Crystallization Behavior of Rutile in the Synthesized Ti-bearing Blast Furnace Slag Using Single Hot Thermocouple Technique

Jing LI, Xidong WANG and Zuotai ZHANG

Department of Energy and Resources Engineering, College of Engineering, Peking University, Beijing, 100871 P.R. China.
E-mail: pkucoelijing@gmail.com, xidong@pku.edu.cn, zuotaizhang@coe.pku.edu.cn

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The present paper constructed the time-temperature-transformation (TTT) diagram of the synthesized titanium-bearing blast furnace (Ti-BF) slag using single hot thermocouple technique (SHTT) in order to study the crystallization behavior of rutile. A combination of X-ray Diffraction (XRD), Electron Probe Micro Analysis (EPMA) and Scanning Electron Microscope (SEM) equipped with Energy-dispersive X-ray spectroscopy (EDX) were applied to determine the structure and the composition of the crystals in the synthesized Ti-BF slag. It was found that rutile with rod shape was formed in the wide range of isothermal temperatures from 1 160°C to 1 320°C, and CaMgSi₂O₆, CaAl₂Si₂O₈ as well as CaTiSiO₅ were precipitated with further decreasing isothermal temperature. At a fixed isothermal temperature, the diameter of rutile increased slightly, whereas the length of rutile increased linearly with holding time. When increasing the isothermal temperature, the diameter of rutile increased linearly, whereas the growth rate of the length of rutile initially increased and followed by a decrease with further increasing isothermal temperature. The growth rate of the length of rutile had a maximum value (7.74 μm/s) at 1 260°C. The mechanism of crystal growth was also discussed, and the results indicated that rutile with one-dimensional growth was observed in the slag melt.

KEY WORDS: Ti-bearing blast furnace slag; rutile; crystallization behavior; TTT diagram; SHTT.

1. Introduction

China has the world’s largest resources of titanium, more than 90% of which is located in the southwest area and existed as the vanadium-titanium magnetite ore. About 54% titanium was enriched into the iron ore concentrate after mineral processing. Generally, blast furnace iron-making process (BF process) is applied to extract the valuable elements (e.g. V, Fe and Ti) from iron ore concentrate. In the BF process, Fe and V are fully extracted, whereas Ti is concentrated into the molten slag, forming the typical Ti-bearing blast furnace slag (Ti-BF slag) containing 22–25 wt% TiO₂. Until now, china has accumulated more than 70 million tons of Ti-BF slag, and it is still increasing at an annual rate of about 3 million tons. Considering that Ti-BF slag is a valuable secondary resource of titanium, a number of studies have been carried out to extract Ti from Ti-BF slag, such as acid leaching, alkaline leaching and high temperature carbonization-low temperature chlorination method, etc. However, the extraction efficiency of Ti from Ti-BF slag strongly depends on the crystallization behavior of rutile, such as crystal size, crystalline fraction and the growth rate. And these crystallization parameters could be studied by constructing the Time-Temperature-Transformation (TTT) diagram using Single Hot Thermocouple Technique (SHTT).

Therefore, selective crystallization and phase separation (SCPS) method was proposed, and a number of researchers have studied the extraction of Ti from Ti-BF slag based on the SCPS method. Many researchers investigated the enrichment behavior of Ti in perovskite in the Ti-BF slag. However, it has been proved that perovskite is hard to be extracted owing to its dendrite structure and the similar density with other phases. In comparison with perovskite, rutile is more appropriate as the Ti-enrichment phase because it has rod-shaped structure and higher density (4.2–4.3 g/cm³) and it was also a kind of high quality raw material to produce the pigment. According to our previous experimental results, Ti could be concentrated into rutile in this synthesized Ti-BF slag, and the composition was shown in Table 1. However, the crystallization behavior of rutile in the slag has not been studied yet. Furthermore, the extraction efficiency of Ti from Ti-BF slag strongly depends on the crystallization behavior of rutile, such as crystal size, crystalline fraction and the growth rate. And these crystallization parameters could be studied by constructing the Time-Temperature-Transformation (TTT) diagram using Single Hot Thermocouple Technique (SHTT).

Table 1. The main chemical composition of the synthesized slag.

<table>
<thead>
<tr>
<th>Synthesized slag</th>
<th>SiO₂ wt%</th>
<th>CaO wt%</th>
<th>Al₂O₃ wt%</th>
<th>MgO wt%</th>
<th>TiO₂ wt%</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Designed composition</td>
<td>40</td>
<td>20</td>
<td>12</td>
<td>6</td>
<td>22</td>
<td>100</td>
</tr>
<tr>
<td>XRF analyzed composition</td>
<td>39.79</td>
<td>20.72</td>
<td>12.43</td>
<td>6.76</td>
<td>20.3</td>
<td>100</td>
</tr>
</tbody>
</table>

Therefore, the aim of this paper is to construct the TTT diagram of this
synthesized Ti-BF slag using SHTT and to investigate the crystallization mechanism of rutile in the synthesized Ti-BF slag.

2. Experimental

2.1. Sample Preparation

In order to eliminate the impact of minor elements in industry slag, such as V, S, Mn, Fe and other elements,20) the synthesized slag was prepared using reagent grade CaO, MgO, SiO₂, TiO₂ and Al₂O₃ with the composition as shown in Table 1. The powder mixture was mixed in ethyl alcohol and dried at 100°C for 12 h. Then 40 g synthesized slag in a molybdenum crucible (Φ40×45×H40 mm) were melted under an argon atmosphere at 1500°C for 1 h in order to homogenize the slag. Subsequently, the liquid slag was poured into water to produce the glassy slag. The glassy slag was dried at 120°C for 12 h and smashed to 300 meshes for the further analysis in SHTT. The composition of quenched slag may differ from those of the designed sample due to evaporation losses. 5 g quenched slag was therefore used for the analysis of chemical composition by X-Ray fluoroscopy (XRF), and the analyzed result was shown in Table 1 for a comparison. It can be seen that the measured values showed a small deviation compared with the designed composition.

2.2. Experimental Procedures

A SHTT was employed to study the crystallization of rutile in the present experiments. The principle of SHTT has been described in detail by Kashiwaya et al.,21) and is briefly summarized here. A Pt-Rh thermocouple (B Type) was used to heat and measure the temperature simultaneously. A microscope equipped with a video camera was applied to observe and record the images of slag, which were sent to a computer and a Video Cassette Recorder (VCR). The heating and cooling processes were controlled by a computer program. During the experiments, about 10 mg slag was mounted on the tip of thermocouple, heated to 1550°C and held for 60 s to eliminate the bubbles and homogenize the slag. And then the slag was rapidly cooled down to a given temperature and held there for 300 s–1500 s. The images of the slag were recorded and temperature-time curves were also documented simultaneously. Then based on the analysis of sample images, the time for the onset of crystallization and the fraction of crystal transformed were determined, and TTT diagram was thereby constructed.

In order to identify the crystal structure of the synthesized slag, the samples were quenched from different temperatures and examined by X-Ray Powder Diffraction (XRD, Rigaku Dmax/2400) analysis in the present experiments. Intensities were collected by 2θ scanning. The instrument parameter was as follows: 40 kV and 100 mA as the generator voltage and tube current, 10–80° as the 2θ scanning range and 8°C/min as the scanning speed, respectively. On the other hand, Electron probe micro analysis (EPMA, JEOL JXA-8100) and Scanning Electron Microscope (SEM, HITACHI S4800) equipped with Energy-dispersive X-ray spectroscopy (EDX, BRUKER) were carried out in order to observe the microstructure of the samples and identify the composition of the crystals in the samples. Back Scattered Electron (BSE) images were obtained in this work.

3. Results and Discussions

3.1. TTT Diagram

Isothermal experiments were carried out in a wide temperature range of 1000–1325°C to construct TTT diagram for the onset of crystallization of the synthesized slag. The time for the beginning of crystallization was defined as 0.5% crystalline fraction. Figure 1 showed the TTT diagram of the synthesized Ti-BF slag. As can be seen, the TTT diagram was divided into two regions above and below 1160°C. This may suggest that there were two different nucleation events in the crystallization process of the synthesized Ti-BF slag and that the crystal morphology drastically changed around 1160°C. Figures 2 through 4 showed the sequence of the precipitation and growth of the crystals in the slag at 1300°C, 1160°C and 1100°C, respectively. It can be seen that the crystals at 1300°C (Fig. 2) appeared as the rod shape and grew along thermocouples toward the center of the sample, which may suggest that the nucleation

![Fig. 1. TTT diagram of the synthesized Ti-BF slag.](image)

![Fig. 2. Crystallization behavior of the synthesized Ti-BF slag at 1300°C.](image)
of the rod-shaped crystal was heterogeneous nucleation. When the experimental temperature decreased to 1 160°C, as shown in Fig. 3, it was found that a new phase with dendritic structure appeared, which was in agreement with the result of the TTT diagram. And with the isothermal temperature further decreasing to 1 100°C (Fig. 4), it was noticed that a large amount of dendritic crystals were formed rapidly in the bulk slag melt. It can therefore be concluded that two kinds of crystals were observed in the slag melt. The first type was the rod-shaped crystal, which was the primary phase of the synthesized Ti-BF slag, appearing in the isothermal temperature ranges from 1 320°C to 1 160°C. The second was the dendritic crystal, which was formed rapidly below 1 160°C in the bulk slag melt.

3.2. Crystalline Phases

In order to identify the structure of the crystals in the slag melt, a Pt pan containing the glassy slag was put into the heating zone of a vertical MoSi2 furnace. The furnace was heated to 1 500°C to homogenize the slag, and then followed by a rapid cooling to the preset isothermal temperature holding for 5 h. The slag samples were then quenched for XRD measurement and SEM analyses. Figure 5 illustrated the XRD patterns of the samples quenched from 1 260°C (a), 1 200°C (b) and 1 100°C (c), respectively. As can be seen, rutile was the only crystal formed at 1 260°C and 1 200°C, whereas silicates (MgSiO3, CaAl2Si2O8 and CaTiSiO5) and rutile were formed at 1 100°C. Figure 6 showed the BSE image of the crystal quenched from 1 260°C, and the results of quantitative analysis by EPMA was listed in Table 2. It was found that the rod-shaped crystal was rutile, which was consistent with the XRD results. Figure 7 displayed the EDX elementary mapping of the crystal quenched from 1 200°C, and the EDX result was listed in Table 3. It can be seen that the crystals mainly consist of Ti and O elements, suggesting that the rod-shaped crystal observed at 1 200°C is rutile. This is also in agreement with the XRD results. Therefore, it can be concluded that the crystal with rod shape formed above 1 160°C in the slag melt was rutile. Figure 8 showed the BSE image of the crystal quenched from 1 100°C by SEM analysis. It was found that the crystals with dendritic structure were silicates, which was consistent with the images observed by SHTT.

In order to better understand the crystalline formation mechanism, the isopleth phase diagram of the synthesized
Ti-BF slag was calculated by FactSage. \(^{22}\) Figure 9 showed the calculated isopleth phase diagram of CaO–SiO\(_2\)–MgO–Al\(_2\)O\(_3\)–TiO\(_2\). The SHTT experimental results were marked in the figure with circles, where the open circles indicated the formation of rutile, and the closed circles indicated the appearance of silicates. As can be seen from the calculated phase diagram, rutile was the primary phase at the temperature range more than 1290°C, which was consistent with the experimental results, \(i.e.,\) rutile was also first precipitated over 1290°C in the present experiments. However, it was also noticed that some deviations were observed by comparing the experimental results with the calculated phase diagram. According to the observation by SHTT and XRD results, rutile was the only crystal formed in the temperature range of 1160°C–1290°C. But the calculated phase diagram showed that some other crystals, such as CaTiO\(_3\), CaTiSiO\(_5\), MgTi\(_2\)O\(_5\) and CaAl\(_2\)Si\(_2\)O\(_8\) were also formed in the temperature range from 1160°C to 1290°C. Furthermore, the crystals appeared at 1100°C (Rutile, CaMgSi\(_2\)O\(_6\), CaAl\(_2\)Si\(_2\)O\(_8\)) in the present experiments were also not in agreement with the prediction by the calculated phase diagram. These could be explained by the following. When the slag was rapidly cooled to the fixed isothermal temperature, it was under a super-cooling condition. But the calculated phase diagram showed the equilibrated phases in the slag.
3.3. Kinetics of Rutile Growth in High Temperature Region

A series of SHTT images were extracted from the recordings and analyzed using Image Tools 2.0 software (The University of Texas Health Science Center at San Antonio, Texas, USA). It was found that the isothermal temperature had a significant effect on the crystal size of rutile. At a fixed isothermal temperature, the diameter of rutile increased slightly, while the length of rutile increased significantly with increasing annealing time. The average diameter of rutile was measured at different temperatures, and the relationship between the diameter of rutile and the isothermal temperature was showed in Fig. 10. The length of the rutile as a function of holding time was also measured in order to calculate the average growth rate of rutile. Figure 11 showed the average growth rate of rutile at different isothermal temperatures. And the average growth rate of rutile as a function of isothermal temperature was illustrated in Fig. 12. These results indicated the following:

(a) The diameter of rutile increased slightly at a fixed isothermal temperature, and it increased linearly with the isothermal temperature increasing.
(b) At a fixed isothermal temperature, the length of the rutile increased rapidly when increasing holding time. And
the growth rate of the length of rutile was found to be linear, indicating that the growth was controlled by crystal/melt interfacial reaction.23)

(c) The growth rate of the length of rutile increased with increasing isothermal temperature, and it reached maximum at 1260°C. After that, it decreased with further increasing temperature. This was consistent with the experimental results in silicate melts.24)

The aforementioned experimental results could be explained by the principal theory of crystallization.25) It is well known that the crystallization involves nucleation and crystal growth. Nucleation is influenced by the under-cooling, and an increasing under-cooling degree could reduce the crystal critical radius and consequently promote the formation of crystal embryo, i.e., the decreasing isothermal temperature is beneficial to nucleation. On the other hand, crystal growth can be controlled by the crystal/melt interfacial reaction and the diffusion of crystal nucleus. And a decreasing isothermal temperature could increase the driving force of the crystal/melt interfacial reaction and the viscosity of the slag. However, the increasing viscosity inhibited the diffusion of crystal nucleus. In view of these two aspects, the growth rate of the length of rutile had a maximum value with a decreasing isothermal temperature, which was consistent with the experimental results in this work.

In addition, with the purpose of determining the growth mechanism of rutile, the Johnson-Mehl-Avrami (JMA) equation26,27) was applied in the present experiments, as shown in Eq. (1),

![Fig. 12. The average growth rate of rutile as a function of temperature.](image1)

![Fig. 13. Measured volume fractions of rutile versus aging time at different isothermal temperatures.](image2)
where X is the crystalline fraction, t is the holding time, K is a constant, n is the Avrami exponent, which represents the mechanism of crystal growth.

In order to determine the volume fraction of rutile (X) at a fixed holding time (t), the rutile was assumed as cuboids and the volume fraction was consequently calculated using the area and the thickness of the sample. The volume fraction was therefore measured and shown in Fig. 13.

Based on the measured volume fraction at different time, as plotted in Fig. 13, the Avrami exponent at different isothermal temperatures were computed, which was in the range of 1.5–1.9. Considering the aforementioned experimental results, these values can be taken as n=2. Considering the aforementioned experimental results, i.e., the growth of rutile was mainly controlled by crystal/melt interfacial reaction. It can therefore be concluded that the growth of rutile was controlled by one-dimensional growth in the slag melt.

This is consistent with the observed results by SHTT.

4. Conclusions

In order to investigate the crystallization behavior of rutile in the synthesized Ti-BF slag, the TTT diagram of the slag was constructed using SHTT. XRD, EPMA and SEM-EDX were applied to identify the chemistry and structure of the crystals. The experimental results were summarized as follows,

1) Rutile with the rod shape was formed in a wide temperature range from 1 160°C to 1 320°C, while silicate appeared with the dendrite structure and may coexist with rutile when the temperature was below 1 160°C.

2) The diameter of rutile was measured with time at different isothermal temperatures. And it was found that the diameter increased slightly at a fixed isothermal temperature and increased linearly with the increasing isothermal temperature.

3) The growth rate of the length of rutile initially increased with the isothermal temperature increasing until it reached the maximum value (7.74 μm/s) at 1 260°C. After that, it decreased with further increasing isothermal temperature.

4) The growth mechanism of rutile was investigated by studying Avrami exponent, and the results indicated that one-dimensional growth of rutile was observed in the slag melt.

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