The Effect of CaF₂ on the Viscosities and Structures of CaO-SiO₂(-MgO)-CaF₂ Slags

JOO HYUN PARK, DONG JOON MIN, and HYO SEOK SONG

The viscosities of CaO-SiO₂(-MgO)-CaF₂ slags were measured to clarify the effect of CaF₂ on the viscous flow of molten slags at high temperatures and the solidification behavior of slags. Furthermore, the infrared (IR) spectra of the quenched slags were analyzed to understand the structural role of CaF₂ in the modification of slag structure. The CaF₂ affects the critical temperature (T_CR) of the slags; that is, the higher the content of CaF₂, the lower the T_CR of the slags. It is suggested that some extent of undercooling as a driving force is needed for the precipitation of solid particles in the melt. In the composition of B = (mass pct CaO)/(mass pct SiO₂) = 1.0, the T_CR was decreased about 150 to 200 K by addition of 10 mass pct MgO, while the T_CR was increased about 100 K by MgO addition at B = 1.3. The effect of CaF₂ on the viscous flow of molten slags can be understood based on a decrease in the degree of polymerization by F⁻ as well as by O²⁻ ions and this was confirmed by the IR spectra of the quenched slags. The relative intensity of the IR bands for [SiO₄]₄-tetrahedra with low NBO/Si decreased, while that of the IR bands for [SiO₄]₄-tetrahedra with high NBO/Si increased with increasing CaF₂ content. The decrease in viscosity of the CaO-SiO₂-MgO-CaF₂ (B = 1.0) system by CaF₂ addition was negligible, while the effect of CaF₂ on the viscosity was significant in the more basic system (B = 1.3).

I. INTRODUCTION

FLUORSPAR is used in primary and secondary steelmaking processes to improve the fluidity of molten slags. The mold fluxes used in continuous casting also contain about 10 to 20 mass pct fluorides. However, the consumption of CaF₂ in the steelmaking industry has been restricted due to its harmful effect on human health, the environment, and operation equipment. The effect of CaF₂ on the viscosity of silicate melts has recently been investigated by some researchers. Shahbazian et al. concluded that the CaF₂ decreased the viscosity of the CaO-SiO₂-CaF₂ ((mass pct CaO)/(mass pct SiO₂), B ≈ 0.6 to 0.9, 13 to 41 mass pct CaF₂) system. Tribe et al. suggested that the solidification temperature of the basic systems (B ≈ 1.3 to 2.5) would be higher than that of the acidic compositions (B ≈ 0.5 to 0.8) in the CaO-SiO₂-MgO-CaF₂ slags. However, the content of CaF₂ in these studies would be significantly high; thus, the effect of CaF₂ on the viscosity, structure, and the solidification behavior of slags with CaF₂ contents less than about 15 mass pct has not yet been clarified.

Therefore, in the present study, the viscosity of the CaO-SiO₂(-MgO)-CaF₂ slags has been measured to clarify the effect of CaF₂ on the viscous flow of molten slags at high temperatures and the solidification behavior of slags. In addition, the infrared (IR) spectra of the quenched slags were analyzed to understand the structural role of CaF₂ in the depolymerization of silicate network in a microscopic view.

II. EXPERIMENTAL

A. Sample Preparation for Viscosity Measurement

All of the slag samples were prepared using reagent-grade chemicals. The master slags were used for the pre-melting of slags, and then, each component was added into the pre-melted 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.

B. Experimental Procedure

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 spindle. The temperature was measured using an R-type (Pt/Pt-13 pct 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 pct Rh spindle, crucibles, and suspending wire, of which dimensions are listed in Table I. 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 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...
Fig. 1—Experimental apparatus for the measurement of slag viscosity.

Table I. Dimensions of the Crucible, Spindle, and Suspending Wire Used in the Measurement of Slag Viscosity

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Inner Diameter (mm)</th>
<th>Inner Depth (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crucible</td>
<td>Pt-10 pct Rh alloy</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Spindle</td>
<td>Pt-10 pct Rh alloy</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>Suspending Wire</td>
<td>Pt-10 pct Rh alloy</td>
<td>2</td>
<td>150</td>
</tr>
<tr>
<td>(lower part)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(upper part)</td>
<td>molybdenum</td>
<td>2</td>
<td>340</td>
</tr>
</tbody>
</table>

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.

In addition, the CaF₂ contents of the slags were analyzed after experiments, because evaporation of the fluoride species from the slags was expected. It was confirmed that the weight loss of CaF₂ by fluoride emission was within about 10 pct of the initial content, as shown in Table II. Hence, the composition in the present article has been expressed as initial contents.

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. The details with regard to the sample preparation and the experimental procedure for the IR spectra measurement have been described previously.\textsuperscript{[3,4,5]}

III. RESULTS AND DISCUSSION

A. CaO-SiO₂-CaF₂ Ternary System

The phase diagram of the CaO-SiO₂-CaF₂ ternary slag is shown in Figure 2 with the experimental compositions.\textsuperscript{[6]}

The dependence of slag viscosity on temperature at different CaF₂ contents is also shown in Figures 3 and 4 for the values of B = 1.0 and 1.3, respectively.

When viscosity measurements are carried out during a cooling cycle, there is a point at which the viscosity increases suddenly and the slag becomes non-Newtonian in behavior. This is variously referred to as the crystallization temperature, the solidification temperature, the break temperature, and the liquidus temperature as well as the critical temperature.\textsuperscript{[7]}

In the present study, the term critical temperature ($T_{CR}$) is used. The critical temperature represents the point at which the activation energy for the viscous flow of slags increases abruptly due to the precipitation of solid phase in the melt.

The critical temperature of the slags (B = 1.0) decreases from about 1753 to 1643 K with increasing CaF₂ content from 5 to 15 mass pct, as shown in Figure 3. This tendency can easily be expected from the phase diagram (Figure 2). 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, as shown in Table III. 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 (CaO-SiO₂).

The $T_{CR}$ of the CaO-SiO₂-15 (mass pct) CaF₂ (B = 1.3) system (Figure 4) is also about 30 K lower than the $T_{LQ}$. However, the viscosity-increasing rate of the 10 mass pct