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# Experimental study on sulfur removal from ladle furnace refining slag in hot state by blowing Air

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**Abstract:** In view of the present problem of sulfur enrichment in the metallurgical recycling process of ladle furnace (LF) refining slag, a simple and efficient method of removing sulfur from this slag was proposed. The proposed method is compatible with current steelmaking processes. Sulfur removal from LF refining slag for SPHC steel (manufactured at a certain steel plant in China) by blowing air in the hot state was studied by using hot-state experiments in a laboratory. The FactSage software, a carbon/sulfur analyzer, and scanning electron microscopy in conjunction with energy-dispersive X-ray spectroscopy were used to test and analyze the sulfur removal effect and to investigate factors influencing sulfur removal rate. The results show that sulfur ions in LF refining slag can be oxidized into $SO_2$ by $O_2$ at high temperature by blowing air into molten slag; $SO_2$ production was observed to reach a maximum with a small amount of blown $O_2$ when the temperature exceeded 1350°C. At 1370°C and 1400°C, experimental LF refining slag is in the liquid state and exhibits good fluidity; under these conditions, the sulfur removal effect by blowing air is greater than 90wt% after 60 min. High temperature and large air flow rate are beneficial for removing sulfur from LF refining slag; compared with air flow rate, temperature has a greater strongly influences on the sulfur removal.

**Keywords:** steelmaking; refining; slag; sulfur removal; oxidation; resource utilization

## 1. Introduction

Steel slag is an auxiliary product in the steelmaking process. Depending on the steelmaking process, steel slag is classified into hot-metal pretreatment slag, basic oxygen furnace slag, electric arc furnace slag, and secondary refining slag. Currently, the utilization rate of steel slag in China is relatively low, and applications of slag tend to focus on basic aspects such as paving materials [1–5], engineering backfill materials [6], and cement [7–12]; however, in all these applications, slag suffers high utilization costs and low utilization values [13]. Because the chemical composition of steel slag (CaO, FeO, MgO, and $Al_2O_3$) [14] is similar to that of flux and slagging material, it has potential applications in metallurgical recycling processes [15]. A schematic of steel slag recycling in a metallurgy process is shown in Fig. 1. The advantages of recycling steel slag in metallurgical processes include reduced raw material consumption, reduced utilization costs, lower emission of steel slag, and decreased environmental pollution; thus, metallurgical recycling is an excellent approach to utilizing steel slag.

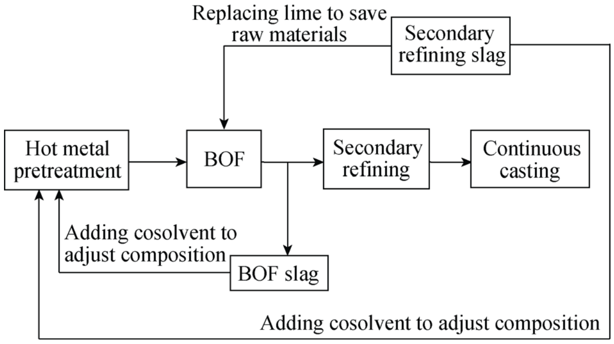

**Fig. 1. Sketch of metallurgical reuse of steel slag in different processes.**

At present, in China, the most common method of refining is ladle furnace (LF) refining, which produces approxi-

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mately 12 million tons of LF refining slag. LF refining slag has high basicity and high sulfur capacity. Fig. 1 shows that LF refining slag has value for recycling in several metallurgical processes; however, the greatest problem during metallurgical recycling is the high sulfur content of LF refining slag. In addition, the sulfur content will increase with each successive recycling of the slag, resulting in sulfur enrichment in the circulating slag, which adversely affects the metallurgical recycling of LF refining slag [16–18].

Many researchers have proposed different methods for desulfurizing LF refining slag. Kobayashi [19] pulverized the cooled refining slag to less than 0.074 mm and injected a mixed gas composed of 79% Ar + 21% $O_2$ at 1100°C for oxidizing, roasting, and desulfurization. They achieved a sulfur removal rate of approximately 50wt%. Bigeev *et al.* [20] placed a flame gun into refining slag before tapping, resulting in desulfurization by the oxidation of the elemental sulfur into gaseous sulfide. Cui *et al.* [21] used two-stage roasting for the desulfurization of LF refining slag and achieved a sulfur removal rate of 71.25wt%. All these methods can move sulfur from LF refining slag to a certain extent. However, the compatibility of these methods with production processes is poor, requiring extensive equipments and technologies, which would adversely affect present manufacturing techniques.

In an actual steel plant, LF refining slag remaining in the ladle will be poured into a container after LF refining. At this stage, refining slag is at a high temperature and in the liquid state with good thermodynamic and kinetic conditions. Therefore, an oxidizing gas can be blown into the LF refining slag at this point to desulfurize the slag by oxidizing sulfur. This method requires only the installation of gas-blowing equipment on the molten slag container. After desulfurization, refining slag can be recycled to the refining process as a slagging constituent, with little influence on existing processes. The specific process is shown in Fig. 2. This method will substantially increase the value of LF refining slag as a metallurgical resource, reduce the amount of slagging constituent and provide economic benefit to steel corporations.

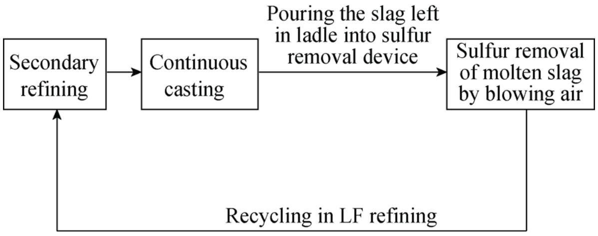

**Fig. 2. A new idea for reusing LF refining slag in the hot state.**

We conducted an experimental study on desulfurization blowing in molten LF refining slag. The effects of desulfurization and factors affecting the desulfurization rate were investigated, and theoretical guidance is provided for the practical application of the thermal desulfurization of LF refining slag in metallurgical processes.

## 2. Experiment

Refining slag (100 g) of SPHC steel was used in the experiments; the composition of the slag is listed in Table 1. As shown in Table 1, both the basicity and sulfur content of refining slag were high.

**Table 1. Composition of experimental LF refining slag** wt%

| CaO | $SiO_2$ | $Al_2O_3$ | MgO | $TiO_2$ | $Fe_2O_3$ | MnO | $P_2O_5$ | $Na_2O$ | BaO | S | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 54.62 | 12.1 | 23.54 | 4.48 | 0.72 | 1.74 | 0.15 | 0.12 | 0.11 | 0.025 | 0.844 | 0.061 |

A $MoSi_2$ tube-type resistance furnace was used to heat slag, during which air served as an oxidizing gas. In the experimental process, refining slag was placed in a MgO crucible with dimensions of ϕ60 mm × 100 mm surrounded by a graphite crucible. The crucible was subsequently placed into a $MoSi_2$ high-temperature box-type furnace to melt LF refining slag at high-temperature range and was subsequently cooled to the experimental temperature. Air was blown into molten LF refining slag through an $Al_2O_3$ tube with a diameter of 8 mm to remove sulfur via oxidation, during which Ar gas was used for protection. The experimental setup is shown in Fig. 3.

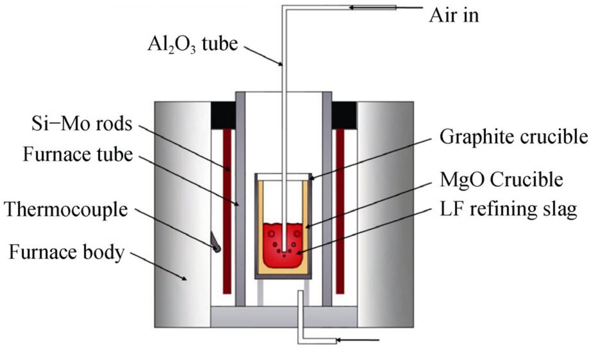

**Fig. 3. Experimental setup used for the laboratory experiments.**

According to the practical manufacturing process, after casting, the LF refining slag temperature in the ladle ranges from 1400°C to 1450°C. To investigate the effects of decreasing temperature, sulfur was removed by oxidation at temperatures of 1400, 1370, and 1350°C. The temperature curve of the resistance furnace is shown in Fig. 4.

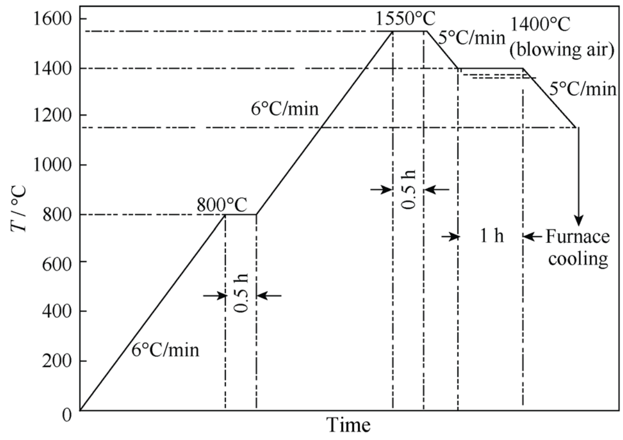

**Fig. 4. Experimental temperature curve.**

During the experiment, samples were collected at four time points: before blowing and after blowing for 10 min, 30 min, and 60 min. The sulfur content was analyzed using a Horiba EMIA-820V (Japan) carbon–sulfur analyzer; the phase morphology and composition were analyzed by scanning electron microscopy (SEM) on a Zeiss EVO-18 microscope equipped with an energy-dispersive X-ray spectroscopy (EDS) unit.

## 3. Results and discussion

### 3.1. Thermodynamic calculations

As shown in Fig. 5, the FactSage thermodynamic software was used to compute the relationship between the amount of blown oxygen and the amount of $SO_2$ produced in 100 g of slag; the calculations were based on the composition of the LF refining slag. The amounts of blown oxygen and the corresponding maximum amounts of $SO_2$ produced are listed in Table 2.

According to FactSage calculation results, S in slag can be oxidized into $SO_2$ by oxygen blown into LF refining slag at high temperatures. As shown in Fig. 1, the corresponding maximum amount of $SO_2$ generated in 100 g of LF refining slag increases with increasing temperature. The increment is small, and the maximum amount of $SO_2$ generated is approximately 1.65 g at different temperatures. In addition, according to Fig. 5, the amount of blown oxygen and corresponding maximum amount of $SO_2$ generated decreases drastically with increasing temperature. However, only a small amount of oxygen needs to be blown into refining slag to maximize the amount of $SO_2$ generated.

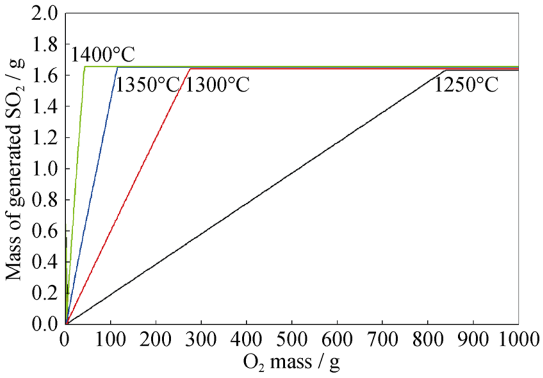

**Fig. 5. Relationship between $O_2$ amount and $SO_2$ production in experimental LF refining slag.**

**Table 2. Sulfur removal rates at different times for four groups of experiments**

| No. | Air-blowing temperature / °C | Gas flow / ($m^3 \cdot h^{-1} \cdot t^{-1}$) | Sulfur removal rate, $\eta$ / % | | |
|---|---|---|---|---|---|
| | | | 10 min | 30 min | 60 min |
| 1 | 1370 | 100 | 47.0 | 74.3 | 88.1 |
| 2 | 1370 | 200 | 48.1 | 75.6 | 90.7 |
| 3 | 1400 | 100 | 64.2 | 87.1 | 96.4 |
| 4 | 1400 | 200 | 71.7 | 88.7 | 95.8 |

### 3.2. Effects of sulfur removal by blowing air

In the experimental process, the LF refining slag is in the liquid state and exhibits excellent fluidity with strong stirring by flowing gas at 1400°C and 1370°C. However, at 1350°C, the slag is a solid–liquid mixture and exhibits poor fluidity; thus, stirring by gas flow is weak and the slag solidifies quickly, leading to a failure to continue to remove sulfur by blowing. Therefore, in subsequent experiments, the effects of sulfur removal by blowing air into LF refining slag and the factors affecting the removal rate of sulfur were studied at 1400°C and 1370°C using different air flows. Four different experiments were conducted. The temperature of blown gas in experiments 1 and 2 was 1370°C, and the corresponding gas flows were 100 $m^3 \cdot h^{-1} \cdot t^{-1}$ and 200 $m^3 \cdot h^{-1} \cdot t^{-1}$, respectively. The temperature of blown gas in experiments 3 and 4 was 1400°C, and the corresponding gas flows were 100 $m^3 \cdot h^{-1} \cdot t^{-1}$ and 200 $m^3 \cdot h^{-1} \cdot t^{-1}$, respectively. In all four experiments, samples were collected prior to blowing and after blowing for 10, 30, and 60 min, and the sulfur content in the samples was analyzed.

The relationship between blowing time and sulfur content in the slag under different experimental schemes is shown in Fig. 6. As shown in Fig. 6, the blowing of air into LF refining slag can achieve remarkable sulfur removal. The sulfur content in the slag decreased with the increasing blowing time, and the sulfur content was decreased to the range lower than 0.1wt% after a blowing time of 60 min.

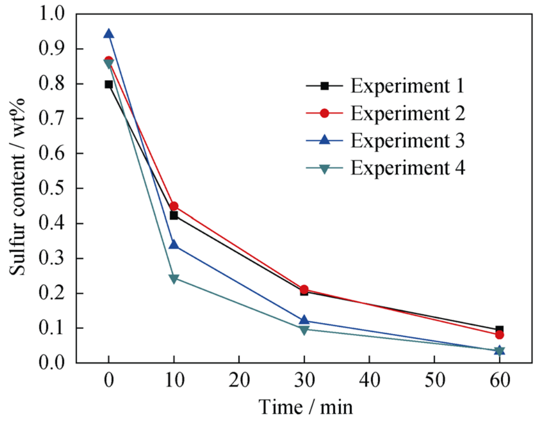

**Fig. 6. Relationship between S content in the slag and air-blowing time.**

The removal rate corresponding to blowing times is defined as follows:

$$\eta = \frac{w_o(S) - w(S)}{w_o(S)} \times 100\% \tag{1}$$

where $w_o(S)$ is the sulfur mass fraction in the slag prior to the blowing of gas, and $w(S)$ is the sulfur mass fraction in the slag after the blowing of gas for a period of time.

The removal rates of sulfur corresponding to 10, 30, and 60 min are listed in Table 2.

As shown in Table 2, the removal rate of sulfur can exceed 47wt% with 10 min of blowing and 74wt% with 30 min of blowing. As a consequence, the removal velocity of sulfur is fast during the initial stage of blowing. After 30 min of blowing, the rate at which the sulfur content in the slag decreases is small and the sulfur content changes little.

### 3.3. Effects of temperature on the gas removal of sulfur

Studies have shown that the reaction at the gas–slag interface under conditions where air is blown into molten slag can be described as follows [22–23]:

$$(S^{2-*}) + \frac{3}{2}O_2^* = SO_2 + (O^{2-}) \tag{2}$$

This equation is the reaction equation of gas desulfurization in molten slag, where $(S^{2-*})$ represents a sulfur ion adsorbed onto the gas–slag interface and $O_2^*$ represents an oxygen molecule adsorbed onto the gas–slag interface.

Wei and Wang [23] proposed that, in the desulfurization of molten $CaO–Al_2O_3–SiO_2$ with gas, the relationship between desulfurization velocity $v_s$ and sulfur content $w(S)$ in the molten slag is given as

$$v_s = -\frac{dw(S)}{dt} = k_1 w(S) \tag{3}$$

The following equation can be deduced:

$$\lg w(S) = -k_2 t + \lg w_o(S) \tag{4}$$

where $t$ is the blowing time for desulfurization, min; and $k_1$ and $k_2$ are constants whose relationship is given as

$$k_1 = 2.30k_2 \tag{5}$$

As a reaction occurs at the gas–slag interface, the interfacial area should be taken into account, where the unit of $v_s$ is denoted as g/min:

$$-\frac{dw(S)}{dt} \cdot \frac{m}{100} = Ak_3 w(S) \tag{6}$$

or

$$-\frac{dw(S)}{dt} = \frac{100Ak_3}{m} w(S) \tag{7}$$

where $A$ is the gas–slag interfacial area, $cm^2$; $m$ is weight of slag, g; and $k_3$ is the reaction rate constant, $g \cdot cm^{-2} \cdot min^{-1}$. By comparing Eqs. (3), (5), and (7), we obtain the following equation:

$$k_3 = \frac{2.30m}{100A} k_2 \tag{8}$$

Wei and Wang [23] observed the following relationship between $\lg k_3$ and temperature:

$$\lg k_3 = -\frac{8190}{T} + 2.09 \tag{9}$$

Fig. 7 shows a comparison of the desulfurization rates at 1370°C and 1400°C. According to Figs. 7(a) and (b), the effect of temperature on the desulfurization rate is remarkable. At an air flow of 100 $m^3 \cdot h^{-1} \cdot t^{-1}$ or 200 $m^3 \cdot h^{-1} \cdot t^{-1}$, the desulfurization rates at 1370°C with 10, 30, and 60 min of blowing are all lower than the corresponding rates at 1400°C. Meanwhile, the reaction rate constant $k_3$ at 1370°C and 1400°C is 0.00127 and 0.00157, respectively, which further indicates that enhancing temperature is beneficial to the gas desulfurization of molten slag.

### 3.4. Effects of gas flow on gas desulfurization

Because of strong stirring of molten slag by the flowing gas, according to Wu *et al.*'s research [24] the diffusion of sulfur ions is no longer the rate-controlling step; the diffusion of oxygen in air at the gas–slag interface is now the rate-controlling step; i.e., the desulfurization velocity is equal to the intensity of blowing oxygen gas.

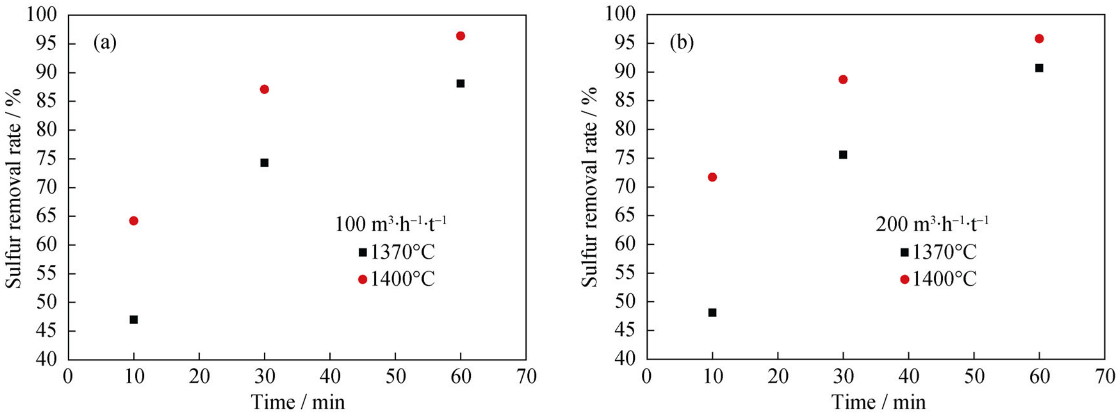

**Fig. 7. Comparisons of sulfur removal rates at different air-blowing temperatures.**

The following equation can be obtained:

$$-\frac{\mathrm{d}w(S)}{\mathrm{d}t}=\frac{2V_{O_2}\times 32\times 10^{-1}}{3m_{\mathrm{slag}}} \tag{10}$$

where $V_{O_2}$ is the intensity of blowing oxygen gas, mol/s; and $m_{\mathrm{slag}}$ is the mass of molten slag, kg. According to Eq. (10), when the slag quality is a certain value, the desulfurization rate is proportional to the intensity of blowing oxygen gas, which indicates that increasing the gas flow is beneficial to gas desulfurization of molten slag.

The effects of gas flow on desulfurization are shown in Fig. 8. According to Figs. 8 (a) and (b), gas flow affects the desulfurization rate to some extent. At two different blowing temperatures and at a gas flow of 100 $m^3 \cdot h^{-1} \cdot t^{-1}$, the desulfurization rates at 10 min and 30 min were lower than the corresponding rates at a gas flow of 200 $m^3 \cdot h^{-1} \cdot t^{-1}$, although the difference is small. At 1370°C, the desulfurization rate at 60 min and at a gas flow of 100 $m^3 \cdot h^{-1} \cdot t^{-1}$ was lower than the corresponding rate at a gas flow of 200 $m^3 \cdot h^{-1} \cdot t^{-1}$. At 1400°C, the desulfurization rate at two gas flows at 60 min was approximately equal. These results demonstrate that a large gas flow facilitates the removal of sulfur from LF refining slag and affects desulfurization less compared to the effect of temperature.

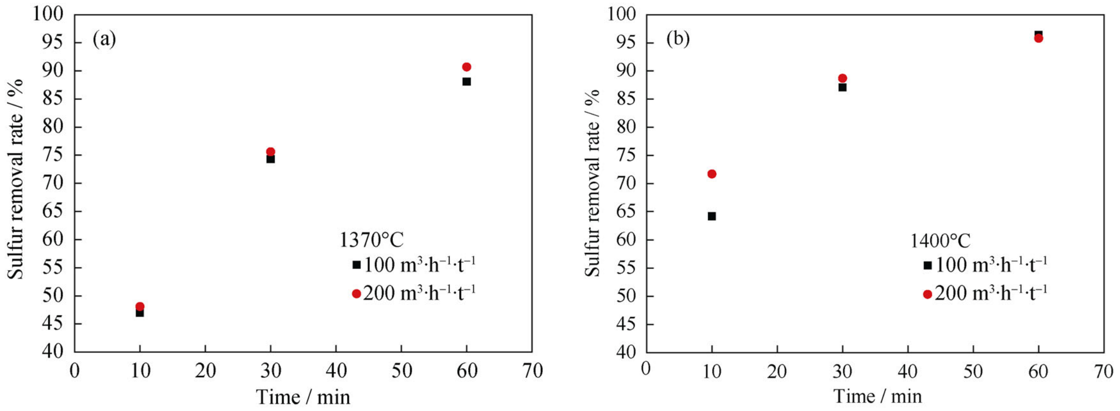

**Fig. 8. Comparisons of Sulfur removal rates with different air flows.**

### 3.5. Microanalyses of LF refining slag before and after desulfurization

SEM images of LF refining slag before and after desulfurization in experiment 2 are shown in Fig. 9. Sample (a) is the sample before blowing, and sample (b) is the slag sample after 60 min of blowing. The two samples were both collected in the liquid state and subsequently quenched in water.

Because of the fast quenching, the slag had insufficient time for growth and nucleation; thus, crystals in phases could not develop into dependent phases with few species of phases. The regions of different colors of the two slag samples were analyzed by EDS; the results are shown in Fig. 10. The black phase is composed of MgO, and the gray phase is $CaO–Al_2O_3–SiO_2–MgO$. The grey phase in sample (a) contains a certain amount of sulfur, whereas the gray phase in sample (b) contains no sulfur. The sulfur in the LF refining slag was almost removed by oxidation after 60 min of blowing.

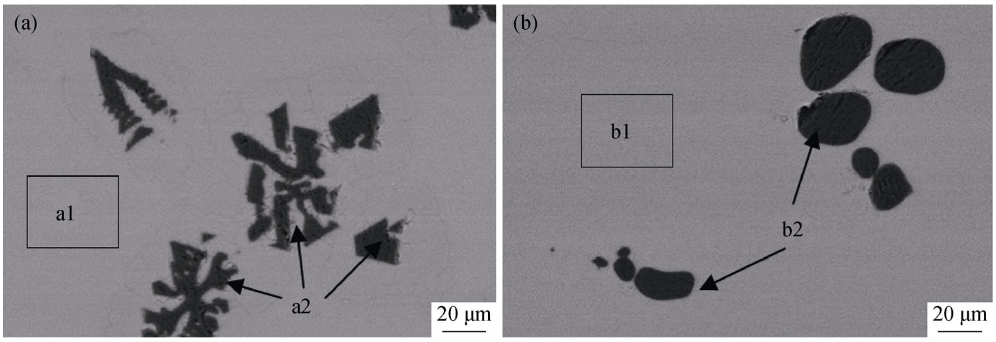

**Fig. 9. Backscattered electron images of experimental LF refining slag before (a) and after (b) sulfur removal.**

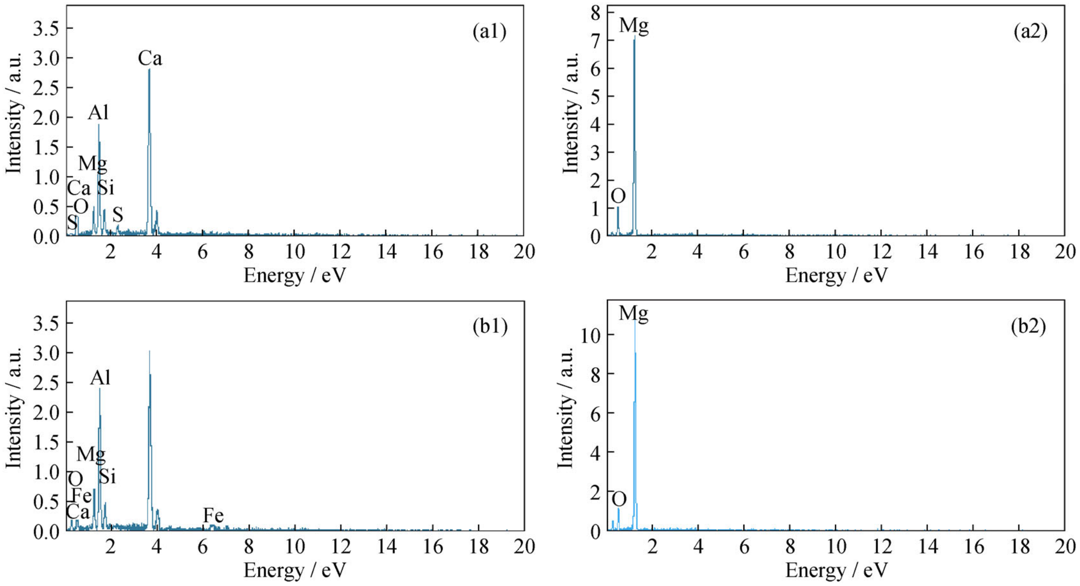

**Fig. 10. EDS spectra for different microregions in experimental samples (a) and (b).**

## 4. Conclusions

At present, sulfur enrichment in the metallurgical recycling of LF refining slag is a widespread problem, substantially restricting the number of times LF refining slag can be recycled in a metallurgical process. In view of this situation, through theoretical calculations and laboratory experiments, the feasibility and factors that influence the removal of sulfur from LF refining slag in a hot state were investigated; as a result, we proposed an efficient method for removing sulfur from LF refining slag. Our research results are summarized as follows:

(1) At the molten state of LF refining slag, sulfur ions in the slag are oxidized into $SO_2$ by $O_2$ in air blown into the molten slag.

(2) FactSage calculations show that, at high temperature, sulfur in LF refining slag can be oxidized to $SO_2$ by blown $O_2$. When the temperature exceeds 1350°C, the production of $SO_2$ reaches a maximum with only a small amount of $O_2$.

(3) At 1370°C and 1400°C, experimental LF refining slag is in the liquid state with good fluidity and the sulfur removal effect of blowing air into the fluid slag is obvious; the sulfur removal was 47wt% at 10 min, greater than 74wt% at 30 min, and greater than 90wt% at 60 min.

(4) High temperatures and large air flows are beneficial for the removal of sulfur from LF refining slag, and, compared to the air flow, temperature has a greater influence on the sulfur removal effect.

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