Influence of Li₂O on the Viscous Behavior of CaO–Al₂O₃–12 mass% Na₂O–12 mass% CaF₂ Based Slags

Gi Hyun KIM and Il SOHN

Department of Materials Science and Engineering, Yonsei University, Seoul, 120-749 Korea. E-mail: ilsohn@yonsei.ac.kr

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The viscous behavior of the CaO–Al₂O₃–12 mass%Na₂O–12 mass%CaF₂ based slag system with various concentrations of Li₂O has been studied using the rotating spindle method to understand the effects on the viscosity with these additives. Li₂O additions up to 1 mass% significantly lowered the viscosity by breaking the [AlO₄]-tetrahedral network structure of molten fluxes, but Li₂O concentrations above this level was comparatively less effective in lowering the viscosity. The viscosity was lower at higher temperatures and from an Arrhenius relationship, the activation energy was calculated to be between approximately 180 to 190 kJ/mol. Fourier Transform Infra-Red (FTIR) analysis of as-quenched slag samples showed the characteristic Al–O stretching vibration in the wavenumber of 800 cm⁻¹ and 660 cm⁻¹. Slags with higher viscosity showed a slightly wider trough near the 800 cm⁻¹ and 660 cm–¹ Al–O stretching bands. XPS analysis of slags with various concentrations of Li₂O indicated the fraction of bridged oxygen (O o) decreased and the non-bridged oxygen (O –) increased with higher concentrations of Li₂O. Li₂O additions up to 1 mass% significantly decreased the bridged oxygen fraction, which seem to correlate well with the viscosity measurements.

KEY WORDS: Li₂O; viscosity; [AlO₄]-tetrahedral network; activation energy; FTIR; XPS; Al–O stretching; depolymerization.

1. Introduction

Maintaining sufficient lubrication in the continuous casting mold is essential to obtaining reliable casting operations and preventing breakouts. Recent developments in steel products for automotive applications such as TRIP (TRansformationInducedPlasticity) and TWIP (TWinningInducedPlasticity) steels contain high concentrations of aluminum, which tend to reduce the main component silica (SiO₂) in the mold flux changing the silica based mold flux to an alumina (Al₂O₃) based mold flux. The kinetics of the reduction reaction may depend on the casting conditions, but thermodynamics dictates the eventual modification to an Al₂O₃ saturated calcium-aluminate flux. With higher Al₂O₃ content, the physical properties of the virgin mold flux drastically changes and thus essential properties such as viscosity and heat transfer characteristics also changes. In particular the viscous behavior of the mold flux plays a vital role in providing sufficient lubrication between the mold and preventing breakouts. To ensure that the viscosity is not excessively high, significant amounts of Na₂O, CaF₂, NaF, and Li₂O is used to compensate for higher Al₂O₃.

In recently published work regarding viscosity of CaO–SiO₂–12 mass% Na₂O–CaF₂–Li₂O, the effect of CaF₂ and Li₂O was studied for the silica-based mold flux. Additions of CaF₂ up to approximately 8 mass% lowered the viscosity, but further additions had little effect since excessive CaF₂ could not dissociate in the molten flux. Li₂O showed a similar behavior at approximately 2 mass% additions. The performance, economical costs, and environmental factors associated with mold flux chemistry are considered, the concentrations of fluxing agents such as CaF₂ and Li₂O when designing mold fluxes should be optimized. In addition, as the flux system changes to the calcium-aluminate flux for high aluminum containing steels, the optimization of CaF₂ and Li₂O additions in calcium-aluminate fluxes is essential to developing high performance fluxes for the next generation of high aluminum steels.

Mills revealed in the CaO–Al₂O₃–CaF₂ ternary slag system at 1873 K (1600°C) that Al₂O₃ additions would increase the viscosity and higher CaF₂ concentrations assisted in modifying the slag and lowering the viscosity. Wen et al. and Sukenaga et al. also showed a decrease in the viscosity with increased Li₂O content. In both papers, the cause for this relationship was explained in terms of the network modification of the molten slag by free oxygen ions (O²⁻) supplied by Li₂O. The free oxygen ions reacts with the bridged oxygen (O⁰) depolymerizing the large silicate networks. Yu et al. in a complex slag system including CaO–SiO₂–Al₂O₃–Na₂O–MnO–CaF₂–Li₂O also discussed the effect of Li₂O additions, where Li₂O additions increases the basicity and because Li⁺ cation is small with a low steric hindrance, it was effective in compensating the charges for complex ionic species of Si–O–Al.

In a detailed study on the FTIR spectra of calcium-aluminate based oxide glasses, Huang and Behrman showed pronounced Al–O tetrahedral stretching bands at wavenumbers near 800 cm⁻¹ and the Al³⁺ ions were found.
The influence of Li$_2$O on the viscous behavior of the slag system based on CaO–Al$_2$O$_3$–12 mass%Na$_2$O–12 mass%CaF$_2$ at a CaO/Al$_2$O$_3$ ratio of 0.8 was investigated using a rotating viscometer. To directly correlate the relationship between slag structure and viscosity, flux samples from the fully liquid region at 1773 K (1500°C) were quenched and analyzed using FTIR (Fourier Transform Infra-Red) spectroscopy and XPS (X-ray Photoelectron Spectroscopy).

### 2. Experimental

Reagent grade chemicals of CaO, Al$_2$O$_3$, CaF$_2$, Li$_2$O, and Na$_2$CO$_3$ were used to produce the slag composition according to Table 1. Li$_2$O experimental range from 0 to 4 mass% was selected, which has been a typical compositional range observed for TRIP and TWIP steel commercial mold fluxes. The CaO/Al$_2$O$_3$ mass ratio was fixed at 0.8 and the samples were premelted at 1773 K (1500°C) for 3 hours under 0.4 l/min of high purity Ar (99.999%) in a Pt-10 mass%Rh crucible to decompose the Na$_2$CO$_3$ carbonate and obtain a homogeneous slag sample of CaO–Al$_2$O$_3$–Na$_2$O–CaF$_2$–Li$_2$O. The homogenized samples were quenched and crushed for the primary experiments. The post-experimental chemical compositions of the fluxes were obtained using X-Ray Fluorescence (XRF) spectroscopy (S4 Explorer; Bruker AXS GmbH, Karlsruhe, Germany). There were slight concentration changes in the concentration of Ca from the XRF result, which suggests some fluorine vaporization for some of the experimental conditions under an Ar flow, but no significant changes in Na and Al. Li was measured using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry, Perkin Elmer) and given in Table 1. Some volatilization was observed from the analysis, but was not significant for the particular slag composition. This was similar to the results observed by Yu et al. where Li$_2$O volatilization in the complex CaO–SiO$_2$–Al$_2$O$_3$–Na$_2$O–MnO–CaF$_2$–Li$_2$O slag system was negligible. The pre and post-experimental composition of the sample slags is given in Table 1.

A calibrated Brookfield digital rheometer (model LVDV-II+; Brookfield Engineering Laboratories, Middleboro, MA) with a rotating spindle was used to measure the viscosity. The experimental apparatus is shown in Fig. 1 and the details provided elsewhere. 

120 g of slag was placed in a Pt-10%Rh crucible and the temperature of the furnace was calibrated using a reference B-type thermocouple and controlled within ±3 K using a PID (Proportional Integral Derivative) controller. Slag samples were heated up to 1773 K (1500°C) and thermally equilibrated for 3 600 s under a flow of Ar gas. Viscosity measurements were taken from 1773 K (1500°C) and at 50 K intervals after 1 800 seconds of soaking with a cooling cycle of 5 K/min until the break temperature (T$_{Br}$) of each slag composition. Preliminary experiments were also carried out during the heating cycle of 5 K/min using identical soaking times resulting in almost identical viscosity measurements when thermally equilibrated. The T$_{Br}$ according to Sridhar et al. and Kim et al. is defined as the point where the measured viscosity changes suddenly during the cooling cycle as shown in Fig. 2. Typical T$_{Br}$ are obtained from the intersection of two tangential linear lines when the natural logarithm of viscosity (ln(η)) is plotted against the reciprocal temperature (1/T). One line is the viscosity measurements at the fully liquid region and the other line at lower temperatures is the viscosity measurements at the liquid/solid coexisting region. Thus, viscosity measurements above T$_{Br}$ are assumed to be taken in the fully liquid region of the slag system.

To identify the molten slag structure using FTIR spectros-
copy (Spectra100; Perkin Elmer, Shelton, CT) and XPS (VG Scientific Instrument, ESCALAB 220i-XL), slag samples were reheated to 1 773 K after the viscosity measurements and quenched. The XRD pattern of the as-quenched slag sample is shown in Fig. 3 and indicates a typical pattern for a homogenous amorphous material for FTIR and XPS analysis. The O1s XPS spectra were analyzed by using a twin X-ray source of Al/Mg. The deconvolution of the main O 1s peak was performed by means of SDP (Spectral Data Processor) software provided by XPS international LLC. The peaks were calibrated by the C1s line of carbon assuming the C1s core level to be 285 eV. After subtraction of the background using Shirley’s method, the peaks were fitted using a nonlinear, least squared routine with a mixed Gauss-Lorentz function.

3. Results and Discussion

3.1. Li2O Effect on the Viscosity

Figure 4 shows the effect of Li2O on the viscosity of the slag based on the CaO–Al2O3–12 mass% Na2O–12 mass% CaF2 system at various temperatures and constant CaO/Al2O3 of 0.8. Within the experimental temperature range of 1 673 K to 1 773 K, the viscosity of the slag decreased with additions of Li2O. 1 mass% Li2O significantly lowered the viscosity and further addition of Li2O is comparatively less effective in lowering the viscosity. In recently published work regarding Li2O additions in the calcium-silicate slag systems, the authors observed Li2O to be less effective in lowering the viscosity above 2 mass% due to the absence of large silicate structures within the molten slag, which was confirmed through XPS and FTIR analysis on as-quenched slag samples. The network forming silicate structures were depolymerized into simpler silicate structures of dimers (Si2O76–) and monomers (SiO44–) with Li2O additions, which lowered the viscosity. Since the present slag system do not contain silicates, the alumina will behave as the network former and the calcium-aluminate slag may behave in a similar manner to the calcium-silicate slags. Within the CaO–Al2O3–Na2O–CaF2–Li2O system and depending on the amount of basic oxides available, Al2O3 can act as an acidic oxide providing an [AlO4]tetrahedral network structure. Higher concentrations of Al2O3 will polymerize the network structure increasing the viscosity. On the other hand as basic oxides such as Li2O are added, free oxygen ions (O2–) are supplied by the dissociation of Li2O into Li+ and O2–. The O2– can modify the large aluminate structures into simpler aluminate structures and thus lower the viscosity. This effect on the slag structure is discussed in the next section with the FTIR and the XPS results.

Above 1 mass% Li2O, Li2O becomes less effective in lowering the viscosity. It is likely that much of the large aluminate network structures have already been modified from the 12 mass% Na2O and the 12 mass% CaF2 and although O2– are continuously supplied with further Li2O additions the amount of large aluminate structures for simplification are comparatively less. In addition, due to the ion compensation effect within a calcium-aluminate based slag with Al3+ ions, Li2O can be more effective in modifying the slag structure compared to the calcium-silicate based slags.

3.2. Li2O Effect on the Molten Slag Structure Using FTIR and XPS

The FTIR results of the CaO–Al2O3–12 mass% Na2O–12 mass% CaF2–Li2O slag system are shown in Fig. 5 for various Li2O concentrations. The typical absorption spectra
for calcium aluminate slags are shown in the FTIR plots. At wavenumbers of approximately 800 cm\(^{-1}\) and 660 cm\(^{-1}\), the stretching vibrations of the Al–O bonding in the \([\text{AlO}_4]\)-tetrahedra are shown.\(^{10}\) There is also the bending vibration of the Al–O–Al bonds at the wavenumber of 450 cm\(^{-1}\).\(^{10}\) These characteristic absorption spectra for the calcium-aluminate type amorphous materials have been studied in great depth for fiber optic applications.\(^{11–13}\) Results of the present study show that the FTIR spectra for the 2 and 4 mass% \(\text{Li}_2\text{O}\) are similar, which suggests the melt structure for these particular samples to be comparable. Thus, if we assume that the viscosity of slags corresponds to the slag structure, the viscous behavior of the 2 and 4 mass% \(\text{Li}_2\text{O}\) samples should also be similar, which was verified in Fig. 4.

For the stretching vibrations of Al–O tetrahedral at 800 cm\(^{-1}\), the trough at the adsorption spectra for 1 mass% \(\text{Li}_2\text{O}\) was slightly wider than the trough for the 2 and 4 mass% \(\text{Li}_2\text{O}\). A wider trough indicates a more structured aluminate tetrahedral network. The weak adsorption peak near 660 cm\(^{-1}\) showed a slightly flatter plateau in Fig. 5 with lower \(\text{Li}_2\text{O}\) suggesting a more complex aluminate network when \(\text{Li}_2\text{O}\) is decreased. These FTIR results are consistent with the viscosity measurements, where significant viscosity changes were observed when 1 mass% \(\text{Li}_2\text{O}\) was added, but beyond 2 mass% the effect was less significant. Figure 6 shows the difference in transmittance spectra (\(\Delta\text{Transmittance}\)) when the FTIR spectra of the CaO–Al\(_2\)O\(_3\)–12 mass\% Na\(_2\)O–12 mass\% CaF\(_2\) were taken as the base and subtracted from the results of the FTIR spectra of slags with \(\text{Li}_2\text{O}\) added. The \(\Delta\text{Transmittance}\) is shown against the baseline. Figure 6 shows more clearly the similarity between 2 mass% \(\text{Li}_2\text{O}\) and 4 mass% \(\text{Li}_2\text{O}\). Although the \(\Delta\text{Transmittance}\) does not significantly deviate from the baseline at the characteristic Al–O stretching vibration near 660 cm\(^{-1}\), the slight positive deviation of the 2 mass% and 4 mass% \(\text{Li}_2\text{O}\) suggests a simpler structure with \(\text{Li}_2\text{O}\) additions. If the results are compared with the viscosity values, the \(\Delta\text{Transmittance}\) shows that the lower viscous behavior can be correlated to the depolymerization of the aluminate network structure and these smaller slag networks is likely related to the Al–O stretching bands near 660 cm\(^{-1}\).

It should also be noted from work done by Yanishevskii\(^{13}\) that FTIR analysis of highly polymerized CaO–Al\(_2\)O\(_3\) glass samples shows the intensity of the 920 cm\(^{-1}\) absorption band to increase with higher Al\(_2\)O\(_3\) concentrations. This band was assumed to be the stretching vibrations of the triple coordination of aluminum by oxygen as AlO\(_3\). In the FTIR observed in Fig. 5, the absorption peaks at 920 cm\(^{-1}\) were not observed, which suggests that large polymerized aluminate structures are unavailable in the current slag system.

The \(\text{O}_{1s}\) XPS spectra for the calcium aluminate slags with \(\text{Li}_2\text{O}\) additions is given in Fig. 7. The deconvoluted peaks of \(\text{O}^2–\), \(\text{O}–\), and \(\text{O}\) as a function of binding energy (eV) is given. Peak fitting resulted in an optimum full width half maximum (FWHM) of less than 2.0 and slightly varying peak binding energies for the bridged oxygen, non-bridged oxygen, and free oxygen. The binding energy of \(\text{O}^2–\), \(\text{O}–\), and \(\text{O}\) is provided in Table 2. From the integrated area of the peak curves of \(\text{O}^2–\), \(\text{O}–\), and \(\text{O}\), the relative fraction of \(\text{O}^2–\), \(\text{O}–\), and \(\text{O}\) in the slag could be obtained.

The change in the various oxygen ion species with \(\text{Li}_2\text{O}\) additions in the CaO–Al\(_2\)O\(_3\)–Na\(_2\)O–CaF\(_2\) system is shown in Fig. 8. In particular, the change in the amounts of bridging oxygen (\(\text{O}^2–\)), non-bridging oxygen (\(\text{O}–\)), and free oxygen (\(\text{O}\)) determine the effect on the slag structure and hence on the viscous behavior of the molten mold flux. According to the results, the fraction of bridging oxygen (\(\text{O}^2–\)) is significantly affected with \(\text{Li}_2\text{O}\) additions at 1 mass%. Qualitatively the amount of \(\text{O}^2–\) in the slag is decreased and the corresponding amounts of \(\text{O}–\) and \(\text{O}\) increase. At 2 mass% \(\text{Li}_2\text{O}\) and above, the change in \(\text{O}^2–\) is not as significant, but the \(\text{O}–\) and \(\text{O}\) change accordingly. The decrease in \(\text{O}^2–\) with \(\text{Li}_2\text{O}\) additions can be correlated with the simplification of the complex silicate structure and subsequent decrease in the viscosity. In addition, since the \(\text{O}^2–\) does not significantly change, but the \(\text{O}–\) continues to increase with higher \(\text{Li}_2\text{O}\) additions, it may be inferred that large network structures are unavailable and significant changes in viscosity can no longer be observed. Any modification of complex slag structures with significant \(\text{O}^2–\) bonds into simpler structures is physically manifested in the viscosity measurements of Fig. 4. The XPS results and the corresponding viscosity
dependence suggest Li$_2$O in the present slag system to behave as a network modifying component providing O$^{2-}$ ions. At 2 mass% Li$_2$O and above, the XPS results suggest that depolymerization is not as significant as the initial addition of Li$_2$O. The results of the XPS seem to strongly correlate with the viscosity measurements in Fig. 4. It should also be noted that there is a very small binding energy shift of the free oxygen (O$^{2-}$) towards higher values with increased Li$_2$O additions even with the C$_{1s}$ calibration. The cause of this possible chemical shift can be speculated to be the increased availability of neighboring oxygen anions, which can provide localized repulsive forces within the molten chemical environment that lowers the tendency of the core electrons to escape from the atom and subsequently increasing the binding energy.

### 3.3. Temperature Dependence and Activation Energy

The temperature dependence of the viscosity for the CaO–Al$_2$O$_3$–12 mass%Na$_2$O–12 mass%CaF$_2$–based slag system is shown in Fig. 9. The viscosity decreases with increasing temperature. In order to calculate the activation energy for viscous flow ($E_{\eta}$), an Arrhenius type relationship was used. The slope from the plot of the natural logarithm of the viscosity ($\ln \eta$) with reciprocal temperature ($1/T$) provides $E_{\eta}$. Assuming an Arrhenius type relationship, Table 3 shows the calculated activation energies in the calcium-aluminate based slag to be between 180 to 190 kJ/mol for various Li$_2$O additions. The values seem reasonable considering the activation energy for the less viscous calcium-silicate slags were calculated to be between 100 kJ/mole to 120 kJ/mol. The results of the activation energy do not seem to directly correlate with the viscous behavior as Li$_2$O content is increased. The direct cause of this phenomenon has yet to be determined. However, the activation energy of viscous flow is well-known to be affected by two main factors that modify the slag network structure, which include viscosity changes through composition manipulation and/or temperature manipula-

![Fig. 7. O$_{1s}$ XPS spectra for CaO–Al$_2$O$_3$–12 mass%Na$_2$O–12 mass%CaF$_2$–xLi$_2$O slags as a function of binding energy at CaO/Al$_2$O$_3$=0.8.](image)

![Fig. 8. XPS result of as-quenched samples with varying Li$_2$O concentration in the CaO–Al$_2$O$_3$–12 mass%Na$_2$O–12 mass%CaF$_2$–xLi$_2$O slags at CaO/Al$_2$O$_3$=0.8.](image)

![Fig. 9. Temperature dependence of the CaO–Al$_2$O$_3$–12 mass%Na$_2$O–12 mass%CaF$_2$–based slag system with Li$_2$O additions and CaO/Al$_2$O$_3$=0.8.](image)

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3.4. Effect of Li$_2$O on the Break Temperature

The measured break temperature given in the following section. The function of reciprocal temperature in the CaO–Al$_2$O$_3$–12 mass%Na$_2$O–12 mass%CaF$_2$–Li$_2$O slag system, additions at constant temperature showed two significantly different slopes below 1 mass% and above 1 mass%. The difference in the effect of Li$_2$O on the break temperature shown in Fig. 10 and the viscosity measurements at constant temperature shown in Fig. 4 suggests that in the present slag system where significant amounts of large network structures have already been modified, the temperature effect with Li$_2$O additions is more of a factor in determining the viscous behavior than the compositional changes with Li$_2$O. Thus, the slag structure, which is directly related to the viscosity, can be a function of both composition and temperature. When much of the aluminates structures have already been modified into simpler units, lowering the temperature is more effective in increasing the viscosity than changing the concentration of Li$_2$O. However, when the amount of fluidizers such as Na$_2$O and CaF$_2$ are less than the current slag system, it may be possible for the compositional effects to become more important.

4. Conclusion

In this study, the effect of Li$_2$O on the viscosity was directly correlated with the slag structure as revealed by FTIR and XPS. Li$_2$O interacts with the slag structure and modifies large aluminates structures to decrease the viscosity. Li$_2$O additions of 1 mass% had significant effect in lowering the viscosity in the calcium-aluminate slags, but higher concentrations seem to have comparatively less of an impact in lowering the viscosity. This was attributed to the presence of highly basic Na$_2$O and CaF$_2$ already in the slag system investigated and the absence of large aluminates structures for modification. Li$_2$O is likely to be more effective in the aluminates slags compared to the silicate slags due to the ion compensation effect. FTIR and XPS results verify the depolymerization of the network structure with additions of Li$_2$O and correlates well with the viscosity measurements. From the effect of the break temperature with Li$_2$O additions and the temperature dependence of the viscosity, temperature can significantly affect the viscosity more significantly than the compositional changes with Li$_2$O additions for the present CaO–Al$_2$O$_3$–12 mass% Na$_2$O–12 mass% CaF$_2$–Li$_2$O slag system.

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