Effect of perovskite phase precipitation on viscosity of Ti-bearing blast furnace slag under the dynamic oxidation condition

L. Zhang [a,*], L.N. Zhang [a], M.Y. Wang [a], T.P. Lou [a], Z.T. Sui [a], J.S. Jang [b]

[a] School of Materials and Metallurgy, Northeastern University, P.O. Box 118, Shengyang, Liaoning 110006, PR China
[b] Korea Atom Energy Institute, Daejeon 305-353, Republic of Korea

Abstract

The effects of the dynamic oxidation on the viscosity of Ti-bearing blast furnace slag, on a selective enrichment, a precipitation and a growth of the Ti component were studied. The oxygen source was the air that was blown into the molten slag through a lance during the dynamic oxidation process. It was found that the oxidation of TiC, metallic Fe, TiO and Ti_2O_3 in the slag was not only in favor of the decrease of the viscosity of the slag, but also for the selective enrichment of the Ti component into the perovskite phase as well as the precipitation and growth of the perovskite phase. As oxidation time increases, the precipitation and growth of the perovskite phase rapidly increased, and the slag changed from the melt to a mixture of the melt and crystalline phase(s), that caused the viscosity of the oxidized slag for 12 min increased rapidly.
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1. Introduction

Every year more than three million tons of blast furnace slag containing 21–24% TiO_2 and 2–4% metallic Fe are produced by smelting V–Ti-bearing magnetite in Panzhihua Iron and Steel Company. The Ti-bearing blast furnace slag is an important man-made resource. Due to the dispersed distribution of Ti component in various fine grained (<10 μm) mineral phases with the complex interfacial combination, it is difficult to recover the Ti component through traditional separation methods [1,2].

On the basis of the point of view of ongoing concern for both economic and resource, several mineral and metallurgy methods have been studied for treating the slag, such as flotation separation, combined with magnetic, hydrometallurgy and melting reduction [2].

However, the recovery and the utilization of each process were poor. So far the slag has not been efficiently utilized those results in a waste of the resource and the pollution of environment [2].

The main mineral phases in Ti-bearing blast furnace slag are titanium carbide, spinel, perovskite, titanaugite, Ti-rich diopside and metallic Fe [1]. The main titanium-containing mineral phases are perovskite, titanaugite and Ti-rich diopside. The perovskite is composed of Ti^{4+}, and the titanaugite and Ti-rich diopside are composed of Ti^{2+} and Ti^{3+}. Based on several studies and practices in a pilot plant on the slag [3–11], blowing air to the molten slag, (Ti^{2+}) and (Ti^{3+}) in the slag were oxidized to (Ti^{4+}), most of the Ti component in the slag was enriched into the perovskite phase which could fully grow and coarsen through the oxidation together with a heat treatment, and the perovskite phase could be separated from the slag by mineral dressing

* Corresponding author. Tel.: +86 24 83681203.
E-mail address: zhl119@263.net (L. Zhang).

method. In order to obtain further information about the precipitation process of the perovskite phase, it is necessary to study the effects of the dynamic oxidation on the precipitation of the perovskite phase in the slag.

The dynamic oxidation of the molten slag remarkably influences the viscosity and chemical composition, which play key role in the selective enrichment, precipitation and growth of the perovskite phase. Obtaining the slag with improved properties for utilization depend not only on the selective enrichment of the Ti component into the perovskite phase, but also on the precipitation, growth and coarsening of the perovskite phase developed through adjusting the viscosity and chemical composition under the dynamic oxidation condition. In other words, the dynamic oxidation of the molten slag is the crucial problem to the selective enrichment, precipitation and growth of the perovskite phase.

The purpose of the present work is to study the effect of the perovskite phase on the viscosity of the slag under the dynamic oxidation condition through two aspects: the viscosity research, the precipitation and growth of the perovskite phase.

2. Experimental

The slag in this study was from the Panzhihua Iron and Steel Company. Chemical composition of the slag is listed in Table 1. Before the experiment, the slag was milled to 120 μm and dried in an oven at 100 °C for 3 h.

The experiments were carried out in a horizontal $MoSi_2$ furnace fitted with an type R thermocouple, which was controlled by the Shimaden SR – 53 temperature programmed control instrument. The length of isothermal section was 60 mm, the temperature accuracy was within ±3 °C. The gas flow rate was controlled by a rotameter. The oxidation gas was compressed air.

The slag samples were melted in a platinum crucible at 1420 °C for 20 min, air was then blown into the molten slag at the flow rate of 1 L/min under isothermal condition for 2, 4, 6, 8, 10 and 12 min, respectively. The slag was then slowly cooled to room temperature at the cooling rate of 5 °C/min. In this process, some samples were obtained by air quenching method at 1420 °C for 2, 4, 6, 8, 10 and 12 min, respectively. The relationships between the viscosity and temperature of the raw slag and the oxidized slag were measured in ZCN-1600 high temperature viscometer. Because the (Ti^{2+}) content in the slag is less, the (Ti^{2+}) content is neglected. The FeO, Fe_2O_3 ($FeO_{1.5}$), Ti_2O_3 and TiO_2 content were measured by chemical titration analyses. The FeO content was determined by *o*-phenanthroline oxida-

tion–reduction titration, and the Fe_2O_3 ($FeO_{1.5}$) content determined indirectly by the TFe content and the FeO content. The Ti_2O_3 content was determined by reduction–oxidation titration, and the TiO_2 content by ammonium ferric sulfate titration. Two repeated measurements were made for each experimental condition. The experimental error was between ±0.06% and ±0.13%.

The experimental apparatus (ZCN-1600) for viscosity measurements consists of a high temperature furnace and viscometer. The raw and the oxidized slag were remelted in a vertical $MoSi_2$ resistance furnace under purified argon atmosphere. A viscometer was conducted by loops to a platinum extension rod and to a measuring spindle made of molybdenum. The viscometer spindle was calibrated against standard oils (Brookfield). The spindle constant was determined by measuring the torque at several rotation speeds at immersion depths. After the molten state of the slag could be verified, the spindle rotating at a speed of 40–60 rpm was lower into the slag. The viscosity of slag was then measured.

The overall experimental errors of the viscosity measurement were estimated using the uncertainties associated with each experimental parameter. The uncertainties in the measurements on the liquid slag arises from the uncertainties of the calibrating oils (2%), viscometer accuracy (1%) and volume expansion of the measuring spindle (4%) and the immersion depth of the spindle (2%). The temperature uncertainty of the high temperature furnace is within ±3 °C. The overall uncertainties of the viscosity measurements are between ±9% and ±13%.

After being polished, the microstructures of the oxidation products were characterized by Quantime520 image analysis, scanning electron microscopy (SEM) with energy dispersive spectrometory (EDS) and X-ray diffraction (XRD). The volume fraction and average grain size of perovskite phase were measured on a Quantime520 image analyzer by the line intercept method (average of 10 fields). The SEM machine is SSX-550, and the EDS machine is TN540. In addition, the XRD machine is D/MAX-RB, and the optical machine is PME OLYMPUS.

The concentrations of crystalline phases can be determined by the volume fraction of the crystalline phases after the dynamic oxidation, but the volume fraction and grain size of crystalline phases (titanaugite and Ti-rich diopside) that are composed of TiO and Ti_2O_3 are very small after the dynamic oxidation, accordingly, it is very difficult to determine the concentrations of titanaugite and Ti-rich diopside by the volume fraction. On the other hand, the volume fraction and grain size of perovskite phase are very large after the dynamic oxidation, hence, the concentration of perovskite phase can be determined by the volume fraction. Analysis uncertainties of the volume fraction and average grain size measurements come from the sample homogeneity, magnification, and number of measured fields. The overall uncertainties of the volume fraction and average grain size measurements are between ±7% and ±15%.

Table 1
Chemical composition of the slag (wt%)

CaO	SiO₂	TiO₂	Ti₂O₃	FeO	Al₂O₃	MgO	MnO	MFe	Others
26.54	24.37	16.9	4.06	1.72	13.76	8.48	0.53	2.52	1.12

Note: M Fe – metallic iron.

3. Results

3.1. Slag viscosity under the isothermal oxidation condition

Fig. 1 shows the relationships between the viscosity and temperature of the oxidized slag for various oxidation time. The viscosity decreased with a longer oxidation time but the viscosity rapidly increased at 12 min.

The viscosity of the slag is concerned with FeO_n ($FeO + FeO_{1.5}$), TiC and crystalline phase formations. The main reason Ti-bearing slag has higher viscosity is that TiC in the slag usually exists in the form of solid state particle [1]. Conversely, it is thought that a higher FeO_n content usually lowers the slag viscosity [11,12]. Compare with FeO_n, the effect of TiC on the viscosity of the slag is more obvious.

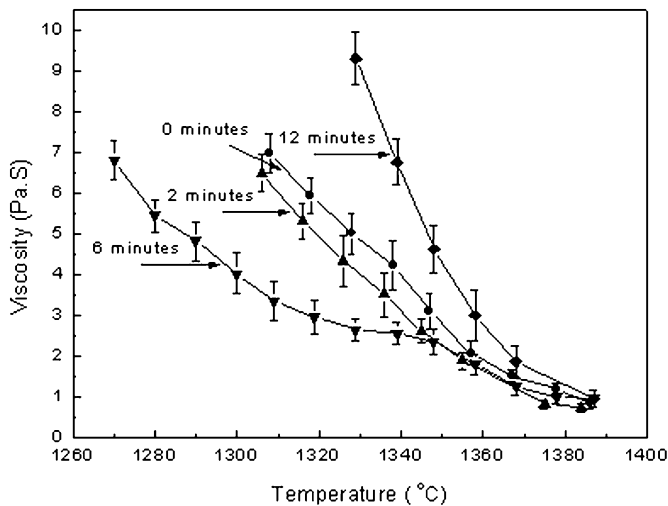Fig. 1. Relationships between the viscosity and temperature of the raw slag and the oxidized slag for various oxidation time.
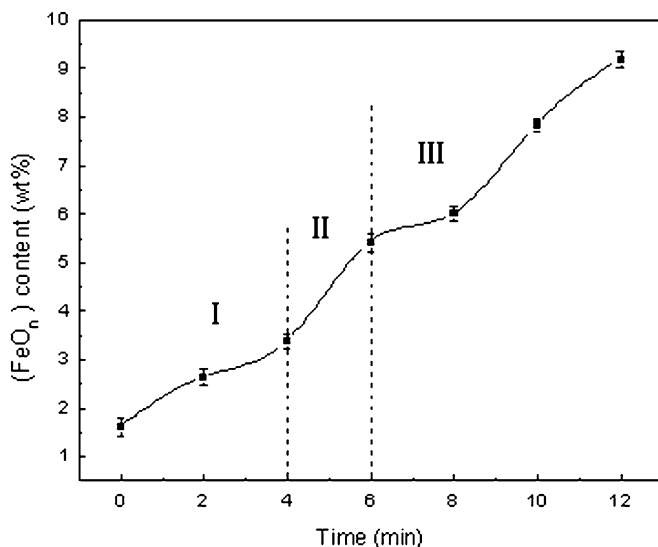
Table 2
Crystalline phases in the un-oxidized slag and oxidized slag

Slag	Crystalline phase observed
Un-oxidized	Perovskite, titanaugite, Ti-rich diopside, spinel, titanium carbide
Oxidized for 2 min	Perovskite, titanaugite, Ti-rich diopside, spinel
Oxidized for 6 min	Perovskite, titanaugite, Ti-rich diopside, spinel
Oxidized for 12 min	Perovskite, spinel, impurity phase

The FeO_n and TiC content changed during the oxidation (in Fig. 2 and Table 2), correspondingly, the viscosity changed. In the earlier stage I (0–4 min), TiC in the slag is oxidized (in Table 2), meanwhile, metallic Fe (in Table 1) is slowly oxidized, the FeO_n content is gradually increased, therefore, the viscosity of the slag is gradually reduced; In the second stage II (4–6 min), TiC gradually vanishes, metallic Fe is rapidly oxidized, and the FeO_n content is rapidly increased, the viscosity is continuously reduced; In the last stage III (6–12 min), although FeO_n is continuously increased, the viscosity of the slag is not continuously reduced but rapidly increased, and that may be due to the formation and growth of the perovskite phase in the oxidized slag.

3.2. Precipitation and growth of the perovskite phase under the isothermal oxidation condition

3.2.1. Crystalline phase analysis under the isothermal oxidation condition

The relationship between the Ti_2O_3 content in the slag and oxidation time is shown in Fig. 3. After cooling, the crystalline phase in the un-oxidized and oxidized slag were examined by XRD, SEM and EDS, and the results are listed in Table 2. The SEM micrograph of the oxidized slag is shown in Fig. 4.
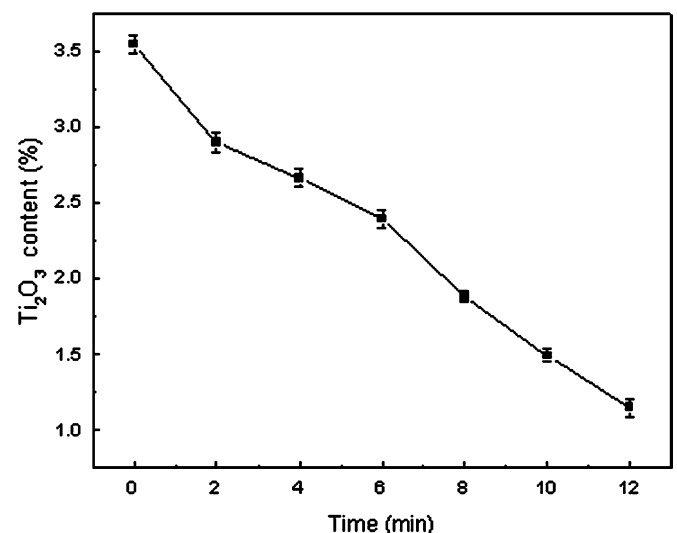

Fig. 2. Relationships between the FeO_n content in the molten slag and oxidation time under the isothermal oxidation condition.

Fig. 3. Relationships between the Ti_2O_3 content in the molten slag and oxidation time under the isothermal oxidation condition.
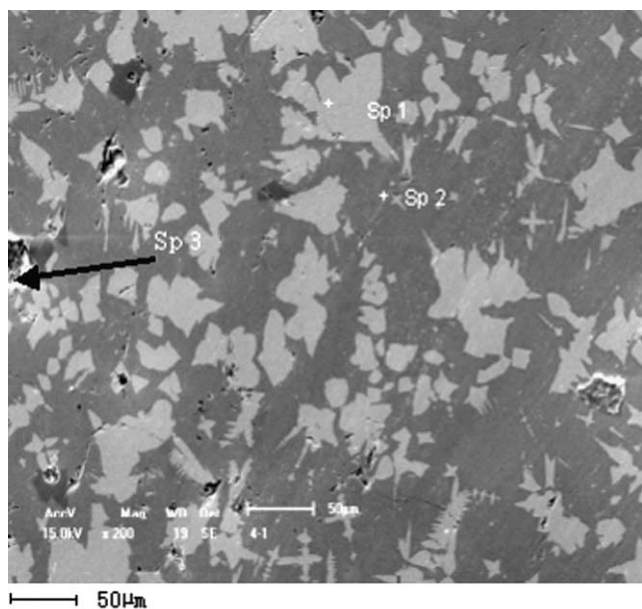
Fig. 4. Back-scattered electron image of the slowly cooling oxidized slag for 12 min (sp 1: perovskite, sp 2: impurity phase, sp 3: spinel).

Fig. 5. Relationships between the ratio of Ti^{4+}/Ti^{3+}, the volume fraction (VF) and grain size of the perovskite phase in the slowly cooling oxidized slag and oxidation time.

It can be seen that the Ti_2O_3 content in the slag decreases with a longer oxidation time, accordingly, the titanaugite $(((Ca_{0.96},Mg_{0.53},Ti_{0.46},Fe_{0.04},M_{0.01})_{2.00}[(Si_{1.28}, Al_{0.72})_{2.00}O_6]))$ and Ti-rich diopside $(((Ca_{0.35},Mg_{0.66},Ti_{0.45}, Fe_{0.03},Mn_{0.01})_{2.00}[(Si_{0.93},Al_{0.84},Ti_{0.23})_{2.00}O_6]))$ which are composed of Ti_2O_3 drop off. As oxidation time approaches 12 min, the Ti_2O_3 content in the slag rapidly decreases, therefore, the titanium carbine, titanaugite and Ti-rich diopside containing Ti_2O_3 almost vanish, and there only exists the perovskite as a main titanium-containing and crystalline phase, the spinel and an impurity phase.

It indicates that most of titania in the slag was enriched into the perovskite phase after air was blown into the molten slag.

3.2.2. Precipitation of the perovskite phase under the isothermal oxidation condition

The relationships between the ratio of Ti^{4+}/Ti^{3+}, the volume fraction of the perovskite phase in the slag and oxidation time are shown in Fig. 5.

It is clearly shown that the ratio of Ti^{4+}/Ti^{3+} and the volume fraction of the perovskite increased with a longer oxidation time. In other words, the ratio of Ti^{4+}/Ti^{3+} increase means that the Ti_2O_3 content in the slag decreases and the TiO_2 content in the slag increases, accordingly, the volume fraction of the perovskite which is composed of TiO_2 increases with a longer oxidation time.

When the oxidizing time is 2 min, the ratio of Ti^{4+}/Ti^{3+} is 5.29 and the volume fraction of the perovskite phase is 22.5%; when the oxidizing time is 12 min, the ratio of Ti^{4+}/Ti^{3+} is 17.72 and the volume fraction of the perovskite phase is 25.8%; meantime, the ratio of Ti^{4+}/Ti^{3+} is 3.56 and the volume fraction of the perovskite phase is 12.0% in un-oxidized slag.
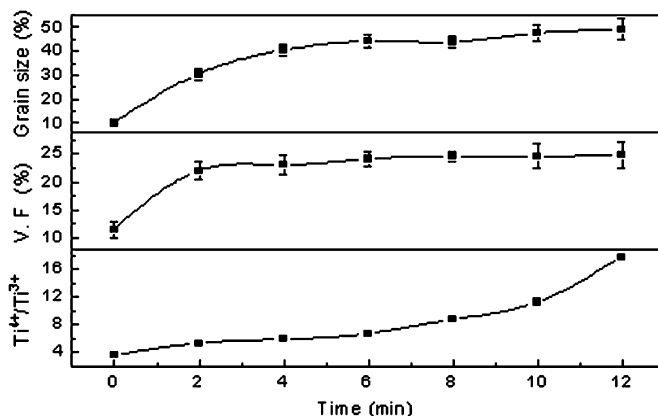
These experimental results indicate that the ratio of Ti^{4+}/Ti^{3+} changes from and the volume fraction of the perovskite changes from 12.0% to 25.8%.

3.2.3. Growth of the perovskite phase under the isothermal oxidation condition

The growth and coarsening of the perovskite phase in the molten slag can be achieved by optimizing the condition such as the oxidation time, as shown in Figs. 5 and 6. It was determined by an image analysis that the average grain size of the perovskite phase changed from 2–10 μm to 40–50 μm in diameter after the dynamic oxidation. As the oxidation time approaches 12 min, the grain size of the perovskite phase and the number of grain over 25 μm in diameter are much greater than those for 2 min (Figs. 5–7), in addition, the viscosity of the oxidized slag for 12 min rapidly increases.

4. Discussion

The experimental results indicate that the volume fraction and grain size of the perovskite increased with a longer oxidizing time. The reason is that the decrease of the viscosity makes the nucleation rate I and crystal growth rate u increased, combination of the two effects accelerate the two precipitation and growth of the perovskite phase. The respective rates can be expressed as follows [13,14]:

$$I = \frac{DN_0}{3\pi\eta a^3} \cdot \exp\left[\left(-b \cdot \frac{\alpha^3\beta}{(\Delta T_r)^2 T_r}\right)\right], \qquad (1)$$

$$U = \frac{kTf}{3\pi\eta a^2} \cdot \left[1 - \exp\left(-\frac{\beta\Delta T_r}{T_r}\right)\right], \qquad (2)$$

where T is the absolute temperature, k is the Boltzmann constant, N_0 is the number of atoms on the surface per unit volume, f is the fraction of sites on the interface where atoms can preferentially be added or removed, a is the interatomic distance, D is the diffusion coefficient, η is the slag viscosity, b is the geometry factor, and α and β is
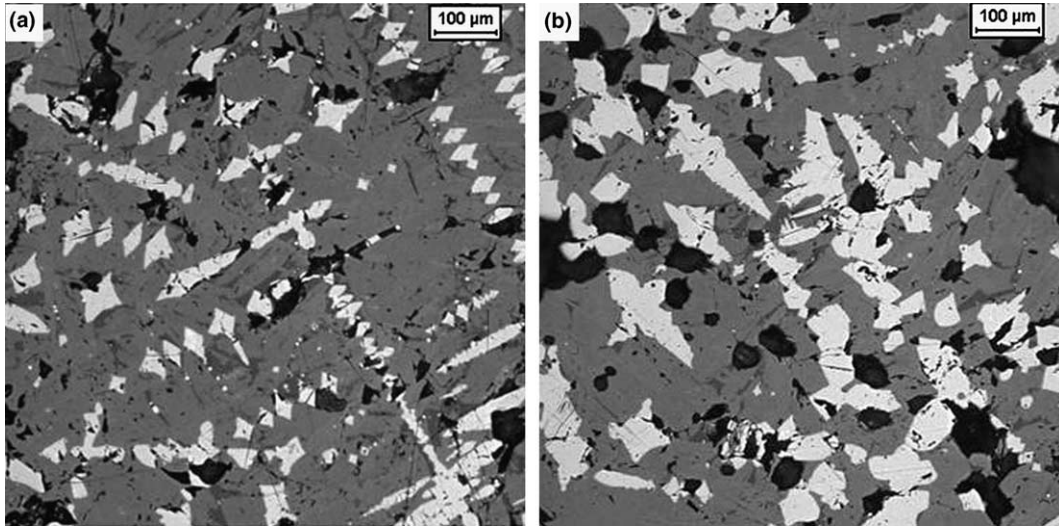
Fig. 6. Micrographs of the slowly cooling oxidized slag for different oxidation time under the isothermal oxidation condition: (a) 2 min and (b) 12 min.
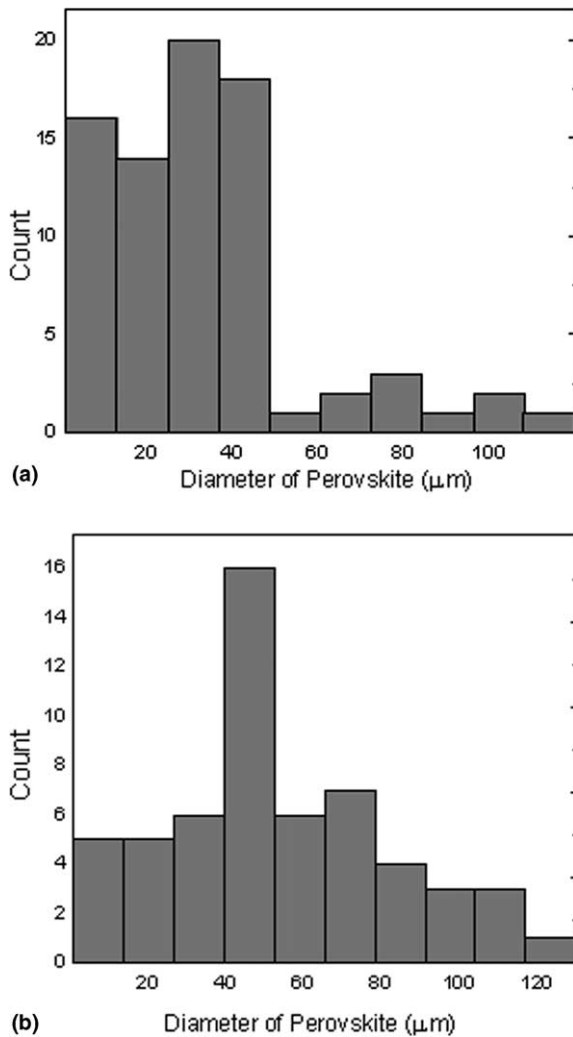

Fig. 7. Size distribution of the perovskite phase in the slowly cooling oxidized slag for different oxidation time: (a) 2 min and (b) 12 min.

the dimensionless parameters related to the liquid–crystal interfacial tension and the entropy of fusion. T_r is the reduced temperature: $T_r = T/T_m$, $\Delta T_r = 1 - T_r$, where T_m is the melting temperature.

For the un-oxidized slag, there exists TiC crystalline phase, which still exists in the form of solid state due to high melting point. Based on several studies [1,12], the TiC solid state particles can cause the viscosity rapidly increased, accordingly, the un-oxidized slag has higher viscosity. According to Eqs. (1) and (2), a higher viscosity is not in favour of the precipitation and growth of the perovskite phase.

In addition, according to the model on the effect of crystalline phases on the viscosity of slag proposed by Annen et al. [12,15], slag could be treated as a mixture of the melt and crystalline phases. The viscosity of the mixture ($\mu_{mixture}$) would be expressed as a function of the liquid's viscosity (μ_{liq}) and the solid content:

$$\mu_{mixture} = \mu_{liq}(1 + 2.5c + 9.15c^2), \tag{3}$$

where c is the volume fraction of crystalline phases. It also indicates that the TiC crystalline phase plays an important role on the viscosity of the un-oxidized slag, In addition, The TiC particles are easy to grow and coarsen during cooling due to high melting point, and the large particle size causes a rapid increase in the viscosity [1,12].

During the dynamic oxidation, the TiC particles gradually drop off. When the oxidizing time is 2 min or 6 min, the TiC particles almost vanish due to the oxidization of the TiC (in Table 2), which causes the decrease of the slag viscosity oxidized for 2 min or 6 min. On the other hand, compared to the slag oxidized for 12 min, only a small quantity of the (Ti^{2+}) and (Ti^{3+}) in the slag oxidized for 2 min or 6 min is oxidized to (Ti^{4+}) (in Fig. 3), accordingly, the precipitation and growth of the perovskite phase is very slow during cooling, and the experimental results of the quenched oxidized slag also indicate that the volume fraction and grain size of the perovskite phase in the slag oxidized for 2 min or 6 min during cooling are much smaller
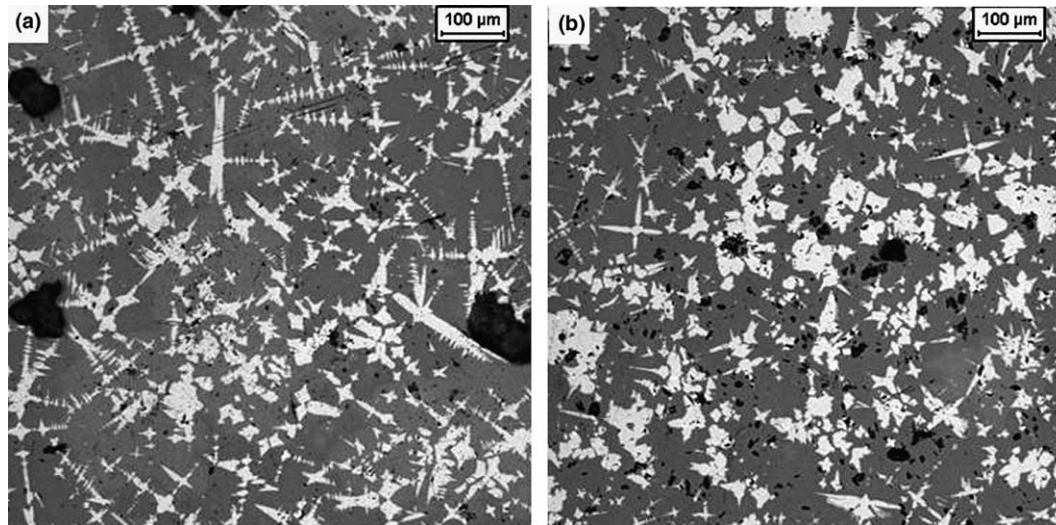
Fig. 8. Micrographs of the quenched oxidized slag for different oxidation time under the isothermal oxidation condition: (a) 2 min and (b) 12 min.

than those in the slag oxidized for 12 min (in Figs. 8 and 9). According to Eq. (3) and several studies [1,12], these small perovskite phases have little effect on the slag viscosity oxidized for 2 min or 6 min. In this case, the decrease of the slag viscosity due to the oxidation of the TiC may be much greater than the increase of the slag viscosity due to the precipitation and growth of the perovskite phase, hence, the viscosity of the slag oxidized for 2 min or 6 min decreases clearly.

As the oxidizing time approach 12 min, although the TiC particles almost vanish (in Table 2), a large quantity of the (Ti^{2+}) and (Ti^{3+}) in the slag is oxidized to (Ti^{4+}) (in Fig. 3), which promotes the rapid precipitation and growth of the perovskite phase by the following reaction: $(Ca^{2+}) + (TiO_3^{2-}) = CaTiO_3$ during cooling, accordingly, the volume fraction and the grain size of the perovskite phase rapidly increases during cooling. The experimental results also indicate that the volume fraction and grain size of the perovskite phase in the slag oxidized for 12 min during cooling are much greater than those in the slag oxidized for 2 min or 6 min (in Figs. 8 and 9). According to Eq. (3), the large volume fraction of the perovskite phase makes the viscosity of the slag oxidized for 12 min rapidly increased. On the other hand, the large grain size makes the slag change from the melt to a mixture of the melt and crystalline phase(s), and these cause the viscosity of the slag oxidized for 12 min increased. In this case, the increase of the slag viscosity due to the precipitation and growth of the perovskite phase may be much greater than the decrease of the slag viscosity due to the oxidation of the TiC, hence, the viscosity of the slag oxidized for 12 min markedly increases, which agrees well with the observation as shown in Figs. 1, 8 and 9.

The increase of the viscosity of the slag oxidized for 12 min is not only due to the rapid increase of the volume fraction and grain size of perovskite phase, but also due to the rise of the melting point of slag. The melting point of
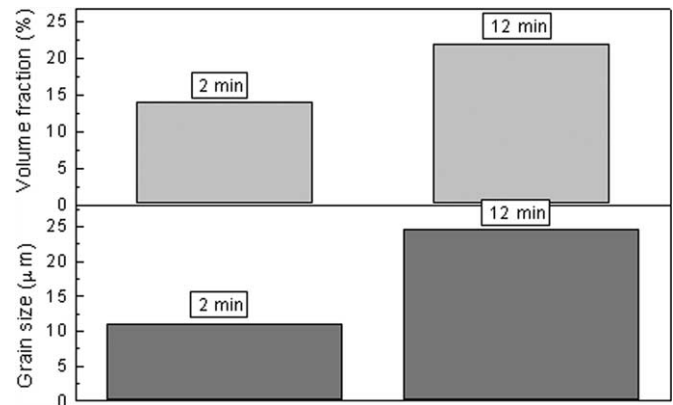

Fig. 9. The volume fraction and grain size of the perovskite phase in the quenched oxidized slag for different oxidation time under the isothermal oxidation condition.

slag can be estimated by determining a temperature (T_L) at which there exists a subsequent rapid increase in the viscosity [16]. The temperature (T_L) is thought to be the melting point of slag [16]. According to the method, the melting point of the slag oxidized for 2, 6 and 12 min are 1336, 1310 and 1350 °C, respectively (in Fig. 1). It is clearly shown that the melting point of the slag oxidized for 12 min particularly rises to near 1350 °C, accordingly, the viscosity of the slag oxidized for 12 min increases rapidly in the temperature range below 1350 °C because temperature of the slag approaches the melting point.

5. Conclusion

During the dynamic oxidation of the molten slag, (Ti^{2+}) and (Ti^{3+}) were oxidized to (Ti^{4+}), and the titanaugite and Ti-rich diopside containing Ti^{3+} gradually vanished. As a result, the Ti component is selectively enriched into the perovskite phase. With a longer oxidation time, the (Ti^{4+}) content rapidly increased and that promoted the

forward of precipitation reaction: $(Ca^{2+}) + (TiO_3^{2-}) = CaTiO_3$, accelerating the enrichment of the Ti component and precipitation of the perovskite phase. Meanwhile, the oxidation of TiC and metallic Fe were not only in favour of the decrease of the viscosity of the slag, but also for the precipitation and growth of the perovskite phase. As the oxidation time approaches 12 min, the precipitation and the grain size of the perovskite phase rapidly increased and the molten slag changed from the melt to a mixture of the melt and crystalline phase(s), causing the viscosity of the oxidized slag for 12 min highly increased.

Acknowledgements

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