Influence of Al₂O₃/TiO₂ Ratio on Viscosities and Structure of CaO–MgO–Al₂O₃–SiO₂–TiO₂ Melts

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The effect of Al₂O₃/TiO₂ ratio on viscosities of CaO–MgO–Al₂O₃–SiO₂–TiO₂ melts was investigated by the rotating cylinder method in this study. In addition, structural characterizations of these quenched vitreous samples were also studied by Raman spectroscopy. It was indicated from the experimental results that viscosity increases as gradually increasing Al₂O₃/TiO₂ ratio while keeping the contents of other components constant. The Raman spectra analyses indicated that TiO₂ mainly exists in the form of [TiO₄] as a network former in composition range of 3–17 mol%. With increasing the Al₂O₃/TiO₂ ratio, the [TiO₄] content decreases and the degree of polymerization of the melt increases resulted from the increase of Al₂O₃ which behaviors as an acidic oxide and incorporates into the SiO₂ network with the charge balance of CaO. Consequently, there will be an increase of viscosity with increasing Al₂O₃/TiO₂ ratio.

KEY WORDS: CaO–MgO–Al₂O₃–SiO₂–TiO₂; viscosity; structure; Raman spectroscopy.

1. Introduction

It is well known that viscosity is an important physical property for aluminosilicate melt. Considerable attentions have been paid on viscosity for its great importance in understanding the fluid dynamic of molten slags and slag-metal reaction kinetics during the pyrometallurgy process. CaO–Al₂O₃–SiO₂ system is a very important fundamental system during the iron-making and steelmaking processes, so it is meaningful to study the viscosities of the CaO–Al₂O₃–SiO₂ based slags. Titanium is a minor element in most rock-forming silicate melts. Nevertheless, this element is petrologically significant. For example, liquidus boundaries between olivine and pyroxene shift toward olivine-rich portions of appropriate systems as TiO₂ is added to the melt.1) Ohno and Ross2) found TiO₂ additions increase the slag viscosity in the CaO–SiO₂–Al₂O₃–TiO₂ slags under reducing atmospheres of C/CO equilibrium mainly because of the reducing the TiO₂. Shankar et al.3) revealed the effect of TiO₂ in the CaO–SiO₂–MgO–Al₂O₃ slag system, where the viscosity decreased with TiO₂ up to 2 mass%. Satio et al.4) found TiO₂ lowered the viscosity in the CaO–SiO₂–MgO–Al₂O₃ slag system as adding 10 mass% and 20 mass% TiO₂. Sohn5) investigated the influence of TiO₂ from 0 to 10 mass% on the viscous behavior of CaO–SiO₂–17 mass%Al₂O₃–10 mass%MgO slags. Both Al₂O₃ and TiO₂ are amphoteric oxides, so it is significant to distinguish their different effects on viscosity. However, there is no related study on the influence of Al₂O₃/TiO₂ ratio. Therefore, in this work, the viscosity variation of CaO–MgO–Al₂O₃–SiO₂–TiO₂ molten slag with Al₂O₃/TiO₂ ratio will be studied. Furthermore, the Raman spectroscopy analyses will also be used to illustrate the structure change corresponding to the viscosity variation.

2. Experimental Procedures

2.1. Viscosity Measurement

Slag samples were prepared using reagent-grade SiO₂, Al₂O₃, MgO, TiO₂, and CaCO₃ powder, all of which were calcined in a muffle furnace at 1 273 K for 10 hours, to decompose any carbonate and hydroxide before use. The detailed information of the chemical reagents was shown in Table 1. Then the prepared CaO and other reagents were precisely weighted according to the compositions shown in Table 2, and then mixed in the agate mortar thoroughly. In each composition of Table 2, contents of CaO, MgO and SiO₂ keep constant, but Al₂O₃/TiO₂ ratio gradually increases. The mixtures were packed into a Mo crucible and pre-melted in an induction furnace at 1 873 K for 3 hours with the protection of Ar gas. After pre-melting, the slag sample, together with the crucible, was preserved in a desiccator.

The viscosity measurement was carried out using the rotating cylinder method. The schematic diagram of the experiment apparatus can be found in our previous paper.6) During the viscosity measurement, both the crucible and the spindle should be properly aligned along the axis of the viscometer, which is very important because a slight deviation from the axis can cause large experimental errors. Then, the furnace was heated up to about 1 823 K and held for 60 min under the protection of Ar gas, before immersing the spindle into the slag and measuring the viscosity. The viscosity measurement was carried out at every 10 K or 25 K interval on TiO₂ molten slag with Al₂O₃/TiO₂ ratio.
cooling. At each experimental temperature before measuring, the melt was kept for 30 min first to ensure the melt uniform. The variations of viscosity due to the different rotating speeds range from 100 to 200 rpm were less than 1.5%, confirming that the molten was Newtonian fluid. The average value was adopted as the viscosity value. All the measured viscosities were given in Table 3. After completing the viscosity measurements, the furnace was reheated up to 1 823 K to pull out the spindle, which was cleaned for the next experiment.

2.2. Raman Spectral Study

Glass samples with different compositions were prepared by conventional melting and quenching method. Raw materials were mixed, put into a platinum crucible and then melted at 1 873 K for 4 hours in Ar atmosphere. After that, the melts were quenched by water to obtain the glass samples which were proved to be amorphous by XRD as shown in Fig. 1.

Raman spectra were acquired using a laser confocal Raman spectrometer (JY-HR800, Jobin Yvon, France). Its precision of wave number is better than 0.01 cm$^{-1}$. The experiments were carried out at room temperature by using excitation wavelength of 532 nm. The light source was a semiconductor laser with power of 1 MW. The frequency band measured in this work was ranged from 100 to 2 000 cm$^{-1}$.

3. Results

3.1. Effect of Al$_2$O$_3$/TiO$_2$ on Viscosity

For four compositions in Table 2 with the same contents of CaO, MgO and SiO$_2$ but different contents of TiO$_2$ and Al$_2$O$_3$, the temperature dependences of viscosity are shown in Fig. 2, from which it can be seen that the Arrhenius law is obeyed and the viscosity decreases as increasing the temperature. Furthermore, the viscosity increases as increasing

| Reagent-powder | Purity | Manufacturer                          |
|----------------|--------|---------------------------------------|
| CaCO$_3$      | AR, ≥99.0% | Sinopharm Chemical Reagent Co., Ltd, China |
| MgO           | AR, ≥98.5% | Sinopharm Chemical Reagent Co., Ltd, China |
| Al$_2$O$_3$   | AR, ≥99.0% | Sinopharm Chemical Reagent Co., Ltd, China |
| SiO$_2$       | AR, ≥99.0% | Sinopharm Chemical Reagent Co., Ltd, China |
| TiO$_2$       | CP, ≥98.0% | Sinopharm Chemical Reagent Co., Ltd, China |

Table 2. Compositions for viscosity measurement (mole fraction).

|        | CaO | MgO | Al$_2$O$_3$ | SiO$_2$ | TiO$_2$ |
|--------|-----|-----|-------------|---------|---------|
| A1     | 0.3 | 0.15| 0.10        | 0.28    | 0.17    |
| A2     | 0.3 | 0.15| 0.14        | 0.28    | 0.13    |
| A3     | 0.3 | 0.15| 0.18        | 0.28    | 0.09    |
| A4     | 0.3 | 0.15| 0.23        | 0.28    | 0.04    |

Table 3. Measured viscosity values for different compositions at different temperatures.

|        | T, K   | $\eta$, dPa.s |
|--------|--------|---------------|
| A1     | 1 808  | 1.29          |
|        | 1 798  | 1.37          |
|        | 1 788  | 1.43          |
|        | 1 777  | 1.51          |
|        | 1 767  | 1.58          |
|        | 1 757  | 1.69          |
|        | 1 731  | 1.96          |
| A2     | 1 809  | 2.16          |
|        | 1 798  | 2.28          |
|        | 1 788  | 2.43          |
|        | 1 778  | 2.81          |
|        | 1 767  | 3.17          |
|        | 1 756  | 3.63          |
|        | 1 730  | 4.76          |
| A3     | 1 803  | 3.66          |
|        | 1 793  | 4.54          |
|        | 1 783  | 5.16          |
|        | 1 773  | 5.99          |
|        | 1 762  | 6.62          |
|        | 1 752  | 7.29          |
|        | 1 727  | 9.19          |
| A4     | 1 860  | 3.81          |
|        | 1 839  | 5.93          |
|        | 1 819  | 8.65          |
|        | 1 798  | 11.39         |
|        | 1 777  | 14.89         |
|        | 1 759  | 16.86         |
|        | 1 738  | 22.08         |

Fig. 1. Typical XRD pattern of the quenched glass sample.
3.2. Structural Characterizations by Raman Spectral

Figure 3 presents the room-temperature Raman spectra of the four glass samples, respectively. All the backgrounds of the measured Raman signals have been subtracted. It is found that the peak of spectra of the glasses become broad and shift to higher frequency from composition A1 to A4.

All the measured Raman spectra are deconvolved by Gaussian-Deconvolution method with the minimum correction coefficient $\geq 0.999$. The squares of the deviations between the observed and calculated Raman envelopes with Gaussian line shapes, $\chi^2$, are also given. The deconvoluted results have been shown in Figs. 4–7. From all the spectra in the figures, obvious bands are found in the frequency of 600–1200 cm$^{-1}$, so the focus of attention in this work is the middle frequency of the Raman spectra. Assignments of Raman peaks have been listed in Table 4. As shown in Figs. 4–7, there exist four bands in the middle frequency range as 700–728 cm$^{-1}$, 820–843 cm$^{-1}$, 940–966 cm$^{-1}$, 1010–1040 cm$^{-1}$, respectively. Area fractions of various bands could be calculated according to the deconvolved spectra data.

Figure 8 shows the area fractions of bands as functions of $x$ (Al$_2$O$_3$)/$x$ (TiO$_2$).

The structure of TiO$_2$-free silicate has been subjected to many studies by Raman spectroscopy, that the peak at about 948 cm$^{-1}$ is due to SiO$_2$ stretching with NBO/T = 2 (non-bridging oxygen per tetrahedrally coordinated cation).
and referred to as \( Q_2 \) (subscript refers to the number of bridging oxygen) species in a chain structure.\(^{13,17,18} \) The 820–843 cm\(^{-1} \) band probably corresponds to the vibration of Ti–O–Si structural group,\(^{17} \) or Ti–O–Ti vibrations,\(^{1} \) or both. It is indicated that Ti\(^{4+} \) exists in the glasses in the form of [TiO\(_4\)]. According to Mysen\(^{1} \) et al.,\(^{1} \) 700–728 cm\(^{-1} \) is probably assigned to deformation of O–Ti–O or O–(Si, Ti)–O in chain or sheet units or both. Based on the reports of You\(^{13} \) et al.,\(^{13} \) Tsunawaki\(^{14} \) and Mcmillan,\(^{15,16} \) the peak around 1 040 cm\(^{-1} \) is due to stretching with NBO/Si = 1 and referred to as \( Q_3 \) species in a sheet structure. In the present spectral, there are no bands at wavenumbers less than 700 cm\(^{-1} \) that could be attributed to Ti–O stretch vibrations of Ti in six-fold coordination.\(^{1} \) Therefore, it is possible that no or very little [TiO\(_6\)] exists in the present system and all the TiO\(_2\) behaves as an acidic oxide.

It is known that Al\(_2\)O\(_3\) is amphoteric oxide and its behavior depends on the basicity of melts to which it is added. Al\(^{3+} \) ions are glass network intermediates and can enter as both the network formers and the network modifiers. For all these four compositions, the contents of basic oxides (CaO + MgO) are higher than that of the Al\(_2\)O\(_3\). Therefore, Al\(_2\)O\(_3\) would behave as an acidic oxide and incorporate into the network of SiO\(_2\) with the charge compensation of basic oxide, which means Al\(^{3+} \) ion enter as the network formers in the form of [AlO\(_4\)]. It also can be seen from the Raman spectroscopic results of Figs. 4–7 that 940–966 cm\(^{-1} \) and 1 010–1 040 cm\(^{-1} \) bands assigned to the \( Q_2 \) and \( Q_3 \), which means Al\(^{3+} \) ion enter as the network formers in the form of [AlO\(_4\)].

Besides, the abundance changes of bridging oxygen are mainly discussed by comparison of areas of two bands 948 cm\(^{-1} \) and 1 040 cm\(^{-1} \). Band 1 040 cm\(^{-1} \) (\( Q_3 \)) refers to the structural unit with more bridging oxygen than band 948 cm\(^{-1} \) (\( Q_2 \)), and the area ratios of \( Q_2 \) to \( Q_3 \) reflect the abundance changes of bridging oxygen. According to Frantz and Mysen,\(^{17,18} \) the mole fractions of different structure units are related to the band areas \( A_i \), according to the equation: 

\[
X_i = \frac{\theta_i A_i}{\theta_i A_i + \theta_2 A_2}
\]

The molar fraction ratio of \( Q_2 \) to \( Q_3 \) could be estimated using Eq. (1). The effects of Al\(_2\)O\(_3\) on the abundance of \( Q_2 \) to \( Q_3 \) can be observed. It can be seen from Fig. 8 that the estimated ratio of \( Q_2 \) to \( Q_3 \) decreases as the content of Al\(_2\)O\(_3\) increases. That means the percentage of \( Q_3 \) increases compared with that of \( Q_2 \), which indicates that the percentage of bridging oxygen increases.

### 4. Discussion

(1) In investigation of the phase relations in the SiO\(_2\)–TiO\(_2\) system, Devries \textit{et al.}\(^{19} \) indeed noticed weight losses that could be attributed to the formation of little Ti\(_2\)O\(_3\), which would have been present in solid solution with TiO\(_2\). As for any redox reaction, the most reduced valence is favored by higher temperatures with the result that the abundance of Ti\(^{3+} \) could become significant in air about 2 000°C at ambient pressure.\(^{20} \) All experimental work mentioned in this study has been performed at temperatures that were not extremely high. Meanwhile, as a matter of fact, Ti\(^{3+} \) ion gives a glass a purple color that is readily observed if this valence state of titanium is present in significant amounts.\(^{20–22} \) However, all glasses of this study are colorless. Therefore, titanium mainly exists in the form of Ti\(^{4+} \) ions.

(2) According to the results of Raman spectroscopic
study, it can be found that, [TiO$_4$] and [AlO$_4$] are the predominant forms of Ti$^{4+}$ and Al$^{3+}$ in the composition range of present study. The reason increasing viscosity is that the Al$^{3+}$ ions enter as the glass network formers in the form of [AlO$_4$] and take place of some Ti$^{4+}$ ions in the network as substituting Al$_2$O$_3$ for TiO$_2$. When Al$^{3+}$ ions enter as the network formers in the form of [AlO$_4$], to keep the equilibrium of electric charge there should be one M$^{2+}$ ion in neighbor of two [AlO$_4$] or one non-bridging oxygen ion as well as one [AlO$_4$]. Therefore, when substituting 1 mol of Al$_2$O$_3$ for 1 mol TiO$_2$, 1 mol [TiO$_4$] disappears but 2 mol [AlO$_4$] adds by consuming 1 mol of CaO which initially behaviors as the network modifier. So, in this study, when the Al$^{3+}$ ions replace Ti$^{4+}$ ions in the network, the number of bridging oxygen ions increases which can be seen from the Raman spectroscopic results of Fig. 8, in which the ratio of Q2 to Q3 gradually decreases, thereby, the degree of polymerization increases, so is the viscosity.

5. Conclusions

(1) In this study, the influence of Al$_2$O$_3$/TiO$_2$ ratio on the viscosity of CaO–MgO–Al$_2$O$_3$–SiO$_2$–TiO$_2$ melts was investigated by using the rotating cylinder method. It was found that viscosity increases as gradually substituting Al$_2$O$_3$ for TiO$_2$.

(2) The Raman spectroscopy technique has been used to provide deep insight into the structure of the CaO–MgO–Al$_2$O$_3$–SiO$_2$–TiO$_2$ melt. Both Ti$^{4+}$ and Al$^{3+}$ mainly enter into the glasses as the network formers in the forms of [TiO$_4$] and [AlO$_4$], respectively. When substituting Al$_2$O$_3$ for TiO$_2$ in CaO–MgO–Al$_2$O$_3$–SiO$_2$–TiO$_2$ melts, the number of non-bridging oxygen decreases, which leads to the increases of viscosity.

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