Combined Effect of SiO₂ and O₂ on the Crystallization Behavior of Modified Ti-Bearing Blast Furnace Slag

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ABSTRACT: FactSage simulation, X-ray diffraction (XRD), and scanning electron microscopy (SEM) coupled to energy-dispersive spectroscopy (EDS) analyses were performed to explore the combined influence of SiO₂ and O₂ on the crystallization behavior of modified Ti-bearing blast furnace slag. The results of FactSage simulation showed that an increase in the added amount of SiO₂ was beneficial to the conversion of Ti-bearing minerals into simple titanium oxides. An increase in oxidation time was conducive to the transformation of low-valent titanium oxides to tetravalent titanium oxide. Therefore, Ti components were precipitated only in the form of rutile under the optimal added amount of SiO₂ (40 g) and the optimum oxidation time (126 s). The results of XRD and SEM analyses were well in agreement with the results of FactSage simulation. Moreover, the mechanism of formation of rutile and glassy phases was discussed.

1. INTRODUCTION

China has abundant titanium resources, 95% of which are in the form of vanadium–titanium magnetite stored in the southwestern part of the country.¹ Currently, ore containing approximately 30% Fe, 10% TiO₂, and 0.3% V₂O₅ is smelted in blast furnaces at Panzhihua Iron and Steel Corporation. Most Ti components in the ore are separated from iron and enriched in the molten slag (22–25% TiO₂). More than 3 million tons of blast furnace slag are generated in China every year. In the last few years, several methods for treating the slag have been studied, such as flotation separation, magnetic separation, hydrometallurgy, and pyrometallurgy.² Nevertheless, the recovery efficiency of Ti components using those methods is relatively low, and the slag has not been used efficiently.³ Owing to the dispersive distribution of Ti constituents in various fine-grained (<10 μm) mineral phases with complex interfacial combinations, it is difficult to recover them via traditional separation methods.¹

Therefore, a method for selective crystallization and separation was proposed.⁴ There are many studies⁵–¹⁶ on enriching the Ti components in blast furnace slag into perovskite. Nevertheless, it has been proved that perovskite is difficult to be extracted due to its dendrite structure and the similar density with other phases. Compared to perovskite, rutile has the advantages of a high added value and high density (4.2–4.3 g/cm³). Therefore, it is appropriate to enrich Ti components to the rutile phase. There are some studies on the selective precipitation and separation of the rutile phase. Li et al.¹⁷ investigated the crystallization behavior of rutile in synthesized Ti-containing blast furnace slag. Sun et al.¹⁸ investigated the effect of P₂O₅ on the crystallization behaviors of synthesized Ti-bear- ing blast furnace slags using the single hot thermocouple technique. In the above two studies, the transformation of perovskite to rutile was realized by adding SiO₂ or P₂O₅ in a neutral atmosphere. However, the products still contain other Ti-bearing phases except rutile, and contain a variety of gangue phases. Zhang et al.¹⁹ studied the crystallization and coarsening kinetics of rutile in modified Ti-bearing blast furnace slag. Zhang et al.²⁰ studied the thermodynamic analysis of the extraction of synthetic rutile from high-titania slag. Zhang et al.²¹ investigated the synthesis of rutile from high-titania slag by pyrometallurgical route. Zhang et al.²² investigated the effect of oxidation on phase transformation in Ti-bearing blast furnace slag. The above four studies were conducted to achieve the transformation of perovskite to rutile by adding SiO₂ or P₂O₅ in an oxidizing atmosphere, and the products contain only rutile and glassy phases. Nevertheless, there are few studies on the mechanism of formation of rutile and glassy phases in the modified slag obtained by adding SiO₂ and O₂.

This study aimed to explore the combined effect of SiO₂ and O₂ on the crystallization behavior of modified Ti-bearing blast furnace slag. The relationships between the added SiO₂ content, oxidation time, and precipitation phases were established using
FactSage simulation. To verify the validity of the FactSage simulation, relevant experiments were carried out. Moreover, the rutile precipitation mechanism was explained by the standard Gibbs free-energy change of reaction, and the mechanism of formation of glassy phase was discussed via the viscosity and structure of molten slag.

2. RESULTS AND DISCUSSION

2.1. FactSage Simulation for the Effect of SiO₂ on Crystallization Behavior. We fixed the oxidation time, the amount of Ti-bearing blast furnace slag, and the amount of titanium slag to 126 s, 222 g, and 278 g, respectively. Then, we used FactSage to simulate the effect of the added amount of SiO₂.
on the crystallization behavior of the modified slag. The simulation results are shown in Figures 1−3.

As shown in Figure 1a−f, the first precipitation phases except rutile and CaO$_2$ are all anorthite. When anorthite starts to precipitate, the amounts of rutile are 183, 193, 208, 213, 214, and 222 g, respectively. As shown in Figure 2, the crystallized temperature of rutile increases with an increase in the added amount of SiO$_2$. The aforementioned results indicate that an increase in the added amount of SiO$_2$ is beneficial to the precipitation of rutile crystals but not to that of other crystals except CaO$_2$. This can be explained by eqs 1 and 2. From the Einstein−Roscoe equation $1,23$ it is known that the viscosity of molten slag increases with increasing volume fraction of rutile. It can be seen from the Stokes−Einstein equation $2,24$ that an increase in viscosity results in a decrease in diffusion coefficient, while a decrease in diffusion coefficient inhibits the precipitation of other crystals except rutile.

$$\eta = \eta_0(1 - \phi)^n$$  \hspace{1cm} (1)

$$D = (kT) / (3\pi\eta d)$$  \hspace{1cm} (2)

Here $\eta$ is the viscosity of the solid−liquid mixture; $\eta_0$ is the viscosity of liquid; $\phi$ is the volume fraction of solid; $a$ and $n$ are constants; $D$ is the diffusion coefficient; $k$ is the Boltzmann constant; $T$ is temperature; and $d$ is the diameter of particle.

As shown in Figure 3, when the added amount of SiO$_2$ is 10 g, the Ti-containing phases are rutile, anosovite, and sphene. As the added amount of SiO$_2$ increases from 10 to 30 g, the amount of rutile increases, the amount of anosovite decreases, and sphene phase disappears. When the added amount of SiO$_2$ increases to 40 g, the amount of rutile increases and anosovite also disappears. As the added amount of SiO$_2$ increases from 40 to 60 g, the amount of rutile remains unchanged. Therefore, the optimal added amount of SiO$_2$ is 40 g. Moreover, the results indicate that an increase in the added amount of SiO$_2$ is beneficial to the conversion of Ti-containing minerals (anosovite and sphene) into rutile.

### 2.2. FactSage Simulation for the Effect of O$_2$ on Crystallization Behavior

We fixed the added amount of SiO$_2$, the amount of Ti-bearing blast furnace slag, and the amount of titanium slag to 40, 222, and 278 g, respectively. Then, we used FactSage software to simulate the effect of oxidation time on the crystallization behavior of the modified slag. The simulation results are shown in Figures 4−6.

**Figure 2.** Relationship between the crystallized temperature of rutile and the added amount of SiO$_2$.

As shown in Figure 4a, when the oxidation time is 0 s, the main Ti-containing phases are anosovite and sphene, while the amount of rutile is extremely low, implying that O$_2$ is essential for the conversion of anosovite and sphene into rutile. As shown in Figure 4b−f, the first precipitation phases except rutile and CaO$_2$ are anosovite, anorthite, anosovite, cordierite, and cordierite, respectively. When these phases start to precipitate, the amounts of rutile are 91, 180, 213, 222, and 228 g, respectively. As shown in Figure 5, the crystallized temperature of rutile increases with an increase in oxidation time. The above results indicate that an increase in oxidation time is beneficial to the precipitation of rutile crystals but not to that of other crystals except CaO$_2$. This can also be explained by eqs 1 and 2.

As shown in Figure 6, as the oxidation time increases from 0 to 126 s, the amount of rutile significantly increases, while anosovite and sphene disappear. When the oxidation time increases to 210 s, the amount of rutile remains unchanged. Thus, the optimum oxidation time is 126 s. It can be concluded that an increase in oxidation time is beneficial to the conversion of Ti-containing minerals into rutile.

### 2.3. Experimental Verification of the Effect of SiO$_2$ on Crystallization Behavior

To verify the authenticity of theoretical analysis, we fixed the oxidation time to 126 s and carried out relevant experiments for the effect of the added amount of SiO$_2$ on phase transformation. The X-ray diffraction (XRD) patterns and scanning electron microscope (SEM) pictures of the modified slag under different added amounts of SiO$_2$ are shown in Figures 7 and 8, respectively. The results of the energy-dispersive spectroscopy (EDS) analysis of each point in Figure 8 are provided in Table 1.

It can be seen from Figure 7 that Ti components existed as anosovite and rutile when the added amounts of SiO$_2$ were 10, 20, and 30 g. However, the Ti-bearing phase was only rutile when the added amount of SiO$_2$ was more than 40 g. As shown in Figure 8 and Table 1, P1, P5, and P9 were rutile, while P3, P7, and P12 were anosovite. It indicated that Ti components were present as rutile and anosovite when the added amounts of SiO$_2$ were 10, 20, and 30 g. As the added amount of SiO$_2$ increased to 40 g, anosovite was not found in the modified slag except rutile. Moreover, with an increase in the added amount of SiO$_2$, the contents of Mg, Al, Fe, and Mn in anosovite phase gradually decreased, while the contents of Mg, Al, Fe, and Mn in the matrix phase gradually increased, implying that an increase in the added amount of SiO$_2$ was conducive to the migration of Mg, Al, Fe, and Mn elements from anosovite to matrix.

**Figure 3.** Relationship between the final amount of Ti-bearing precipitation phases and the added amount of SiO$_2$.
results of SEM analysis were well in agreement with the results of XRD analysis, i.e., an increase in the added amount of SiO₂ promoted the conversion of anosovite into rutile, which was consistent with the results of FactSage simulation.

2.4. Experimental Verification of the Effect of O₂ on Crystallization Behavior. We fixed the added amount of SiO₂ to 40 g and carried out relevant experiments for the effect of oxidation time on phase transformation. The XRD patterns and SEM pictures of the modified slag under different oxidation times are shown in Figures 9 and 10, respectively. The results of the EDS analysis of each point in Figure 10 are provided in Table 2.

Figure 4. Relationship between oxidation time and precipitation phases: (a) 0 s, (b) 42 s, (c) 84 s, (d) 126 s, (e) 168 s, and (f) 210 s.
As shown in Figure 9, when the oxidation time was 0 s, Ti compositions were present as anosovite. When oxidation times were 42 and 84 s, Ti components existed as anosovite and rutile, respectively. When the oxidation time was greater than 126 s, Ti-bearing mineral phase was only rutile. As shown in Figure 10 and Table 2, the points P2−P5 were all anosovite, implying that Ti components were present as anosovite when the oxidation time was 0 s. The points of P6 and P8 were anosovite and rutile, respectively, and the points of P10 and P12 were anosovite and rutile, respectively. It indicated that Ti components existed in the form of anosovite and rutile when oxidation times were 42 and 84 s, respectively. As the oxidation time increased to 126 s, anosovite was not found in the modified slag except rutile. In a word, the results of SEM analysis were well in agreement with the results of XRD analysis, i.e., an increase in oxidation time promoted the conversion of anosovite into rutile, which corresponded with the results of FactSage simulation.

It was found by the XRD analysis (Figures 7 and 9) that there were rutile and anosovite in the modified slag. However, it can be observed from the SEM analysis (Figures 8 and 10) that there were three phases in the modified slag, i.e., rutile, anosovite, and matrix. It indicated that the matrix phase of the modified slag was the glassy phase.

From the results of FactSage simulation, the phase compositions of the modified slag consisted of rutile, anosovite, sphene, clinopyroxene, anorthite, etc. From the experimental results, the modified slag only contained rutile, anosovite, and glassy phases. The reason why the results of FactSage simulation were different from the experimental results was that the simulation cannot consider the effect of dynamics on crystallization behavior.

2.5. Mechanism of Formation of Rutile. To study the mechanism of formation of rutile, we calculated the standard Gibbs free-energy changes of reactions 3−12 by FactSage software. The results are shown in Figure 11.

\begin{align*}
\text{CaO} + \text{SiO}_2 + \text{TiO}_2 &= \text{CaSiTiO}_5 \\
\text{CaO} + 2\text{SiO}_2 + \text{MgO} &= \text{CaMgSi}_2\text{O}_6 \\
\text{CaO} + 2\text{SiO}_2 + \text{Al}_2\text{O}_3 &= \text{CaAl}_2\text{Si}_2\text{O}_8 \\
2\text{TiO}_2 + \text{MgO} &= \text{MgTi}_2\text{O}_5 \\
\text{TiO}_2 + \text{Al}_2\text{O}_3 &= \text{Al}_2\text{Ti}_5\text{O}_8 \\
2\text{TiO}_2 + \text{TiO} &= \text{Ti}_3\text{O}_3 \\
\text{TiO}_2 + \text{Ti}_2\text{O}_3 &= \text{Ti}_3\text{O}_5 \\
2\text{TiO} + \text{O}_2 &= 2\text{TiO}_2 \\
2\text{Ti}_3\text{O}_5 + \text{O}_2 &= 4\text{TiO}_2 \\
2\text{Ti}_3\text{O}_5 + \text{O}_2 &= 6\text{TiO}_2
\end{align*}

It is well known that the molecular formula of anosovite can be represented by \((\text{AO} \cdot 2\text{TiO}_2) \cdot (\text{B}_2\text{O}_3 \cdot \text{TiO}_2)\). In this work, AO are divalent oxides including MgO and TiO, and B2O3 are trivalent oxides containing Al2O3 and Ti2O3. Therefore, the precipitation reactions of anosovite can be expressed by reactions 6−9. As shown in Figure 11a, the standard Gibbs free-energy changes of reactions 4 and 5 are less than those of reactions 3, 6, and 7, which implies that reactions 3, 6, and 7 are inhibited with an increase in the added amount of SiO2, i.e., the precipitation of anosovite and sphene (CaSiTiO5) is restrained. Therefore, Ti components can only exist as simple titanium oxides, such as TiO, Ti2O3, Ti3O5, and TiO2.

As shown in Figure 11b, the standard Gibbs free-energy changes of reactions 10, 11, and 12 are less than those of reactions 8 and 9, indicating that reactions 8 and 9 are inhibited with an increase in oxidation time, i.e., the precipitation of anosovite is restrained. Hence, Ti components are present as TiO2.

In summary, when O2 and SiO2 are simultaneously added to the modified slag, it can be seen from Figure 11 that reactions 3, 6, 7, 8, and 9 are inhibited and Ti components can only exist in the form of TiO2. Therefore, TiO2 converts into rutile at a high
temperature. This indicates that the addition of SiO₂ and O₂ is indispensable for the preparation of rutile.

2.6. Mechanism of Formation of Glassy Phase. To study the mechanism of formation of the glassy phase, some slags with a temperature of 1300 °C were quenched in water, and the viscosity of the modified slag was measured. The metallographic pictures, rutile volume fraction, and viscosity are shown in Figures 12–14, respectively.

As shown in Figures 12 and 13, the volume fraction of rutile crystals increased with an increase in the added amount of SiO₂ and oxidation time, implying that an increase in the added amount of SiO₂ and oxidation time is beneficial to the precipitation of rutile crystals. It can be seen from formula 1 that an increase in the volume fraction of rutile crystals increased the viscosity of molten slag. It can also be observed from Figure 14 that an increase in the added amount of SiO₂ and oxidation time increased the viscosity of the molten slag. Thus, it can be concluded from formula 2 that an increase in the viscosity of molten slag decreased the diffusion coefficient, thereby inhibiting the precipitation of other crystals except rutile. This is the main reason for the formation of glassy phase.

Table 1. EDS Analysis of Each Point in Figure 8

| points | O (%) | Mg (%) | Al (%) | Si (%) | Ca (%) | Ti (%) | Mn (%) | Fe (%) |
|--------|-------|--------|--------|--------|--------|--------|--------|--------|
| P1     | 35.03 |        |        |        |        |        |        | 0.75   |
| P2     | 41.00 | 6.54   | 11.38  | 16.77  | 15.07  | 2.09   | 3.28   | 3.87   |
| P3     | 42.04 | 7.92   | 6.56   |        |        | 40.03  | 0.81   | 2.64   |
| P4     | 41.41 | 6.67   | 11.37  | 16.31  | 14.49  | 2.50   | 3.33   | 3.92   |
| P5     | 32.02 |        |        |        |        |        |        |        |
| P6     | 38.76 | 7.95   | 11.43  | 16.18  | 15.68  | 2.49   | 3.14   | 4.35   |
| P7     | 41.46 | 5.59   | 4.95   |        |        | 44.97  | 1.13   | 1.90   |
| P8     | 38.78 | 7.86   | 11.25  | 16.65  | 15.52  | 2.57   | 3.08   | 4.29   |
| P9     | 35.78 |        |        |        |        |        |        | 0.58   |
| P10    | 37.14 | 8.40   | 13.02  | 16.94  | 13.95  | 2.71   | 3.45   | 4.39   |
| P11    | 37.09 | 8.52   | 12.96  | 16.63  | 14.13  | 2.97   | 3.37   | 4.33   |
| P12    | 40.67 | 3.54   | 2.47   |        |        |        |        | 51.83  |
| P13    | 40.9  |        |        |        |        |        |        | 0.65   |
| P14    | 40.9  |        |        |        |        |        |        | 0.84   |
| P15    | 40.9  |        |        |        |        |        |        |        |
| P16    | 40.9  |        |        |        |        |        |        |        |
| P17    | 40.9  |        |        |        |        |        |        |        |
| P18    | 36.26 | 9.71   | 13.83  | 16.04  | 14.21  | 1.56   | 3.63   | 4.76   |

2.6. Mechanism of Formation of Glassy Phase. To study the mechanism of formation of the glassy phase, some slags with a temperature of 1300 °C were quenched in water, and the viscosity of the modified slag was measured. The metallographic pictures, rutile volume fraction, and viscosity are shown in Figures 12–14, respectively.

As shown in Figures 12 and 13, the volume fraction of rutile crystals increased with an increase in the added amount of SiO₂ and oxidation time, implying that an increase in the added amount of SiO₂ and oxidation time is beneficial to the precipitation of rutile crystals. It can be seen from formula 1 that an increase in the volume fraction of rutile crystals increased the viscosity of molten slag. It can also be observed from Figure 14 that an increase in the added amount of SiO₂ and oxidation time increased the viscosity of the molten slag. Thus, it can be concluded from formula 2 that an increase in the viscosity of molten slag decreased the diffusion coefficient, thereby inhibiting the precipitation of other crystals except rutile. This is the main reason for the formation of glassy phase.
According to the theory of molten slag structure, Si$^{4+}$ was to form a $[\text{SiO}_4]^{4-}$ tetracoordinate ion and acted as a network former, which interconnected and finally formed three-dimensional networks in the molten slag. Ti$^{3+}$ was to form a hexacoordinate ion and acted as a network modifier, which broke the oxygen bonds of $[\text{SiO}_4]^{4-}$ and played the role of molten slag depolymerization. Ti$^{4+}$ can form a $[\text{TiO}_4]^{4-}$ tetracoordinate ion, which usually fits into the three-dimensional silicate units and enhances the overall polymerization of the molten slag. When O$_2$ was flowed into the molten slag, low-valent titanium elements (the raw materials mainly contained Ti$^{3+}$) were oxidized to Ti$^{4+}$, resulting in the increase of the $[\text{TiO}_4]^{4-}$ tetracoordinate ion. Therefore, the addition of SiO$_2$ and O$_2$ was conducive to the increase of tetracoordinate ions, which increased the viscosity of molten slag and promoted the formation of glassy phase.

### 3. CONCLUSIONS

To study the combined effect of SiO$_2$ and O$_2$ on the crystallization behavior of the modified slag, FactSage simulation and relevant experiments were performed. Moreover, the mechanism of formation of rutile and glassy phases was discussed. The results were summarized as follows:

1. An increase in the added amount of SiO$_2$ was beneficial to the conversion of Ti-bearing minerals into simple titanium oxides, such as TiO, Ti$_2$O$_3$, Ti$_3$O$_5$, and TiO$_2$.
2. An increase in oxidation time was conducive to the transformation of low-valent titanium oxides to tetravalent titanium oxide.
3. Ti components in the modified slag were precipitated only in the form of rutile under the optimal added amount of SiO$_2$ (40 g) and the optimum oxidation time (126 s).
4. The crystallized temperature of rutile increased with an increase in the added amount of SiO$_2$ or oxidation time.

![Figure 10. SEM pictures of the modified slag under different oxidation times: (a) 0 s, (b) 42 s, (c) 84 s, and (d) 126 s.](image)

| points | O (%) | Mg (%) | Al (%) | Si (%) | Ca (%) | Ti (%) | Mn (%) | Fe (%) |
|--------|-------|--------|--------|--------|--------|--------|--------|--------|
| P1     | 37.51 | 8.33   | 13.31  | 16.36  | 13.97  | 3.15   | 2.92   | 4.45   |
| P2     | 36.26 | 2.31   | 1.97   | 58.45  | 0.37   | 0.64   |
| P3     | 35.87 | 2.42   | 1.86   | 58.85  | 0.31   | 0.69   |
| P4     | 36.45 | 2.16   | 2.07   | 58.28  | 0.46   | 0.58   |
| P5     | 36.53 | 2.08   | 2.14   | 58.16  | 0.35   | 0.74   |
| P6     | 36.98 | 2.01   | 2.18   | 57.77  | 0.44   | 0.62   |
| P7     | 37.36 | 8.25   | 13.68  | 16.57  | 14.04  | 2.58   | 3.15   | 4.37   |
| P8     | 33.75 |       |        |        |        | 66.25  |
| P9     | 37.52 | 8.16   | 13.49  | 16.44  | 13.87  | 2.98   | 3.29   | 4.25   |
| P10    | 38.14 | 1.85   | 1.93   | 57.14  | 0.36   | 0.58   |
| P11    | 37.78 | 8.39   | 13.72  | 16.32  | 13.95  | 2.73   | 3.07   | 4.04   |
| P12    | 36.19 |       |        |        |        | 63.81  |
| P13    | 37.93 | 8.16   | 13.66  | 16.59  | 14.12  | 1.87   | 3.34   | 4.33   |
| P14    | 40.9  |       |        |        |        | 59.1   |
| P15    | 40.9  |       |        |        |        | 59.1   |
| P16    | 40.9  |       |        |        |        | 59.1   |
| P17    | 40.9  |       |        |        |        | 59.1   |
| P18    | 40.9  |       |        |        |        | 59.1   |
| P19    | 40.9  |       |        |        |        | 59.1   |
| P20    | 36.26 | 9.71   | 13.83  | 16.04  | 14.21  | 1.56   | 3.63   | 4.76   |

Table 2. EDS Analysis of Each Point in Figure 10
The precipitation of rutile significantly inhibited the precipitation of other phases and promoted the formation of glassy phase.

The addition of SiO2 and O2 increased the viscosity of molten slag and promoted the formation of glassy phase.

4. MATERIALS AND METHODS

4.1. Materials. In this study, Ti-bearing blast furnace slag was obtained from Panzhihua Iron and Steel Research Institute (Sichuan Province, China). Based on previous research, titanium slag was prepared from titanium middling ore. The additive SiO2 was of analytical grade and provided by China National Medicines Corporation Ltd. O2 was provided by Shenyang Shuntai Gas Corporation Ltd., and its purity was 99% (mass fraction). The chemical compositions and XRD patterns of Ti-bearing blast furnace slag and titanium slag are shown in Table 3 and Figure 15, respectively. It can be seen that Ti-bearing blast furnace slag mainly contains perovskite (CaTiO3), akermanite (Ca2Mg(Si2O7)), diopside (CaMgSi2O6), and spinel (MgAl2O4). Anosovite and anorthite (CaAl2(SiO4)2) are the main phases in titanium slag.

4.2. Experimental Section. 4.2.1. FactSage Simulation. The combined influence of SiO2 and O2 on the crystallization behavior of modified Ti-bearing blast furnace slag was simulated by FactSage. The initial chemical components of Ti-bearing blast furnace slag and titanium slag were chosen according to the results shown in Table 3. The Scheil−Gulliver cooling method in the Equilib module of FactSage was used to build the relationships between the added amount of SiO2, oxidation time, and precipitation phases. The cooling temperatures used in the simulation ranged from 1000 to 1450 °C. The FToxid and FactPS databases were used in the simulation.

4.2.2. Modified Experiments. The modification experiments were performed in a vertical MoSi2 furnace with B-type thermocouple. It was estimated that the overall absolute temperature accuracy of the experiment was ±3 °C. The oxidation gas was O2, and the flow ratio of O2 was regulated by a rotameter.

According to the aforementioned thermodynamic calculation, 222 g of Ti-bearing blast furnace slag, 278 g of titanium slag, and a certain amount of SiO2 (10, 20, 30, 40, 50, and 60 g) were loaded into a crucible under an Ar atmosphere at 1450 °C for 20 min to melt it fully, and then O2 was blown into the molten slag with a certain time (0, 42, 84, 126, 168, and 210 s) and a flow ratio of 5 L/min under an isothermal condition. When the specified oxidation time was reached, the O2 valve was closed. Since it took few seconds to close the O2 valve, the added amount of O2 was slightly excessive. Hereafter, the modified slag was slowly cooled to room temperature at a cooling ratio of 5 °C/min and analyzed by XRD, SEM, and EDS.

During the cooling process, the mechanism of formation of glassy phase was studied. When temperature decreased to 1300 °C, a small amount of slag was taken through a straw immediately, and the samples were quenched in water. After being polished, the samples were observed under a metallographic microscope. The volume fraction of rutile crystals was

Figure 11. Standard Gibbs free-energy changes of (a) reactions 3−7 and (b) reactions 8−12.

Figure 12. Quenched metallographic pictures: (a−c) when the added amounts of SiO2 are 20, 40, and 60 g, respectively, and (d−f) when oxidation times are 42, 126, and 210 s, respectively.
measured on a Quantime520 image analyzer by the line intercept method (average 15 fields). Moreover, the modified slag was reheated to 1450 °C to determine the relationship between viscosity and temperature during the cooling process.

4.3. Characterization. The phase compositions of the solid samples were identified by XRD analysis (X’Pert PROMPD/PW3040, PANalytical B.V. Corp., the Netherlands) using Cu Kα radiation for 7 min from 10 to 90 °. The microscopic observation and element distribution in the samples were conducted by SEM on a scanning electron microscope (TESCAN VEGA III) equipped with an EDS spectrometer (INCA Energy 350). Quenched samples were observed by a metallographic microscope (201A−D) to study the mechanism of formation of glassy phase. The viscosity of molten slag was

| Table 3. Chemical Components of Samples (% Mass Fraction) (1: Ti-Bearing Blast Furnace Slag; 2: Titanium Slag; MFe Represents Metallic Iron Content) |
|---|
| sample | CaO | SiO₂ | TiO₂ | Ti₂O₃ | Al₂O₃ | MgO | FeO | MFe |
| 1 | 26.87 | 25.13 | 17.58 | 3.86 | 14.08 | 7.86 | 1.51 | 2.18 |
| 2 | 4.32 | 8.85 | 60.72 | 14.65 | 2.64 | 2.02 | 0.96 |

Figure 13. Relationship between rutile volume fraction and the added amount of SiO₂ and oxidation time.

Figure 14. Relationship between viscosity and temperature (20, 40, and 60 represent the added SiO₂ amounts of 20, 40, and 60 g; 42 and 126 represent the oxidation times of 42 and 126 s).

Figure 15. XRD patterns of raw materials: (a) Ti-bearing blast furnace slag and (b) titanium slag.
measured through the rotating spindle method by a ZCN-1600 melt physical property comprehensive testing instrument with a digital viscometer.

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