Influence of TiO$_2$ on the Viscous Behavior of Calcium Silicate Melts Containing 17 mass% Al$_2$O$_3$ and 10 mass% MgO

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1. Introduction

Iron ores consisting of significant TiO$_2$ such as ilmenite are low cost ores, but due to the high TiO$_2$ content its use may result in significant issues within the blast furnaces such as lower reduction degree,$^1$–$^4$ changes in the liquidus temperature in slag,$^5$–$^7$ lower residual removal by the slag,$^8$–$^{10}$ and viscosity changes within the bosch and hearth.$^{11}$–$^{15}$ However, potential benefits of TiO$_2$ in the blast furnace slags have also been known by forming a protective layer of titanium carbo-nitride on the refractory brick and inhibiting the premature failure and erosion of the hearth.$^9$,$^{15}$–$^{18}$ Ohno and Ross$^{13}$ found TiO$_2$ additions increase the slag viscosity in the CaO–SiO$_2$–TiO$_2$ slags under reducing atmospheres of C/CO equilibrium. Shankar et al.$^{19}$ revealed the effect of TiO$_2$ in the CaO–SiO$_2$–MgO–Al$_2$O$_3$ slag system, where the viscosity decreased with TiO$_2$ up to 2 mass%.$^5$–$^{10}$ Saito et al.$^{14}$ found TiO$_2$ lowered the viscosity in the CaO–SiO$_2$–MgO–Al$_2$O$_3$ slag system at 10 mass% and 20 mass% TiO$_2$. However, the viscosity data between 0 to 10 mass% TiO$_2$ is still ill-defined. In this study, the influence of TiO$_2$ from 0 to 10 mass% on the viscous behavior of CaO–SiO$_2$–17 mass% Al$_2$O$_3$–10 mass% MgO slags have been investigated and correlated to the slag structure using XPS (X-Ray Photoelectron Spectroscopy).

2. Experimental Methods

Samples were synthesized using reagent grade chemicals of CaO, SiO$_2$, MgO, Al$_2$O$_3$, and TiO$_2$. The samples were premelted at 1773 K under 0.4 L/min of Ar in a Pt crucible to obtain a homogeneous slag sample. Post-experimental chemical composition using X-Ray Fluorescence (XRF) spectroscopy (S4 Explorer; Bruker AXS GmbH, Karlsruhe, Germany) showed and no apparent change and is given in Table 1.

The viscosity of 120 g of slag placed in a Pt crucible was measured using a rotating spindle connected to a calibrated Brookfield digital rheometer (model LVDV-II+; Brookfield Engineering Laboratories, Middleboro, MA) details of which have been given elsewhere.$^{20}$–$^{22}$ Measurements were taken at each target temperature during a 5°C/min cooling cycle after 30 minutes of soaking and in the fully liquid region of the slag system well above the break temperature (T$_{Br}$) of each slag composition.$^{20}$,$^{21}$ After completing the viscosity measurements, slag samples were reheated to 1773 K and quenched on a water-cooled copper plate to confirm the slag structure using XPS (VG Scientific Instrument, ESCALAB 220i-XL).

3. Results and Discussion

3.1. Effect of TiO$_2$ on the Viscosity

Figure 1 shows the viscosity of the CaO–SiO$_2$–17 mass% Al$_2$O$_3$–10 mass% MgO based slag with TiO$_2$ additions and a constant CaO/SiO$_2$ of 0.8 at various temperatures. TiO$_2$ additions at 5 and 10 mass% decreased the viscosity and the effect of TiO$_2$ is more pronounced at lower temperatures. At higher temperatures of 1723 K and above, TiO$_2$ additions above 5 mass% has only a slight effect in lowering the viscosity. The present study seems to show that TiO$_2$ additions decrease the viscosity and since the viscous behavior of molten slags is closely related to the slag structure, the decrease in the viscosity with TiO$_2$ additions seems to suggest that TiO$_2$ behaves as a basic oxide and modification of the network structure is likely.

![Fig. 1. Effect of TiO$_2$ additions on the viscosity in the CaO–SiO$_2$–17 mass% Al$_2$O$_3$–10 mass% MgO–x TiO$_2$ slag system at constant CaO/SiO$_2$ of 0.8 and various temperatures.](image-url)

Table 1. Chemical composition and measured viscosities of CaO–SiO$_2$–Al$_2$O$_3$–MgO–TiO$_2$ slags.

<table>
<thead>
<tr>
<th>No</th>
<th>C/S</th>
<th>Composition (mass%)</th>
<th>Viscosity (Pa·s)</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>CaO</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>1</td>
<td>0.8</td>
<td>53.2</td>
<td>39.8</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>50.9</td>
<td>37.1</td>
</tr>
<tr>
<td>3</td>
<td>0.8</td>
<td>28.6</td>
<td>34.4</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>36.5</td>
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<td>34.0</td>
</tr>
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<td>1.0</td>
<td>31.5</td>
<td>31.5</td>
</tr>
<tr>
<td>7</td>
<td>1.2</td>
<td>40.6</td>
<td>32.4</td>
</tr>
<tr>
<td>8</td>
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<td>9</td>
<td>1.2</td>
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<td>28.0</td>
</tr>
</tbody>
</table>
TiO₂ lowers the viscosity in the CaO–SiO₂ of 0.8 to 1.2 range. From comparison of the initial slope of 5 mass% TiO₂ additions and the slope between 5 mass% and 10 mass% TiO₂ additions, it can be inferred that the effect of TiO₂ additions becomes less pronounced at higher TiO₂ concentrations. The results of Saito et al.¹⁴) seems to show a similar decreasing trend. Saito et al.'s viscosity measurements were slightly higher, which is likely due to the absence of MgO and a higher Ar flowrate.

3.2. Effect of CaO/SiO₂ on the Viscosity

Figure 3 shows the effect of CaO/SiO₂ at constant TiO₂ content of 5 and 10 mass% at 1773 K. In both cases, higher CaO/SiO₂ or higher apparent basicity (aO₂⁻) lowers the viscosity of the present slag system. This has been typically observed in other slag systems due to the supply of free oxygen ions (O₂⁻) with increased CaO/SiO₂ and the subsequent modification of the large silicate network. Comparison of the 5 and 10 mass% TiO₂ at constant basicity seems to also indicate that the effect of basicity is more significant in modifying the slag viscosity.

3.3. Effect of TiO₂ on the Slag Structure Using XPS

Figure 4 shows an example of the deconvoluted peaks of O°, O⁻, and O²⁻ as a function of O₁S binding energy (eV) for the CaO–SiO₂ of 1.2. Peak fitting resulted in an optimum full width half maximum (FWHM) of less than 2.0 and the subsequent peak binding energies for the various oxygen ion species after background removal and C₁S calibration are given in Table 2. These binding energies of O° between 531.86 to 532.00 eV agree well with Park et al.²³) at 532.12 eV and previously published work of the authors.²¹)

The results of oxygen ion species with TiO₂ additions at CaO/SiO₂ of 0.8 and 10 mass% TiO₂, respectively. The fraction of bridged oxygen (O°) and the non-bridged oxygen (O⁻) decreased with TiO₂ additions, but the free oxygen (O²⁻) increased with TiO₂ additions. Thus, higher TiO₂ content seems to provide a higher potential to depolymerize the slag network structure. Similar trends were observed for constant CaO/SiO₂ of 1.2. It should be noted that the additions of TiO₂ above 5 mass% at constant CaO/SiO₂ of 0.8 had comparatively less effect on changing the fraction of O°, O⁻, and O²⁻, which seems to correlate well with the viscosity measurements in Fig. 2. Similar correlations can be made from the results of CaO/SiO₂ at 1.2 in Figs. 5(b) and 2.

3.4. Temperature Dependence and Activation Energy

The temperature dependence of the viscosity at CaO/SiO₂ of 0.8 and various TiO₂ content is shown in Fig. 6. As expected, the viscosity decreases with increasing temperatures. Although not shown, similar trends were obtained for CaO/SiO₂ of 1.0 and 1.2. In order to calculate the activation energy for viscous flow (Eᵥ), the Arrhenius type relationship of Eq. (1) was used and the slope from the plot of the natural logarithm of the viscosity (ln η) with reciprocal temperature (1/T) provided Eᵥ.

\[ \eta = \eta_0 \exp \left( -\frac{E_v}{RT} \right) \]  \hspace{1cm} (1)
various slag compositions, where values between 195 kJ/mol to 262 kJ/mol were calculated depending on the various slag compositions. These values are comparable to the results obtained by Saito et al.\textsuperscript{14}) between 150 to 210 kJ/mol for CaO–SiO\textsubscript{2}–20 mass% Al\textsubscript{2}O\textsubscript{3} slags at constant CaO/SiO\textsubscript{2} of unity and containing either MgO or TiO\textsubscript{2}. Kim et al.\textsuperscript{20}) has also published activation energy values of viscous flow from 200 to 240 kJ/mol for the CaO–SiO\textsubscript{2}–20 mass% Al\textsubscript{2}O\textsubscript{3}–10 mass% MgO slags at CaO/SiO\textsubscript{2} from 0.8 to 1.2, which is also comparable to the present study.

4. Conclusion

TiO\textsubscript{2} additions lowered the viscosity by depolymerizing the slag network structure. The XPS results showed the fraction of bridged oxygen (O\textsuperscript{\textdegree}) decreased with TiO\textsubscript{2} additions and free oxygen (O\textsuperscript{2–}) increased. The additions of TiO\textsubscript{2} above 5 mass% at constant CaO/SiO\textsubscript{2} of 0.8 had comparatively less effect on changing the fraction of O\textsuperscript{\textdegree}, O–, and O\textsuperscript{2–}, which seems to correlate well with the viscosity measurements. Increasing basicity seems to be more effective in decreasing the viscosity compared to TiO\textsubscript{2} additions. From the temperature dependence, the activation energy of viscous flow was calculated between 195 kJ/mol to 262 kJ/mol depending on the slag composition.

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