Influence of TiC on the Viscosity of CaO–MgO–Al₂O₃–SiO₂–TiC Suspension System

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The present study investigated the influence of TiC particle addition on the viscosity of CaO–MgO–Al₂O₃–SiO₂ melts by using the rotating cylinder method. It was found viscosity increased as increasing the volume fraction of TiC, but decreased as enhancing the rotation speed. The temperature dependence of viscosity for the same composition can be described by the Arrhenius law. However, temperature has little influence on the relative viscosity of TiC bearing slag. There is also no obvious difference of activation energies for different compositions with or without the addition of TiC solid particle. Therefore, the activation energy of solid-liquid mixture may be mainly determined by the composition of liquid phase. Two kinds of TiC with the particle sizes of 1.0 μm and 10 μm were used to study the influences of solid size on viscosity, and it was found the TiC particle with a small size can increase the viscosity much more greatly. The Einstein-Roscoe equation cannot be used directly to the TiC containing two-phase mixtures. By modifying the parameter, it can well describe the viscosity variation behavior. According to the calculated results, the maximum volume fraction increases as increasing the rotation speed or decreasing the particle size of TiC. The apparent volume of TiC is about 2.2–3.3 times of its real volume.

KEY WORDS: suspension system; relative viscosity; TiC; slag.

1. Introduction

During the high temperature smelting process, slags always play a significant role. The performance of slags is decided by its physicochemical properties, of which viscosity is the most important one. It is closely related to the mass transfer velocity in the slag which determines the reaction kinetics, as well as the effectively separation of slag and metal, etc. Lots of experimental1–2) and theoretical studies3–5) have been done to investigate the viscosity variation regularity of fully liquid slags. However, in many pyrometallurgical processes, there are always suspension systems composed of liquid slags and insoluble solid particles, for instance, liquid blast furnace slag containing TiC solid particle during the smelting of titanium bearing ore; convert slags containing CaO and 2CaO·SiO₂ solid particles; copper slags containing solid magnetite (Fe₃O₄) during the copper smelting if the atmosphere becomes too oxidized at the operating temperature.

However, due to the extremely difficulties in carrying out the viscosity measurement for the solid-liquid two-phase system at high temperature, the viscosity data about this kind of system is scarce. Wright et al. measured the viscosity of calcium ferrite slags and calcium alumino-silicate slags containing spinel particles.6,7) Seok et al. studied the viscous behavior of CaO–SiO₂–FeO–MgO slags saturated with dicalcium silicate (2CaO·SiO₂) with 8 mass% MgO at 1 873 K.8) Liquid-2CaO·SiO₂ mixtures and liquid-MgO mixtures were studied at the steelmaking temperature by Du et al.9) Bai et al. investigated the viscosities of CaO–MgO–Al₂O₃–SiO₂–TiO₂ blast furnace type slag containing TiC, but was short of systematic study and didn’t consider the possible reaction between TiO₂ and TiC.10) Study about the viscosity of this kind of high temperature suspension system not only has the meaning of engineering application, but also is helpful to the theoretical research. By comparing the measured viscosities with the calculated viscosities by different models, Du et al. concluded that Einstein-Roscoe equation was the only model applicable for the systems of Liquid-2CaO·SiO₂ mixtures and liquid-MgO mixtures at the steelmaking temperature, and no modification of the model parameter was found necessary, though the particles were not spherical.9) However, both Wright et al.7) and Seok et al.8) found that the parameters of Einstein-Roscoe equation should be adjusted to describe the viscosity variation behavior of suspension system.

Study about the influence of TiC particle on the viscosity of CaO–MgO–Al₂O₃–SiO₂ slag system at different temperatures, and assess the validation of Einstein-Roscoe equation. Meanwhile, in order to distinguish the effect of particle size of TiC on viscosity, two different kinds of TiC will be used.

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2. Experiment

Slag samples were prepared using reagent-grade SiO$_2$, Al$_2$O$_3$, MgO, and CaCO$_3$ powders. The particle sizes of the TiC were 1.0 μm and 10 μm. All the oxides reagents were calcined in a muffle furnace at 1273 K for 10 hours, to decompose any carbonate and hydroxide before use. Then the prepared CaO and other reagents were precisely weighed according to the compositions shown in Table 1, and then mixed in the agate mortar thoroughly. The composition of A0 without TiC addition is shown in Table 1. Based on the composition of A0, different volume percentages of TiC were added to prepare other compositions. Groups A and B include TiC particles with 1.0 and 10 μm in diameter, respectively. The mixtures of CaO, MgO, Al$_2$O$_3$ and SiO$_2$ were packed into a Mo crucible and pre-melted in an induction furnace at 1873 K for 2 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 by using the rotating cylinder method. The schematic diagram of the experimental apparatus can be found in our previous paper. The viscometer was calibrated by using castor oil at room temperature. 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 1823 K and retained for 60 min under the protection of Ar gas. Once the slag was melted, TiC particles were added to the melt, before immersing the spindle into the slag and measuring the viscosity. The bottom end of the spindle was 10 mm away from the crucible. Before viscosity measurement, sufficient stirring was exerted to make TiC solid particles distribute uniformly in the melt. After experimental measurements, the scanning electron microscope technology was used to check the distribution of TiC in the quenching sample after polishing. Figure 1 is the scanning micrograph of the quenched samples A2 and B2 I) in the middle position along the central axis of crucible; II) in the bottom position along the central axis; III) near the crucible wall in the position of half high, from which it can be concluded that TiC distributed uniformly during the viscosity measurement. The small white dots are the precipitated phase when cooling from the high temperature.

The viscosity measurement was carried out at every 25 K interval on cooling. At each experimental temperature before measuring, the melt was kept for 30 min first to ensure the melt uniform. Then, the measurements were carried out three times with different rotated speeds as 100, 150 and 200 rpm. All the measured viscosities were given in Table 2. After completing the viscosity measurements, the furnace was reheated up to 1823 K to pull out the spindle, which was cleaned for the next experiment.

3. Results

3.1. Influences of Rotation Speed and Temperature on Viscosity

The viscosity data for different compositions at different temperatures and rotation speeds are shown in Table 2. The variations of viscosity with temperature and rotation speed for composition A0 is shown in Fig. 2, from which it can be seen that the temperature dependence of viscosity for A0 can be described by the Arrhenius law, furthermore, for the

Table 1. Compositions for viscosity measurement.

| Sample | CaO mol fraction | MgO mol fraction | Al$_2$O$_3$ mol fraction | SiO$_2$ mol fraction | TiC volume fraction |
|--------|------------------|------------------|--------------------------|---------------------|---------------------|
| A0     | 0.42             | 0.12             | 0.09                     | 0.37                | 0                   |
| A1 and B1 |                  |                  |                          |                     | 0.02                |
| A2 and B2 |                  |                  |                          |                     | 0.04                |
| A3 and B3 |                  |                  |                          |                     | 0.06                |

Fig. 1. Scanning micrograph of the quenched samples A2 and B2 I) in the middle position along the central axis; II) in the bottom position along the central axis; III) near the crucible wall in the position of half high.
melt without TiC addition, rotation speed has little influence on the viscosity, thereby, the melt behaviors as Newtonian fluid. Figures 3–8 show the viscosity variation behavior of

Table 2. Measured viscosity values for different compositions at different temperatures.

| Composition | T, K | 1810 | 1784 | 1758 | 1733 | 1708 | 1682 |
|-------------|-----|------|------|------|------|------|------|
| A0 100 rpm | η, dPa.s | 3.54 | 4.16 | 5.07 | 6.16 | 7.58 | 9.71 |
| A1 100 rpm | η, dPa.s | 4.18 | 5.14 | 6.24 | 7.65 | 9.29 | 11.67 |
| A2 100 rpm | η, dPa.s | 5.58 | 6.86 | 8.11 | 10.12 | 12.57 |
| A3 100 rpm | η, dPa.s | 7.68 | 9.34 | 11.47 | 13.98 | 17.31 |
| B1 100 rpm | η, dPa.s | 3.99 | 4.85 | 5.88 | 7.24 | 8.92 | 11.13 |
| B2 100 rpm | η, dPa.s | 5.01 | 6.06 | 7.36 | 8.97 | 10.96 | 13.98 |
| B3 100 rpm | η, dPa.s | 6.94 | 8.38 | 10.16 | 12.39 | 15.37 | 19.51 |

Fig. 2. Viscosity variation of composition A0 with temperature and rotation speed.

Fig. 3. Viscosity variation of composition A1 with temperature and rotation speed.

Fig. 4. Viscosity variation of composition A2 with temperature and rotation speed.

Fig. 5. Viscosity variation of composition A3 with temperature and rotation speed.
compositions A1, A2, A3, B1, B2 and B3, respectively. From these figures, the temperature dependence of viscosity for all the compositions strictly fulfills the Arrhenius law. However, for both groups A and B, the influence of rotation speed becomes more and more remarkable at high volume fraction of TiC. When TiC addition is small such as A1 and B1, viscosity changes a little with rotation speed. But, as increasing the volume percentage of TiC, the slag system gradually departs from the Newtonian fluid behavior. The rotation speed dependence of viscosity for suspension system may be resulted from the reason that the rotation speed affects the apparent volume fraction of solid particle in the melt which will be discussed in the following sections.

3.2. Influence of Temperature on Relative Viscosity

The relative viscosity as the viscosity ratio of solid-liquid mixture to pure liquid is generally used in the suspension system. According to the data shown in Table 2, changes of relative viscosity with temperature for different compositions are shown in Fig. 9. The influence of temperature is seldom studied for the experimental difficulties that the volume percentage of solid phase and the composition of liquid phase will be change by precipitation or dissolution of solid phase as decreasing or increasing the temperature. However, in the present study, the temperature dependence of viscosity could be investigated since there is no chemical reaction between CaO–MgO–Al2O3–SiO2 liquid slag and TiC solid particle. From Fig. 9, temperature has little influence on the viscosity. This may be meaningful to the viscosity estimation of high temperature suspension system. It is not necessary to measure the viscosity value at many temperatures, but only viscosity value at one temperature. By combining with the viscosity data of pure liquid from measurement or calculation, the viscosity of suspension system at other temperatures can be obtained.

3.3. Influences of Rotation Speed, Particle Size and Volume Percentage of TiC on Relative Viscosity

According to the above analyses, the viscosity values at different temperatures for the same composition measured at the same rotation speed are almost the same, consequently, the average value at different temperatures was adopted. Figure 10 is the variation of relative viscosity with the rotation speed, particle size and volume percentage of TiC. It can be clearly seen that the relative viscosity decreases as increasing the rotation speed. The TiC containing high temperature solid-liquid mixture behaves as a shear thinning melt. It can also be concluded that the small TiC particle could increase the viscosity much more greatly than the large particle when the volume fraction is the same. However, all the theoretical models for describing the viscosity of suspension system didn’t consider the influence of particle size, such as the most widely used Einstein-Roscoe model shown in Eq. (1)

$$\eta = \eta_0 (1 - af)^{-n}$$

where $\eta$ and $\eta_0$ are the viscosity of solid-containing and solid-free melt, respectively; $f$ is the volume fraction of solid particles in the melt; $a$ and $n$ are constants. For spherical particles of a uniform size, Roscoe suggested $a$ and $n$ to be 1.35 and 2.5, respectively. From Fig. 10, it can also be found that relative viscosity increases as increasing the volume percentage of TiC, and the increment is much larger when the volume percentage of TiC is higher.
4. Discussion

(1) Since the temperature dependence of viscosity for all the compositions obeys the Arrhenius law, the activation energy of viscosity can be obtained as shown in Table 3. From Table 3, the activation energy is almost not affected by the rotation speed, volume percentage and the particle size of TiC. Consequently, the composition of liquid slag should be the main factor affecting the activation energy of suspension system.

(2) Even if Du et al. stated that the Einstein-Roscoe equation can be used directly with no modification required, but from Fig. 10, it can be seen that the calculated relative viscosities are much lower than the measured values. It was suggested the best fit can be obtained by allowing the parameters $a$ and $n$ or only $a$ to vary. The constant $n$ is related to the geometrical particle shape and can be assumed to be 2.5 for spherical solid particles. From Einstein-Roscoe Eq. (1), it can be seen that when the volume fraction of solid equals to the reciprocal value of $a$, the viscosity will become “infinite”. Therefore, $1/a$ represents the maximum volume fraction of solid $f_{\text{max}}$ that the melt could accommodate before the viscosity becomes “infinite”. In order to quantify the influence of solid phases on slag viscosity by Einstein-Roscoe equation, only parameter of $a$ is allowed to be changed to fit the experimental results. Parameter $a$ is optimized for groups A and B at different rotation speeds. The optimized values are shown in Table 4. Examples of the fitting effects for groups A and B at the rotation speed of 150 rpm are shown in Fig. 11. The maximum volume fraction $f_{\text{max}}$ of TiC can be estimated to be from 22% to 34% in the present experimental condition. It increases as enhancing the rotation speed. Furthermore, there is also a larger value of $f_{\text{max}}$ when the particle size of TiC is smaller. Roscoe used Eq. (1) (with the parameter values of $a$ and $n$ to be 1.35 and 2.5) to fit the experimental measured viscosity value to obtain the apparent volume fraction of solid phase. Following his treatment, the ratio of apparent volume fraction to the real volume fraction can be obtained (which is equal to the ratio of value of $a$ to 1.35) to be 3.28, 3.03 and 2.87, as well as 2.93, 2.44 and 2.21 for groups A and B at the rotation speed of 100, 150 and 200 rpm, respectively. Therefore, the apparent volume of solid particle is always several times of its real volume. Furthermore, the ratio of apparent volume fraction to the real volume fraction increases as the diameter of TiC powder decreases. In TiC, $x$ is always less than 1, the valency of Ti ion is unsaturated. Therefore, the Ti ion in the surface of TiC particle can absorb the nearby anion which results in lots of liquid slags moving with TiC during the viscous flow, thus a large apparent volume of TiC. Because the existence of the adsorption layer is resulted from the unsaturated Ti ion near the surface of particle, it is reasonable to consider that the thickness of adsorption layer should not increase linearly as increasing the TiC size, and there should be a smaller increment for a larger particle.

![Fig. 9. Change of relative viscosity with the temperature.](image1)

![Fig. 10. Change of relative viscosity with the volume fraction of TiC and the rotation speed.](image2)

| Table 3. Activation energy of different slags at different rotation speeds. |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Activation Energy (kJ/mol)  | A0                         | A1                         | A2                         | A3                         |
| 100 rpm                     | 199.75                     | 200.02                     | 201.81                     | 201.52                     |
| 150 rpm                     | 201.95                     | 201.02                     | 203.96                     | 199.70                     |
| 200 rpm                     | 202.01                     | 200.44                     | 204.35                     | 196.29                     |
| average                     | 201.24                     | 200.49                     | 203.37                     | 199.17                     |

| Table 4. Values for parameters $a$ and $f_{\text{max}}$ at different rotation speeds. |
|------------------------|------------------------|------------------------|------------------------|
| Parameter              | Group                  | 100 rpm                | 150 rpm                | 200 rpm                |
| $a$                    | Group A                | 4.43                   | 4.09                   | 3.87                   |
|                       | Group B                | 3.95                   | 3.29                   | 2.98                   |
| $f_{\text{max}}$      | Group A                | 0.226                  | 0.244                  | 0.258                  |
|                       | Group B                | 0.253                  | 0.304                  | 0.336                  |
The present study measured the influence of TiC particles addition on the viscosity of CaO–MgO–Al₂O₃–SiO₂ melts by using the rotating cylinder method. The following conclusions can be drawn.

(1) Viscosity increases as increasing the volume fraction of TiC solid particle, but decreases as enhancing the rotation speed.

(2) The temperature dependence of viscosity for the same composition can be described by the Arrhenius law. However, temperature has little influence on the relative viscosity. The activation energies of different compositions with or without TiC addition are almost the same. Therefore, the composition of the liquid phase is the main factor affecting the activation energy.

(3) For the same volume fraction of TiC addition, the composition with the smaller TiC particle will has a larger viscosity.

(4) The Einstein-Roscoe equation cannot be used directly to the TiC containing two-phase mixtures. By allowing the parameter a to vary with the rotation speed and the particle size of TiC, the Einstein-Roscoe can well describe the viscosity variation behavior. According to the model calculated results, the maximum volume fraction increases as increasing the rotation speed or decreasing the particle size of TiC. The apparent volume of TiC is calculated to be 2.2–3.3 times of its real volume. The large apparent volume of TiC particle may be resulted from the liquid slags adsorbed on the TiC solid particle which move together with TiC particle under the external force.

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