Viscosity Measurement of Calcium Ferrite Based Slags during Structural Relaxation Process

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In the present study, we measured the viscosity change with the melting time (melting temperature: 1 873 K, 1 773 K or 1 673 K, atmosphere: air) of calcium ferrite (CaO·Fe2O4(CF)) based slags (CF, CF–5wt%SiO2 and CF–5wt%Al2O3) by the rotating crucible method. Moreover, the viscosity changes were discussed from the viewpoints of the iron oxidation states (Fe2+ and Fe3+) and the coordination number of Fe3+.

Viscosity of the CF based slags decreased with the melting time at all the temperature (1 673 K, 1 773 K or 1 873 K). Viscosities of the slags became constant after the melting time of 120 min at 1 873 K and at 1 773 K. In the case of the melting at 1 673 K, the viscosity of the slags became constant after 240 min. The results of the chemical analysis indicated that the oxidation state of iron ions in the quenched CF slag was not changed during the viscosity measurements. We could not directly observe the change in the coordination structure of Fe3+ in CF based slags during the melting time, because the CF based slag could not be vitrified due to the limitation of quenching rate in the present study. However, the data of the viscosity and the structural information for 40CaO–40SiO2–20Fe2O3 (mol%) slag indicated that the coordination structure of Fe3+ strongly affect the viscosity of iron-containing slags. The decreases in the viscosity of the CF based slags would be also controlled by the change in the coordination number of Fe3+.

KEY WORDS: viscosity; iron oxide containing slag; calcium ferrite; melt property; structural relaxation; iron ore sinter.

1. Introduction

In recent years, use of low quality ores, such as pisolite and marra mamba ores, is increasing in amount with the decline in the production of Australian high quality ores.1) Therefore, developments of sintering technology, which will convert the low quality ores into high quality raw materials, are strongly desired. It is well known that the quality of iron ore sinter (reducibility, strength, and so on) is influenced by the microstructure of the sinters. Generally, the iron ore sinter is produced by a liquid-phase sintering at temperature range of 1 473–1 673 K. Some physical properties of the generated liquids, which are mainly composed of calcium ferrite (CaO·Fe2O4 (CF)) and gangue mineral (SiO2, Al2O3 or MgO),2) is considered to affect the microstructure of the iron ore sinter.3) For instance, the penetration behavior of the generated melts into the bulk ores are reported to be controlled by the viscosity and the surface tension of the generated melts.4,5) However, published data of physical properties for ferrite-based system is very limited and heavily outnumbered by that for silicate-based system. Figure 1 represents the temperature dependences of the viscosity for CaO–Fe2O3 melts (CaO content: 18.9–20 wt%, Fe2O3 content: 80–81.1 wt%) reported by several researchers.6–8) As shown in the figure, the temperature dependences of the viscosity for CaO–Fe2O3 melts have large differences among the researchers, despite these melts are comparable in chemical compositions. Therefore, highly reliable data of physical property for CaO–Fe2O3 system is demanded. Moreover, one of the authors9) reported that the CaO–Fe2O3 based melts had the isothermal...

Fig. 1. Temperature dependences of viscosity for CaO–Fe2O3 system reported by several researchers.4–8)
melting time dependence on the viscosity, which would have academic interests.

The aim of the present study is to clarify the melting time dependences of the viscosity for CF based slag as a first step of the physical property study for the liquids generated during the process of iron ores sintering. Namely, the viscosity changes with melting time (melting temperature: 1 673 K, 1 773 K or 1 873 K) of CF based slags (CF, CF–5wt%SiO₂, or CF–5wt%Al₂O₃) were measured by the rotating crucible method. Additionally, the viscosity change has been discussed from the viewpoints of change in the oxidation states of iron ions (Fe²⁺ and Fe³⁺) and the coordination number of Fe³⁺.

2. Experimental Procedure

2.1. Viscosity Measurement

2.1.1. Sample Synthesis

CF based slags and 40CaO–40SiO₂–20Fe₂O₃ (mol%) slag were employed for viscosity measurements in the present study. Initial compositions of CF based slags are listed in Table 1. The slag samples were pre-melted and then employed as starting materials for the viscosity measurements. The details of pre-melting procedure were as follows. Firstly, the appropriate proportions of reagent grade CaCO₃, Fe₂O₃, SiO₂, and Al₂O₃ powders were weighed and mixed in a mullite mortar. The mixtures were then placed in a Pt crucible (30 cc) and melted in an electric furnace at 1 773 K under air. Melting time for the CF based slags and for the 40CaO–40SiO₂–20Fe₂O₃ slag were 30 min and 120 min, respectively. Then after that, the melts were quenched on a copper plate. These quenched slags were ground into a powder and employed as starting materials for viscosity measurement.

2.1.2. Apparatus for Viscosity Measurement

Figure 2 represents the schematic illustrations of the rotating crucible viscometer, which consists of a rotating system, a heating system and a measuring system. An electric resistance furnace with six U-shape MoSi₂ heating elements was employed for heating and melting. The differential transformer (Fig. 2(a)) was developed by improving a commercially available rotation angle detector. A crucible and a bob, both with Pt–20wt%Rh, were used in the experiments. The dimensions of the crucible and the bob are given in Fig. 2(b).

The viscometer was calibrated by using several kinds of silicone oil standards with viscosities of 0.01–0.1 Pa·s at room temperature before the each measurement. The calibration of the viscometer at high temperature were also made by using reference slag (SRM2). The errors of the viscosity measurements were within ±3% at all the experiments.

2.1.3. Temperature Profiles for Viscosity Measurement

Figure 3 illustrates temperature profiles for viscosity measurements. In the case of profile (a), (b) and (c), we measured the viscosity change with the melting time and (d), we measured viscosity at 25 K interval on cooling.

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ture) in temperature profile (d). The experimental conditions used in the present study are summarized in Table 2.

2.2. Oxidation State Analysis of Iron Ions in the CF Slag

CF slags, which were synthesized with the same procedure as the starting material for the viscosity measurements, were melted in a Pt crucible (amount of the slag sample: 50 g, internal diameter of the crucible: 30 mm) at 1773 K under air (temperature profile: (b)) and quenched with copper plates after the melting time of 0, 30, 60, 120 and 240 min. The oxidation states of the iron ions (Fe$^{2+}$ and Fe$^{3+}$) for these quenched slags were quantitatively determined by chemical analysis.10)

3. Results and Discussion

3.1. Viscosity Change of the Calcium Ferrite Based Slags with the Melting Time

Figures 4–6 indicate the changes in the viscosity of the CF based slags (CF, CF–5wt%SiO$_2$, CF–5wt%Al$_2$O$_3$) with the melting time. The viscosities of the CF based slags (CF, CF–5wt%SiO$_2$, CF–5wt%Al$_2$O$_3$) were found to be decreased with the melting time at all the examined temperatures. The viscosity of the CF based slags became constant after the melting time of 120 min at 1873 K and at 1773 K. In the case of melting at 1673 K, the viscosity of the CF based slags became constant after the melting time of 240 min.

Figure 7 shows the viscosity changes in the CF based slags during the melting time at 1773 K. As shown in the figure, the viscosities of the CF based slags became constant after 120 min, which was independent on the slag compositions. In addition, the viscosity of the CF slag was increased with the addition of SiO$_2$ or Al$_2$O$_3$. SiO$_2$ has been widely realized as a strong network-former. Besides, Al$_2$O$_3$ has been categorized as an amphoteric oxide, and also behave as a network-former in a highly basic system.11) Therefore the increase in viscosity of CF slag is considered to be due to the increase in the size of flow units with the addition of SiO$_2$ or Al$_2$O$_3$.

Iron ions have two kinds of oxidation states (Fe$^{2+}$ and Fe$^{3+}$) in the molten slag and the redox equilibrium between Fe$^{2+}$ and Fe$^{3+}$ is influenced by the basicity of the slag, the
melting temperature and the oxygen partial pressure. Fe$^{2+}$ in the melts is thought to be octahedrally coordinated by oxygen and behave as network modifier. Meanwhile, Fe$_2$O$_3$ (Fe$^{3+}$) is categorized as one of the amphoteric oxide. Additionally, Dingwell reported that the viscosity of the iron oxides containing silicate melts decreased with increasing the ratio of Fe$^{2+}$ to the total Fe. There was a possibility that the change in the oxidation state of iron ions might affect the viscosity of the CF based slags during the melting time. Consequently, the oxidation state analysis of the quenched CF slag has been conducted.

3.2. Change in the Oxidation States of Iron Ions in the CF Slag

Figure 8 reveals the ratio of Fe$^{2+}$ to total-Fe and the viscosity with the melting time in the CF slag. As denoted in the figure, the viscosity of the CF slag decreased with the melting time. However, no significant difference in the ratio of Fe$^{2+}$ to total-Fe (7.3±0.5%) was observed with the melting time. From the result of oxidation state analysis, we can conclude that the viscosities of the CF based slags are not controlled by the change in the oxidation state of the iron ions during the melting. As mentioned above, Fe$_2$O$_3$ (Fe$^{3+}$) has been categorized as an amphoteric oxide. Namely, Fe$^{2+}$ is octahedrally coordinated by oxygen (Fe$^{3+}$ (6)) in a highly basic system and behave as a network modifier. On the contrary, Fe$^{3+}$ is tetrahedrally coordinated by oxygen (Fe$^{3+}$ (4)) in a highly basic system and behave as a network former. In other words, the changes in the coordination number of Fe$^{3+}$ has would affect the viscosity of the calcium ferrite slags. In the following section, the effect of the change in the coordination number of Fe$^{3+}$ on the viscosity has been discussed. However, the CF based slag could not be vitrified due to the limitation of quenching rate in the present study. Accordingly, the viscosity change of 40CaO–40SiO$_2$–20Fe$_2$O$_3$ (mol%) slag, the coordination structure of which were reported by Nagata et al., have been measured.

3.3. Viscosity and Structural Change with the Melting Time of 40CaO–40SiO$_2$–20Fe$_2$O$_3$ (mol%) Slag

Figure 9 shows the change in the viscosity and the fraction of Fe$^{2+}$, Fe$^{3+}$ (4) and Fe$^{3+}$ (6) ions for 40CaO–40SiO$_2$–20Fe$_2$O$_3$ (mol%) slag with the melting time at 1 773 K under air. Reference 14 employed as the fraction data of Fe$^{2+}$, Fe$^{3+}$ (4) and Fe$^{3+}$ (6) ions for 40CaO–40SiO$_2$–20Fe$_2$O$_3$ (mol%) slag. The starting material of the viscosity measurement was pre-melted under air for 120 min, which have the same thermal history as the reference.15 As shown in Fig. 9, the viscosity of 40CaO–40SiO$_2$–20Fe$_2$O$_3$ (mol%) slag decreased with the melting time. The fraction of Fe$^{2+}$ was not changed during the melting time, which indicates that the oxidation state of iron was equilibrated during the pre-melting process of the starting material. In contrast, Fe$^{3+}$ (4) decreased with the increase in fraction of Fe$^{3+}$ (6) with the melting time. The coordination structure of Fe$^{3+}$ was equilibrated after 120 min. From the viscosity and the reported data of the structural characterization, the decrease in the viscosity of 40CaO–40SiO$_2$–20Fe$_2$O$_3$ (mol%) slag was considered to be due to the increase in Fe$^{3+}$ (6) with the melting time. Therefore the viscosity change in the CF based slags with the melting time is also thought to be controlled by the same mechanism.

In the following section, temperature dependence of viscosity for the CF slag will be discussed.

3.4. Temperature Dependence of Viscosity for the Calcium Ferrite Slag

Figure 10 represents the temperature dependences of the viscosity for the CF slag with reported data of Sumita et al. The viscosity of the CF slag after the enough melting time (1 873 K and 1 773 K: the viscosity at the melting time of 300 min, 1 673 K: the viscosity at the melting time of 600 min) was employed as the equilibrated value. As shown in the figure, the viscosity of the CF slag (equilibrated value) decreased linearly with increasing temperature. However, in the present study, the temperature dependence of the viscosity for the CF slag (equilibrated value) was stronger than that of the reference data. In the present work in the temperature profile, if they could measure the viscosity without melting until the slag viscosity becoming constant at each of the examined temperature, the difference in the thermal history would affect the temperature dependence of the viscosity. Consequently, the viscosity...
measurement at temperature profile (d) has been conducted to clarify the effect of the thermal history on the temperature dependence of the viscosity for the CF slag. As shown in Fig. 10, the temperature dependence of viscosity for the CF slag at temperature profile (d) is in good agreement with that of the reference data. This agreement clearly indicates that the difference in the temperature dependence of viscosity for the CF slag was not based on the difference in researchers, but on the difference in the thermal history of the slag. Therefore, we conclude that the viscosity of the CF based slags is unveiled as a thermal history sensitive property. That is simply because CF based slag requires long time (120–240 min) to equilibrate the coordination structure of Fe$^{3+}$. Therefore, in the case of using the viscosity data of the calcium ferrite based slag, it is necessary to have a careful consideration on the thermal history of the slag. Otherwise the viscosity data of the slag might be somewhat misleading.

4. Conclusion

The viscosity changes of the CF based slags (CF, CF–5wt%SiO$_2$ or CF–5wt%Al$_2$O$_3$) with the melting time have been measured in the present study. The viscosity of the CF based slags decreased with the melting time at all the examined temperature. We could not directly observe the structural change of the CF based slag with the melting time at elevated temperature in the present work. However, the results of the oxidation state analysis for the quenched CF slag and the viscosity-structure relation of 40CaO–40SiO$_2$–20Fe$_2$O$_3$ (mol%) slag indicated that the decrease in the viscosity has been controlled by change in the coordination number of Fe$^{3+}$ in the CF based slags. In addition, the viscosity of the CF based slag was found to be sensitive on the thermal history before measurement. That is simply because CF based slag requires long time to equilibrate the coordination structure of Fe$^{3+}$ at each of the examined temperature.

The present work was a first step for clarifying the physical property of CF based slags. Accordingly, more of the measurements of physical property and in-situ observations of the structural change with melting time in the CF based slag have been required for goal understanding of the physical properties for the calcium ferrite based slags.

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