Note

Separation of Olivine Crystals and Borate Containing Slag from CaO–SiO₂–B₂O₃–MgO–Al₂O₃ System by Utilizing Super-Gravity

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The olivine crystals and borate containing slag were effectively separated from the CaO–SiO₂–B₂O₃–MgO–Al₂O₃ system at an optimum precipitating temperature of olivine by utilizing super-gravity. The borate containing slag melt went through the filter, whereas the olivine crystals with a larger size of 300 μm –2 500 μm were intercepted by the filter. Consequently, after super-gravity separation with $G=900$ at 1 463 K for 5 minutes, the mass fraction of B₂O₃ in separated borate containing slag was 30.17 wt%, while that of the separated olivine was only 0.009 wt%, and the recovery ratio of boron in separated borate containing slag thus was up to 99.97%.

KEY WORDS: olivine crystals; borate containing slag; precipitation; separation; super-gravity; CaO–SiO₂–B₂O₃–MgO–Al₂O₃ system.

1. Introduction

The boron-bearing slag is a main byproduct of blast furnace ironmaking process by using ludwigite as raw material.¹⁾ Although the content of B₂O₃ (boron oxides) in the slag was up to 10–22 wt%, it was hard to apply the traditional physical separation techniques to recover boron due to its dispersive distribution and complex combination in various minerals.^{2,3)} Fortunately, many novel technical methods have been proposed for recovering boron from the slag, mainly including the acid leaching process,^{4,5)} and the precipitation and crystallization method.^{6,7)} Sui proposed⁷⁾ that the efficiency of boron extraction from boron-bearing slag was related to the precipitating amount of suanite (Mg₂B₂O₅) and kotoite (Mg₃B₂O₆), and the optimum precipitating temperature of boron appeared at 1 373 K. Xia⁸⁾ suggested further that the temperature range of 1 473 K–1 373 K was beneficial for the nucleation and growth of suanite precipitate. Liu⁹⁾ proposed that the boron extraction rate in a low temperature range reduced with the decrease of cooling-rate in a high temperature range. Additionally, Zhang¹⁰⁾ reported that the precipitation of suanite was replaced by olivine (Mg₂SiO₄) at 1 573 K–1 373 K

when cooling-rate was below 2 K/min. Moreover, Wang⁴⁾ proposed that some fine suanite intermixed with larger olivine particles appeared in the slag after furnace cooling. In light of the fine size and fragile state of boron precipitates, especially the intimate intermixing of boron with other precipitates, it was difficult to separate boron precipitate from other minerals directly by beneficiation methods.¹¹⁾ Considering olivine was the first precipitate from boron-bearing slag with temperature decreasing based on B₂O₃–MgO–SiO₂ phase diagram, while kotoite and suanite precipitated at lower temperatures and uniformly distributed among the first precipitated olivine,^{5–11)} the separation of olivine precipitate and borate containing slag thus would be another feasible choice for recovering boron from the slag. Consequently, the precipitation behavior of olivine in CaO–SiO₂–B₂O₃–MgO–Al₂O₃ system was investigated, and then the separation of olivine crystals and borate containing slag melt by utilizing super-gravity was conducted in current study, which under the inspiration of successful application of super-gravity on some other melts.^{12–15)} Simultaneously, the effects of gravity coefficient on the microstructure, the mineral compositions, and the content and recovery ratio of boron in separated samples were investigated further.

2. Experimental

The chemical agents were well mixed based on the main compositions of real boron-bearing blast furnace slag from Liaoning province of China, which was called simulated slag as shown in **Table 1**. The samples were filled in some graphite crucibles and heated to 1 773 K for 30 minutes under argon atmosphere in a muffle furnace to ensure fully melting. Thereafter, the melted slag was sequentially cooled to 1 723 K, 1 673 K, 1 623 K, 1 573 K, 1 523 K, 1 473 K, 1 423 K, 1 373 K or 1 323 K at 50 K intervals, and then slowly cooled from one to the next temperature at a cooling-rate of 0.5 K/minute, respectively. After that, the samples obtained in different temperature ranges were water-quenched and measured further by X-ray diffraction (XRD) and scanning electron micrograph and energy-dispersive spectrum (SEM-EDS) to gain the variations in precipitation behaviors of olivine with the decreasing temperature.

Based on preliminary precipitation experiment results, the slag was melted at 1 773 K and slowly cooled from 1 523 K to 1 373 K at a cooling-rate of 0.5 K/minute for promoting the precipitation and crystallization of olivine, and then water-quenched. Afterwards, the separation experiments of olivine crystals and borate containing slag melt were conducted in a centrifugal apparatus as depicted in **Fig. 1**, in which a heating furnace heated by resistance and a counterweight were fixed symmetrically onto a centrifugal rotor for generating a stable and adjustable super-gravity field, which rotated from vertical to horizontal once the

Table 1. Chemical compositions of the boron-bearing blast furnace slag and the simulated slag (wt%).

Compositions	B ₂ O ₃	MgO	SiO ₂	CaO	Al ₂ O ₃
Real slag	10.00–22.00	35.00–45.00	20.00–32.00	5.00–8.00	5.00–10.00
Simulated slag	20.00	40.00	25.00	7.00	8.00

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Fig. 1. Schematic diagram of centrifugal apparatus: 1 counter weight, 2 centrifugal axis, 3 conductive slipping, 4 heating furnace, 5 temperature controller, 6 thermocouple, 7 resistance coil, 8 olivine crystals, 9 fiber, 10 filter, 11 borate containing slag melt.

centrifugal rotor started running. 15 grams water-quenched slag were placed onto a graphite filter with a pore size of 0.5 mm, and a graphite felt with a pore size of 0.01 mm was embedded between them, which were put further onto a graphite crucible with an inner diameter of 19 mm. The sample was heated to 1 463 K in the heating furnace for 10 minutes, and then the centrifugal apparatus was adjusted to angular velocity of 1 036 r/min, 1 465 r/min or 1 794 r/min, namely $G=300$, $G=600$ or $G=900$ as calculated *via* Eq. (1), at the constant temperature for 5 minutes, respectively. After that, the apparatus was shut off, and the sample was water-quenched. Furthermore, the parallel experiment was conducted at 1 463 K for 15 minutes without super-gravity treatment.

$$G = \frac{\sqrt{g^2 + (\omega^2 R)^2}}{g} = \sqrt{1 + \left(\frac{N^2 \pi^2 R}{900}\right)^2} \dots\dots\dots (1)$$

where, G is gravity coefficient, g is normal-gravitational acceleration ($g=9.8 \text{ m/s}^2$), ω is angular velocity (rad/s^{-1}), N is rotating speed (r/min), R is the distance between centrifugal axis and sample center ($R=0.25 \text{ m}$).

The samples obtained by super-gravity with different gravity coefficients were sectioned longitudinally along the center axis to gain a macrograph. Thereafter, the separated samples were measured by XRD and SEM-EDS methods for analyzing the mineral compositions and microstructures, and characterized further by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to determine the mass fractions of B_2O_3 . Conclusively, the recovery ratio of boron was calculated *via* Eq. (2).

$$R_B = \frac{m_s \times \omega_B}{m_o \times \omega_o + m_s \times \omega_B} \times 100\% \dots\dots\dots (2)$$

where, R_B is the recovery ratio of boron in separated borate containing slag, m_o and m_s are the mass of separated olivine and borate containing slag, ω_o and ω_B are the mass fractions of B_2O_3 in separated olivine and borate containing slag.

3. Results and Discussion

Combined with the variations in mineral compositions and microstructures of slag melt with temperature decreasing as shown in **Fig. 2**, it was obvious that the fine equiaxed olivine crystals first precipitated at temperature below

Fig. 2. Variations in XRD patterns and SEM photographs of the slag melt with temperature decreasing: (a) XRD patterns, (b) SEM of 1 523 K–1 473 K, (c) SEM of 1 473 K–1 423 K, (d) SEM of 1 423 K–1 373 K.

Fig. 3. Vertical profiles of the sample obtained by super-gravity compared with the parallel sample: (a) $G=1$, (b) $G=600$. (Online version in color.)

1 573 K. With temperature decreasing from 1 523 K to 1 373 K, the diffraction peak intensity of olivine gradually increased, and the fine olivine precipitates transformed into a larger columnar crystals, whereas the boron remained in slag melt rather than forming suanite or kotoite precipitates due to the decrease of concentration and migration rate of magnesium ion with the adequately precipitating of olivine. When temperature decreased further to below 1 373 K, the diffraction peak intensity of olivine tended to decrease, while a weak diffraction peak of kotoite started to appear. This indicated that 1 523 K–1 373 K was the optimum temperature range for a single olivine adequately precipitating from the slag melt during slowly cooling process.

The vertical profiles of the sample obtained by super-gravity with $G=600$ compared with the parallel sample are illustrated in **Fig. 3**. Obviously, the whole sample with a uniform structure was blocked by filter in a normal-gravity field as shown in Fig. 3(a). In contrast, two separated samples that went through and held above the filter were obtained by super-gravity treatment as shown in Fig. 3(b). Moreover, the sample above filter appeared in a white porous structure, while the sample below filter presented in a transparent glassy state, respectively.

Compared with the XRD patterns of separated samples obtained by super-gravity as shown in **Fig. 4**, only the diffraction peak of olivine obviously appeared in the upper sample, whereas that of the lower sample presented as a typical dispersive peak. Furthermore, the SEM photographs and EDS data of separated samples are shown in **Fig. 5** and **Table 2**, respectively. Most of magnesium (39.59–41.62 wt%), silicon (22.87–24.70 wt%) and oxygen

Fig. 4. XRD patterns of the separated samples obtained by super-gravity.

Fig. 5. SEM photographs of the separated samples: (a) and (b) separated olivine, (c) separated borate containing slag, pt.1 and pt.2 olivine crystals, pt.3 and pt.4 inlay material. (Online version in color.)

Table 2. EDS data of the separated olivine obtained by super-gravity (wt%).

No.	Positions	Mg	Si	O	C
Pt. 1	Fig. 5(a)	41.62	24.70	33.68	–
Pt. 2	Fig. 5(b)	39.59	22.87	37.54	–
Pt. 3	Fig. 5(a)	–	–	24.61	75.39
Pt. 4	Fig. 5(b)	–	–	24.05	75.95

(33.68–37.54 wt%) apparently precipitated into the olivine, and the separated olivine crystals appeared in a larger three-dimensional structure, which was regarded as a square or a diamond shape with size of 300–500 μm in one plane as shown in Fig. 5(a), while presented as a spatulate shape with size of 2 000–2 500 μm in the vertical plane as shown in Fig. 5(b). However, the compounds of calcium, aluminum, magnesium, silicon, and boron, which were confirmed by the ICP-AES results, formed slag melt, it was scarcely possible to find any olivine grains in the separated slag melt as shown in Fig. 5(c). It was evidenced that all olivine crystals were intercepted by filter, while the borate containing slag melt went through the filter forced by super-gravity and thus effectively separated from the olivine crystals.

Figure 6 presents the variations in mass fractions and recovery ratios of B_2O_3 in separated samples obtained by super-gravity with different gravity coefficients. Generally, due to the higher viscosity of slag melt in a lower separating temperature, some slag melt could not be effectively separated from the olivine crystals instead including in the gaps among them, thus increasing gravity coefficient was definitely beneficial for the reinforced separation between two phases. In the case of 1 463 K, $G=900$ and $t=5$ min, the mass fraction of B_2O_3 in separated borate containing slag was up to 30.17 wt%, while that of the separated olivine

Fig. 6. Variations in mass fractions and recovery ratios of B_2O_3 in the separated samples obtained by super-gravity with different gravity coefficients.

was only 0.009 wt%. The recovery ratio of boron in separated borate containing slag was up to 99.97%. Considering the olivine crystals adequately precipitated and effectively separated from the borate containing slag melt by utilizing super-gravity in current study, some works thus on following separation of boron precipitates from the separated borate containing slag are needed to increase the efficiency of boron extraction further.

4. Conclusion

It was confirmed by the experimental results that separation of olivine crystals and borate containing slag from $\text{CaO-SiO}_2\text{-B}_2\text{O}_3\text{-MgO-Al}_2\text{O}_3$ system at an optimum precipitating temperature of olivine by utilizing super-gravity was an effective method. In a super-gravity field, the borate containing slag melt went through the filter, whereas the olivine crystals with a larger size of 300 μm –2 500 μm were effectively intercepted by the filter, and increasing gravity coefficient definitely enhanced the solid-liquid separation.

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