O\(_3\) concentrations in the melt as expected, which correlates well with the FTIR results. According to the Raman analysis, the substitutional effect of SiO\(_2\) with Al\(_2\)O\(_3\) suggests the major structural species to be alumino-silicates with some highly complex alumimates (Al–O\(^0\)) to exist and increase with higher Al\(_2\)O\(_3\). There is also a pronounced increase in the alumino-silicate and highly complex Al–O\(^8\) structural units at Al\(_2\)O\(_3\) concentrations of 20 mass\% and higher, which correlate well with the viscosity measurements in Fig. 2 and the results of the
CaO–SiO$_2$–Al$_2$O$_3$–12 mass% Na$_2$O–12 mass% CaF$_2$. Although the present slag system is CaF$_2$ free and contains 5 mass% Li$_2$O, the critical Al$_2$O$_3$ concentration at 20 mass%, where the viscosity and slag structure changes significantly is similar to the CaF$_2$ containing CaO–SiO$_2$–Al$_2$O$_3$–Na$_2$O slag previously mentioned. Thus, a common condition is likely to exist at this particular composition, which is a topic for future endeavors.

Figure 8 shows the fraction of structural units as a function of CaO/(SiO$_2$+Al$_2$O$_3$) obtained from the deconvoluted Raman spectra. In the present CaO–SiO$_2$–30 mass% Al$_2$O$_3$–12 mass% Na$_2$O–5 mass% Li$_2$O slag composition, the slag’s structural network is seen to be alumino-silicate dominant as observed from Fig. 7. As the CaO/(SiO$_2$+Al$_2$O$_3$) increases, there are slight changes in the amount of the complex Si–O–Al and Al–O$^0$ structural units suggesting some depolymerization is occurring. Thus, the changes observed in the viscosity at high aluminate content seem to correlate to the changes observed in the complex structural units of Si–O–Al and Al–O$^0$.

3.4. Temperature Dependence of the Viscosity and the Apparent Activation Energy

From the temperature dependence of the viscosity for the present slag system, the slope of the natural logarithm of the viscosity (ln$\eta$) as a function of the reciprocal temperature (1/T) allows the calculation of the activation energy for viscous flow, which is the resistance of the liquid to shearing.

$$\eta = \eta_0 \exp\left(\frac{E_{\eta}}{RT}\right)$$

where $\eta$ is the viscosity (Pa·s), $E_{\eta}$ is the activation energy for viscous flow (J/mol), $R$ is the ideal gas constant (8.314 J/molK), and $T$ is the absolute temperature (K). Activation energy for viscous flow is plotted in Fig. 9. The linear slope was obtained by the least square method and the activation energy with the standard deviation is provided in Table 4.

The activation energy for the present slag system was between 129 kJ/mol to 226 kJ/mol, which is within expected values compared to other slag systems. Melts with higher viscosity have higher resistance to shear resulting in higher activation energies. Therefore, higher viscosity can typically be correlated to higher activation energies of viscous flow. Higher Al$_2$O$_3$ at fixed CaO/(SiO$_2$+Al$_2$O$_3$) of 0.8 resulted in higher activation energies. In Fig. 10, above 20 mass%
Al<sub>2</sub>O<sub>3</sub>, the activation energy significantly increases, which correlates well with the viscosity measurements and the increment in the slope of the viscosity above 20 mass% Al<sub>2</sub>O<sub>3</sub> observed in Fig. 2. Changes in the activation energy for CaO/(SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>) of 1.2 resulted in abnormally large activation energy of over 226 kJ/mol. Due to the high melting temperatures at high basicity, the temperature dependence experiments of the viscosity at a CaO/(SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>) of 1.2 was limited to a narrow temperature region and thus large errors is likely to have occurred for this particular set of experiments. Considering the comparably negligible changes in the viscosity measurements as a function of CaO/(SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>), the activation energy as a function CaO/(SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>) is likely to be similar and thus near 150 to 160 kJ/mol.

### Acknowledgements

This study was partially supported by the Brain Korea 21 (BK21) Project at the Division of the Humantronics Information Materials and the National Science Foundation of Korea Project No. 2012-80486.

### References