Amphoteric Behavior of Alumina in Viscous Flow and Structure of CaO-SiO₂ (-MgO)-Al₂O₃ Slags

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The viscosity of CaO-SiO₂ (-MgO)-Al₂O₃ slags was measured to clarify the effects of Al₂O₃ and MgO on the structure and viscous flow of molten slags at high temperatures. Furthermore, the infrared spectra of the quenched slags were analyzed to understand the structural role of Al₂O₃ in the polymerization or depolymerization of silicate network. The Al₂O₃ behaves as an amphoteric oxide with the composition of slags; that is, the alumina behaves as a network former up to about 10 mass pct Al₂O₃, while it acts as a network modifier, in parts, in the composition greater than 10 mass pct Al₂O₃. This amphoteric role of Al₂O₃ in the viscous flow of molten slags at the Newtonian flow region was diminished by the coexistence of MgO. The effect of Al₂O₃ on the viscosity increase can be understood based on an increase in the degree of polymerization (DOP) by the incorporation of the [AlO₄]-,tetrahedra into the [SiO₄]-tetrahedral units, and this was confirmed by the infrared (IR) spectra of the quenched slags. The influence of alumina on the viscosity decrease can be explained on the basis of a decrease in the DOP by the increase in the relative fraction of the [AlO₆]-octahedral units. The relative intensity of the IR bands for the [SiO₄]-tetrahedra with low NBO/Si decreased, while that of the IR bands for [SiO₄]-tetrahedra with high NBO/Si increased with increasing Al₂O₃ content greater than the critical point, i.e., about 10 mass pct in the present systems. The variations of the activity coefficient of slag components with composition indirectly supported those of viscosity and structure of the aluminosilicate melts.

I. INTRODUCTION

The amphoteric behavior of alumina in aluminosilicate melts has been an issue for several decades in the fields of metallurgy as well as glass and geo-sciences. Thus, many researchers have focused on the structural role of alumina in aluminosilicate systems by measuring the physical properties such as viscosity and thermal or electrical conductivities, measuring the spectroscopic properties such as infrared (IR) and Raman spectra, and by employing thermodynamic calculations. In alkaline (or alkaline earth) silicate melts containing alumina, Al-O coordination would be tetrahedral, i.e., [AlO₄] just like [SiO₄]-tetrahedra, when the molar ratio Al₂O₃/MO (MO is basic oxide) is less than unity. When this ratio exceeds 1.0, Al³⁺ ions would have octahedral coordination with oxygen and enter interstices in the structure. These structural changes in aluminosilicate melts could affect their physical properties. The viscosity of the MO-SiO₂-Al₂O₃ slags increases as MO is replaced by Al₂O₃, for a given SiO₂ content, until the molar ratio Al₂O₃/MO is about unity as a result of a decrease in the concentration of nonbridging oxygen in the melt, and vice versa above this ratio. Turkdogan and Bills indicated that this behavior would be evidence of the amphoteric nature of alumina. However, [AlO₄]₅⁻-tetrahedral units have a different charge to [SiO₄]⁴⁻-tetrahedra, and thus, cations are needed to provide electrical charge balance, e.g., [Na(AlO₄)]⁴⁻ or [1/2Ca(AlO₄)]²⁺; thus, the Na⁺ or Ca²⁺ ions must be sited close to the Al atom. With regard to these estimations, Duan et al. reported that the change of glass structure would be concerned with the stability of the structural units. They introduced the stable energy, $u = u_{att} + u_{rep}$, by combining the Coulomb attraction energy and repulsion energy $u_{rep} = \frac{B}{r^n}$, where $B$ and $n$ are constants, and $r$ is the distance between ions, respectively) and $u_{att} = \frac{Z_1Z_2e^2}{r}$, where $Z_1$ and $Z_2$ are electric charges of positive and negative ions, and $e$ and $r$ are the charge on an electron and the distance between ions, respectively).

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METALLURGICAL AND MATERIALS TRANSACTIONS B
VOLUME 35B, APRIL 2004—269
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 premelting of slags, and then, each component was added into the premelted 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. Procedure of Viscosity Measurement

The rotating cylinder method was used in the present study and a schematic diagram of the experimental apparatus is shown in a previous article. A rotating viscometer (Brookfield, model RVDV-II/H11001, 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 the 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 1600 to 1823 K.

The measurements of viscosity in the present study were made using a Pt-10 pct Rh spindle, crucibles, and a suspending wire. 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 performed during cooling cycles under an Ar atmosphere. 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. Finally, some slag samples were reheated to about 1823 K after viscosity measurements, and then water quenched to measure the IR spectra of the slags.

C. Procedure of IR Spectra Measurement

The structure of the investigated slags was analyzed by Fourier transform infrared (FT-IR) spectroscopy (Nicolet, Avatar 360, Woburn, MA). The FT-IR 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. A spectral resolution of 2 cm$^{-1}$ was chosen. Each sample of 2.0 mg was mixed with 200 mg of KBr in an agate mortar, and then pressed into pellets of 13-mm diameter. The spectrum for each sample represents an average of 20 scans, which were normalized to the spectrum of the blank KBr pellet.

III. RESULTS AND DISCUSSION

A. CaO-SiO$_2$-Al$_2$O$_3$ Ternary System

The phase diagram of the CaO-SiO$_2$-Al$_2$O$_3$ ternary slag is shown in Figure 1 with the experimental compositions. The dependence of slag viscosity on temperature at different Al$_2$O$_3$ contents is also shown in Figures 2 and 3 for the value of $B$ (mass pct CaO)/(mass pct SiO$_2$) = 1.0 and 1.3, respectively. The data from the literature are also shown in Figures 2 and 3 to enlarge the effect of Al$_2$O$_3$ on the viscosities, which have not been measured in the present work.

The viscosity of the slags ($B = 1.0$) at 1823 K exhibits a maximum value of about 0.8 Pa·s at 10 mass pct Al$_2$O$_3$, and this trend is observed through the entire temperature range measured. This could be attributed to the amphoteric behavior of Al$_2$O$_3$ in the aluminosilicate melts. The viscosity of the slags with $B = 1.3$ (Figure 3) at 1823 K decreases from