Thermodynamic Simulation of Viscosity of TiO$_2$-Ti$_2$O$_3$-CaO Ternary Slag

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Abstract. The viscosity of high titanium slag at high temperature is one of the key factors of slag-iron separation. Based on the Einstein-Roscoe equation, thermodynamic simulation of viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag is studied by using FactSage$^*$ software, and the effects of temperature, CaO content and solid-phase particles on the viscosity of slag were studied. The results show that the increase of CaO content has the effect of reducing melting temperature and viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag. After the TiO$_2$-Ti$_2$O$_3$-CaO ternary slag is completely melted, the increase of temperature has little effect on viscosity of slag, and the viscosity is about 110~125mPa·s. When the temperature is lower than melting temperature, TiO$_2$-Ti$_2$O$_3$-CaO ternary slag will precipitate solid-phase particles, and the precipitation process is carried out in stages, and with the decrease of temperature, the precipitation will increase and the viscosity will sharply increase. TiO$_2$-Ti$_2$O$_3$-CaO ternary titanium slag has obvious characteristics of short slag.

1. Introduction
There is a wealth of titanium resources in China, but it is mainly for the ilmenite with the low grade and high impurity content, which will limit the production of titanium dioxide and sponge titanium. With the rapid development of titanium dioxide and sponge titanium industry, the demand for high-grade titanium concentrates is increasing. Therefore, the processing of rich ilmenite resources into titanium-rich material is the urgent task for the development of titanium dioxide and titanium materials industry in China [1].

High titanium slag is a high quality raw material in the production process of titanium dioxide and sponge titanium. Electric furnace smelting is one of the main methods to prepare high titanium slag at present. The good effect of slag-iron separation in the smelting process is the key to ensuring the smooth production and the quality of the product. The viscous flow characteristics of high titanium slag in the furnace are especially important [2].

Due to the high melting point and complex composition of high titanium slag, the related research on the viscosity of high titanium slag at home and abroad is rare. In 1957, Researchers at the Soviet Academy of Sciences pioneered a study of the impact of the composition on the viscosity of titanium slag [3]. In the 1960s, a group of foreign researchers for viscosity of titanium slag was related to explore. Until today, foreign reports on the viscosity of titanium slag is still less [4,5]. In the last century 80's, the domestic began to study the viscosity of titanium slag [6].
There is large inequality on high titanium slag with its high demand and research results of viscosity. Solving the blank problem of viscosity of some slag system has become a task that researchers need to solve urgently.

In the past, the researchers mainly got through the experimental method to study the change rules of viscosity of high titanium slag. Due to high melting point and other properties of high titanium slag, it leads to difficult test and high cost. In this study, thermodynamic simulation of viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag was studied by using FactSage® software. The effects of temperature, CaO content and solid-phase particles on the viscosity of slag were studied. Fill the gaps in the domestic viscosity data of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag.

2. Research methods

In 1906, Einstein [7] proposed a method for describing the viscous behavior of melting containing solid-phase particles, as shown in equation (1). Einstein pointed out that the equation is applicable regardless of the size distribution of the sphere.

$$\eta = \eta_0 (1 + 2.5c)$$  (1)

Where $\eta$ is the viscosity of melting containing the solid-phase particles; $\eta_0$ is the viscosity of melting in the fully molten state; and $c$ is the volume concentration.

With the advancement of the theory, the researchers have improved the equation (1), where the typical model is Einstein-Roscoe equation [8], as shown in equation (2).

$$\eta = \eta_0 (1 - af)^{-n}$$  (2)

Where $f$ is the volume fraction of solid-phase particles; $a$ and $n$ are constants. Roscoe assumes that the solid-phase particles are spherical, and he gives $a$ and $n$ values. According to Seong-Ho S [9], it is assumed that the density values of the solid-phase particles and the melting are the same, that is, the solid volume fraction is equal to the solid mass fraction.

FactSage is one of the representative thermodynamic software, developed by the FACT thermodynamics database developed by Canada, and integrated with the Germany developed ChemSage database to become a large thermal chemical database running on Windows. It is widely used in pyrometallurgy, materials science, hydrometallurgy and other fields [10].

This paper bases on the Einstein-Roscoe equation, uses the Equilib and Viscosity modules of FactSage® thermodynamics software and selects the FToxid database to study the viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag. According to the phase diagram of slag, the temperature range of the study is 1620 ~ 1750 °C (step 5 °C). The pressure is a standard atmospheric pressure. The phase diagram of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag is shown in Figure 1.

Simulation scheme of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag was determined by the composition of high titanium slag in Wuding Company of Yunnan Metallurgical New Titanium Industry: reduction degree was 0.35 ~ 0.39 and the CaO content was 0.4% ~ 2%. The chemical composition of high titanium slag of the factory is shown in Table 1, simulation scheme of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag system is shown in Table 2.

The reduction degree ($R$) is calculated as:

$$R = \frac{M_{TiO_2}}{1.111 \times M_{TiO_2} + M_{Ti_2O_3}} \times 100\%$$  (3)

Where $M_{TiO_2}$ and $M_{Ti_2O_3}$ respectively represent the mass of TiO$_2$ and Ti$_2$O$_3$. 

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Figure 1. The phase diagram of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag

Table 1. The chemical composition of high titanium slag (wt\%).

|       | TiO$_2$ | Ti$_2$O$_3$ | FeO  | MnO  | CaO  | MgO  | SiO$_2$ | Al$_2$O$_3$ | Cr$_2$O$_3$ | ZrO$_2$ |
|-------|---------|-------------|------|------|------|------|---------|-------------|-------------|---------|
| wt\%  | 55.441  | 35.172      | 2.417| 1.245| 0.177| 0.861| 2.104   | 1.824       | 0.058       | 0.186   |

Table 2. Simulation Scheme of TiO$_2$-Ti$_2$O$_3$-CaO Ternary Slag System (wt\%).

|       | TiO$_2$ | Ti$_2$O$_3$ | CaO |
|-------|---------|-------------|-----|
| R=0.35| 63.33   | 36.27       | 0.40|
|       | 63.08   | 36.12       | 0.80|
|       | 62.82   | 35.98       | 1.20|
|       | 62.57   | 35.83       | 1.60|
|       | 62.31   | 35.69       | 2.00|
| R=0.37| 61.17   | 38.43       | 0.40|
|       | 60.92   | 38.28       | 0.80|
|       | 60.68   | 38.12       | 1.20|
|       | 60.43   | 37.97       | 1.60|
|       | 60.19   | 37.81       | 2.00|
| R=0.39| 59.00   | 40.60       | 0.40|
|       | 58.76   | 40.44       | 0.80|
|       | 58.52   | 40.28       | 1.20|
|       | 58.29   | 40.11       | 1.60|
|       | 58.05   | 39.95       | 2.00|

3. Results and discussion

3.1. Effect of temperature on the viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag

Temperature is one of the main factors on affecting viscosity. The melting property of the high titanium slag is expressed by melting temperature and melt-property temperature. Melting temperature is the temperature at which the solid-phase disappears completely during the heating of titanium slag. Melt-property temperature indicates the lowest temperature at which the slag is free to flow. Melting temperature (A) and melt-property temperature (B) of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag is simulated by
FactSage® software as shown in Figure 2. It can be seen from Figure 2 that the reduction degree and the CaO content can affect melting temperature and melt-property temperature of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag system. When the CaO content is the same, melting temperature and melt-property temperature of high titanium slag decreases with the increase of reduction degree. When the reduction degree is the same, melting temperature and melt-property temperature of high titanium slag decreases with the increase of CaO content. In this study, melting temperature of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag is 1675 °C ~ 1705 °C, melt-property temperature of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag is 1655 °C ~ 1700 °C. Under the same conditions, melt-property temperature is lower than melt temperature of 5 °C ~ 20 °C.

![Figure 2. The melting property of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag](image)

Effect of temperature on the viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag was calculated. The results are shown in Figure 3, for the given composition of slag, when the temperature is higher than melting temperature, with the temperature increases, the viscosity value is almost unchanged, and the viscosity value is low, about 110 ~ 125 mPa·s; when the temperature is lower than melting temperature, with the temperature decreases, the viscosity value increases rapidly. There is a distinct turning-point in the viscosity-temperature curve, TiO$_2$-Ti$_2$O$_3$-CaO ternary slag has obvious characteristics of short slag.

![Figure 3. Effect of temperature on the viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag](image)

### 3.2. Effect of CaO content on the viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag

The effect of CaO content on the viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag is shown in Figure 4. The slag temperature of both groups (1) and (2) is higher than their melting temperature, and high titanium slag is completely melted. With the increase of CaO content, the viscosity value decreases slowly. (3) and (4), with the decrease of CaO content, the slag temperature is lower than melting temperature, and the solid-phase particles precipitate from molten slag, and the viscosity value increases. The increase
of CaO content can reduce the viscosity of slag, and the flowability becomes better, that is to say, CaO is a good cosolvent.

![Figure 4](image)

**Figure 4.** Effect of CaO content on the viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag

3.3. Effect of solid-phase particles on the viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag

The phase and viscosity of TiO$_2$-Ti$_2$O$_3$-1.2%CaO (R=0.37) ternary slag are shown in Figure 5. It can be seen from Figure 5 that melting temperature of TiO$_2$-Ti$_2$O$_3$-1.2%CaO (R=0.37) ternary slag is 1690.24 °C, when the temperature is higher than melting temperature, titanium slag is in the completely molten state, the viscosity value is almost constant; when the temperature is lower than melting temperature, solid-phase particles in the molten titanium slag are formed, which is not conducive to the movement. With the decrease of the temperature, the precipitation of solid-phase particles increases abruptly, the viscosity value increases rapidly, and the flowability becomes poor. When the temperature drops to 1660 °C, the mass fraction of solid-phase particles in the slag is 43.731%, the viscosity value is about 1351 mPa·s, and the flowability was poor. When the temperature drops to about 1375 °C, the liquid phase completely disappears, leaving only Ti$_x$O$_y$ and Perovskite (CaTiO$_3$).

![Figure 5](image)

**Figure 5.** Phase and viscosity of TiO$_2$-Ti$_2$O$_3$-1.2%CaO (R=0.37) ternary slag.

The effect of solid mass fraction on the relative viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag is shown in Figure 6. It can be seen from Figure 6 that the relative viscosity increases with the increase of the mass fraction of solid, and the curve have obvious turning-point when the mass fraction of solid is about 53%.
4. Conclusions
1) When the TiO$_2$-Ti$_2$O$_3$-CaO ternary slag is completely melted, the temperature has little effect on the viscosity of slag, and the viscosity value is low (about 110 ~ 125mPa·s). When the temperature is lower than melting temperature, the viscosity value increases sharply with the decrease of the temperature; the slag system has obvious characteristics of short slag.
2) CaO content can reduce the melting temperature and viscosity of TiO$_2$-Ti$_2$O$_3$-CaO ternary slag.
3) When the temperature is lower than melting temperature, TiO$_2$-Ti$_2$O$_3$-CaO ternary slag will precipitate solid-phase particles, the viscosity value will increases rapidly.

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