

## Influence of $\text{Na}_2\text{CO}_3$ as Additive on Direct Reduction of Boron-bearing Magnetite Concentrate

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**Abstract:** Boron-bearing magnetite concentrate is typically characterized by low grade of iron and boron ( $w_{\text{TFe}} = 51\% - 54\%$ ,  $w_{\text{B}_2\text{O}_3} = 6\% - 8\%$ ), as well as the close intergrowth of ascharite phase and magnetite phase. A promising technology was proposed to separate iron and boron by coupling the direct reduction of iron oxides and Na activation of boron minerals together. The influence of  $\text{Na}_2\text{CO}_3$  as additive on the direct reduction of boron-bearing magnetite was studied by chemical analysis, kinetic analysis, XRD analysis and SEM analysis. The results showed that the addition of  $\text{Na}_2\text{CO}_3$  not only activated boron minerals, but also reduced the activation energy of the reaction and promoted the reduction of iron oxides. Besides, the addition of  $\text{Na}_2\text{CO}_3$  changed the composition and melting point of non-ferrous phase, and then promoted the growth and aggregation of iron grains, which was conducive to the subsequent magnetic separation. Thus, the coupling of the two processes is advantageous.

**Key words:** ludwigite; kinetic analysis; direct reduction; magnetic separation; sodium carbonate

There is quite abundant ludwigite ore in Liaoning province, China. The total reserve of ludwigite ore is about 280 Mt, of which about 21.84 Mt is  $\text{B}_2\text{O}_3$ , accounting for 58% boron reserves in China<sup>[1]</sup>. Because of the low grade of boron ( $w_{\text{B}_2\text{O}_3} = 6\% - 8\%$ ) and iron ( $w_{\text{TFe}} = 27\% - 30\%$ ), and the complex intergrowth of different minerals, boron minerals and magnetite cannot be separated and enriched effectively by traditional mineral processing methods. Some results indicated that  $\text{B}_2\text{O}_3$  in boron-bearing magnetite concentrate ( $w_{\text{TFe}} = 51\% - 54\%$ ,  $w_{\text{B}_2\text{O}_3} = 6\% - 8\%$ ) accounted for more than 30% of total  $\text{B}_2\text{O}_3$  in ludwigite<sup>[2,3]</sup>. It is obvious that the key problem in exploring ludwigite is the further separation of boron and iron in boron-bearing magnetite concentrate.

The separation of boron and iron in boron-bearing magnetite concentrate has been investigated by many researchers, and several processes have been proposed, including hydrometallurgical, pyrometal-

lurgical and Na-activation roasting processes, etc.<sup>[4-8]</sup>. However, none of these processes has been found to be effective and economically feasible.

Recently, a promising process was proposed<sup>[9]</sup>. The boron-bearing magnetite concentrate was first homogenized with sodium salt and coal, and then heated in a reducing atmosphere for a certain period of time. After that, the roasted product was subjected to wet grinding and water leaching to obtain boron-rich leaching solution, and the leaching residue was used to extract metallic iron powder by low intensity magnetic separation. Boron-rich leaching solution can be used to produce borax by carbonization technology, and metallic iron powder can be used to steelmaking. New technology shortened the process and reduced energy consumption by coupling the direct reduction of iron oxides and Na activation of boron minerals together. Preliminary test results showed that the iron grade and recovery of iron product were up to 92.94% and 87.33%, respectively, while the

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leaching rate of boron was 91.45% under the condition of temperature of 1100 °C, holding time of 90 min, coal dosage of 20% and Na<sub>2</sub>CO<sub>3</sub> dosage of 30%. However, the influence of Na activation reaction on the reduction of iron oxides is not very clear.

In this paper, some tests were carried out in a muffle furnace, using boron-bearing magnetite concentrate, coal and sodium carbonate as raw materials. The purpose of this research is to study the influence of Na<sub>2</sub>CO<sub>3</sub> as additive on the direct reduction of boron-bearing magnetite. The results of this study can provide a theoretical basis for the low-cost, short process, iron-boron efficient separation technology.

## 1 Experimental

### 1.1 Materials

The sample used in this research is boron-bearing magnetite concentrate, and its main chemical compositions are 53.01% Fe, 3.67% B<sub>2</sub>O<sub>3</sub>, 0.35% CaO, 11.39% MgO, 3.97% SiO<sub>2</sub>, and 0.11% Al<sub>2</sub>O<sub>3</sub>.

The concentrate belongs to multi-component and low grade ore, and the particle size of the boron-bearing magnetite concentrate is 40% passing 74 μm.

The crystalline phases of the boron-bearing magnetite concentrate were investigated by powder XRD technique, and the pattern was analyzed by the search-match software. The mineral components of the boron-bearing magnetite concentrate are shown in Fig. 1.

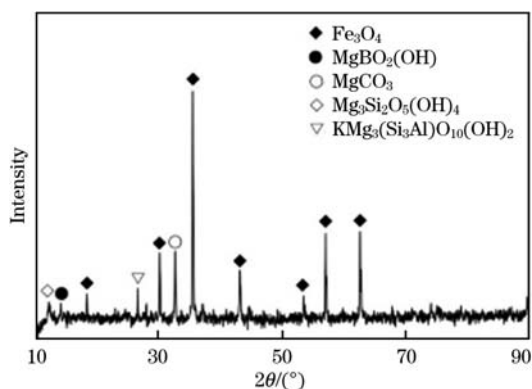


Fig. 1 XRD pattern of boron-containing magnetite concentrate

As shown in Fig. 1, magnetite (Fe<sub>3</sub>O<sub>4</sub>) and magnesite (MgCO<sub>3</sub>) are major phases, while szaibelyite (MgBO<sub>2</sub>(OH)), phlogopite (KMg<sub>3</sub>(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>2</sub>) and lizardite (Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) are minor phases.

A coal with 0.51% water, 15.01% ash, 23.82% volatile matter and 60.66% fixed carbon was used as the reductant, and sodium carbonate (AR) was used as additives. The particle size of coal was controlled

below 1 mm.

### 1.2 Experimental procedure

Boron-bearing magnetite concentrate was first homogenized with 20% coal and 30% Na<sub>2</sub>CO<sub>3</sub>, and then placed into graphite crucibles with a lid. The samples were heated in a muffle furnace for different time at different pre-set temperatures; after that, the samples were removed from the furnace and cooled to room temperature in an inert atmosphere. The cooled products were analyzed to determine the degree of reduction after grated to -74 μm. Direct reduction tests without Na<sub>2</sub>CO<sub>3</sub> were carried out at the same time as controlled experiment.

Because of the presence of carbonates, the degree of reduction could not be directly calculated by mass loss of mixed materials. The degree of reduction (*D*) is defined as follows:

$$D = \frac{\Delta W_t}{\Delta W_T} \times 100\% \quad (1)$$

where,  $\Delta W_t$  is the oxygen loss of iron oxides in time *t*; and  $\Delta W_T$  is the total oxygen content of iron oxides.

## 2 Results and Discussion

### 2.1 Effect of Na<sub>2</sub>CO<sub>3</sub> on degree of reduction

To identify the effect of Na<sub>2</sub>CO<sub>3</sub> on the degree of reduction, several comparative tests about sodium additive were carried out at different temperatures and for different time. The results are shown in Fig. 2.

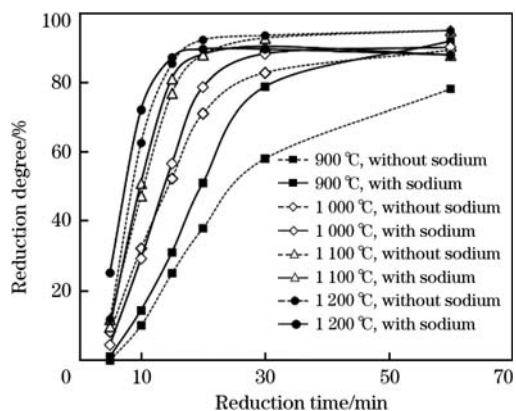


Fig. 2 Isothermal reduction curve of boron-bearing magnetite concentrate

Fig. 2 shows that the reduction degree of boron-bearing magnetite gradually increased with the increase of reaction time. The increase rate was faster in the first 30 min, and then became slow. Besides, there was a proportional relationship between temperature and reduction degree when the reaction time was fixed. It is obvious that raising the temper-

ature and increasing the reduction time are both conducive to the reduction of boron-bearing magnetite, which is consistent with previous study<sup>[10]</sup>.

Compared with direct reduction without sodium, the addition of sodium increased the reduction degree of boron-bearing magnetite significantly at 900 °C. As the temperature increased, the increase amplitude of reduction degree gradually decreased. However, when the temperature reached 1100 °C, the reduction degree became lower than that without the addition of sodium. To further explain different effects of  $\text{Na}_2\text{CO}_3$  on the reduction degree at different temperatures, the reduction rate at different time and temperatures was calculated, as shown in Fig. 3.

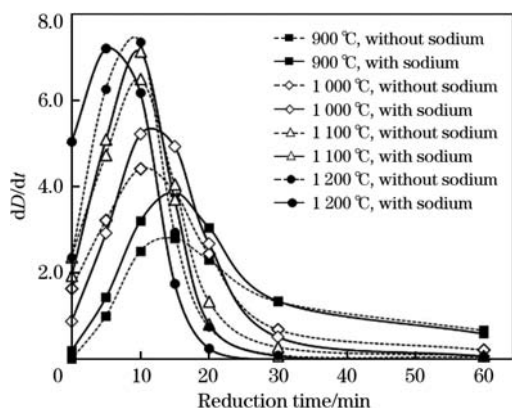


Fig. 3 Reduction rate curve of boron-bearing magnetite concentrate

From Fig. 3, it is obvious that the reduction rate increased at the beginning and then decreased with the increase of reduction time. The maximum reduction rates are reached mainly in 5–15 min, and the higher the temperature is, the sooner the maximum reduction rate is achieved. Besides, the maximum reduction rate increased gradually with the increase of temperature. Thus, when the reaction time is fixed, increasing temperature can increase the reduction rate, and then increase the reduction degree, which is consistent with the results in previous reduction degree analysis.

Compared with direct reduction without sodium, the addition of sodium improved the reaction rate. Besides, with the increase of temperature, the increase amplitude of maximum reduction rate gradually decreased, and the maximum reaction rate gradually appeared in advance. Some researchers believed that the gasification of carbon was an important step of direct reduction, and sodium could contribute to carbon gasification reaction<sup>[11,12]</sup>. Because the carbon gasification reaction is slow at lower temperatures,

the role of sodium in promoting carbon gasification is more obvious. However, as the temperature increased, the carbon gasification rate was gradually approaching to the limit, and the role of sodium is waning with the increase of temperature.

## 2.2 Effect of $\text{Na}_2\text{CO}_3$ on reduction kinetics

Reduction of iron oxides is a typical gas-solid reaction, and the reaction is carried out from outside to inside step by step until the end of the reaction. Scholars idealized the characteristics of gas-solid phase reaction, and constructed a reaction model, called the unreacted shrinking core model, as shown in Fig. 4.

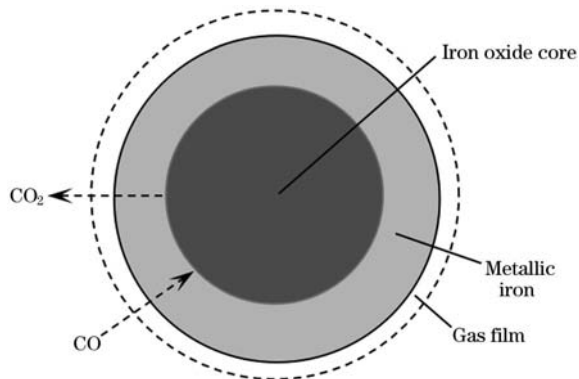


Fig. 4 Shrinking core model of reduction of iron oxide

In order to facilitate the expression, the iron ore is taken as the standard sphere, so the spread of surface chemical reactions can be simplified to a one-dimensional problem. The overall reaction process can be divided into the following steps:

- (1) CO diffuses to the reaction product surface (Fe). This process is called external diffusion.
- (2) CO diffuses to the reaction interface (Fe and iron oxides) through reaction product. This process is called internal diffusion.
- (3) Iron oxides are reduced to metallic iron in the interface. This process is referred to as chemical reaction.
- (4)  $\text{CO}_2$  generated by the reaction diffuses to the outside through the product layer.
- (5)  $\text{CO}_2$  gas diffuses from gas film around product to the air current.

Reduction kinetic differential equations can be established based on the shrinking core model. The overall reaction can be considered to consist of outside diffusion, internal diffusion and chemical reactions. If there is one particularly slow step, other steps will reach equilibrium, and then this step will become the rate-controlling step. Different control

model equations are given as follows<sup>[13-15]</sup>:

$$f_1(t) = D \tag{2}$$

$$f_2(t) = 1 - 3(1 - D)^{2/3} + 2(1 - D) \tag{3}$$

$$f_3(t) = 1 - (1 - D)^{1/3} \tag{4}$$

where,  $f(t)$  is a function.

If  $f_1(t)$  and  $t$  show an apparent linear relationship at a certain time, external diffusion can be considered as the rate-controlling step at this part; while if  $f_2(t)$  and  $t$  exhibit an apparent linear relationship at a certain time, internal diffusion can be considered as the rate-controlling step at this part. If  $f_3(t)$  and  $t$  reveal an apparent linear relationship at a certain time, chemical reaction can be considered as the rate-controlling step at this part.

Fig. 5 shows the relationship of  $1 - (1 - D)^{1/3}$  and  $t$  without  $\text{Na}_2\text{CO}_3$  at different temperatures, and Fig. 6 shows the relationship of  $1 - (1 - D)^{1/3}$  and  $t$  with 30%  $\text{Na}_2\text{CO}_3$  at different temperatures. It is obvious that  $1 - (1 - D)^{1/3}$  and  $t$  show the apparent linear relationship either without  $\text{Na}_2\text{CO}_3$  or with 30%  $\text{Na}_2\text{CO}_3$ . Thus, the reduction of boron-bearing magnetite is controlled by chemical reaction. Fig. 7 shows the Arrhenius curve of reaction rate constant  $k$  and  $T$ , calculated from the slope of Figs. 5 and 6. Therefore, the activation energy can be calculated by the Arrhenius equation:

$$\ln k = \ln A - \frac{E}{RT} \tag{5}$$

where,  $A$  is frequency factor,  $\text{s}^{-1}$ ;  $E$  is activation energy,  $\text{J/mol}$ ;  $R$  is gas constant,  $8.314 \text{ J/(mol} \cdot \text{K)}$ ; and  $T$  is temperature,  $\text{K}$ .

Fig. 7 shows that the slope ( $-E/R$ ) of Arrhenius curve were 8648 and 6868, respectively. Thus, the activation energy of direct reduction without  $\text{Na}_2\text{CO}_3$  was 71.90  $\text{kJ/mol}$ , whereas the activation energy of direct reduction with  $\text{Na}_2\text{CO}_3$  was 57.10  $\text{kJ/mol}$ . It is obvious that after 30%  $\text{Na}_2\text{CO}_3$  was added,

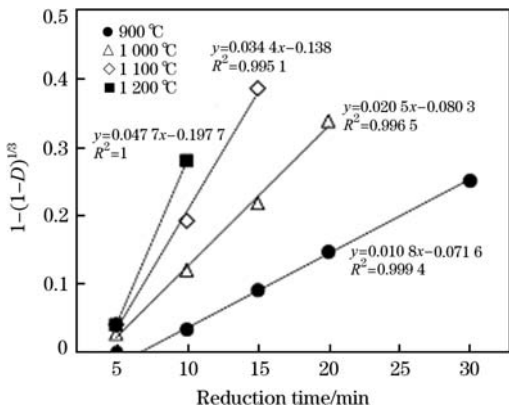


Fig. 5 Relationship of  $1 - (1 - D)^{1/3}$  and  $t$  without  $\text{Na}_2\text{CO}_3$

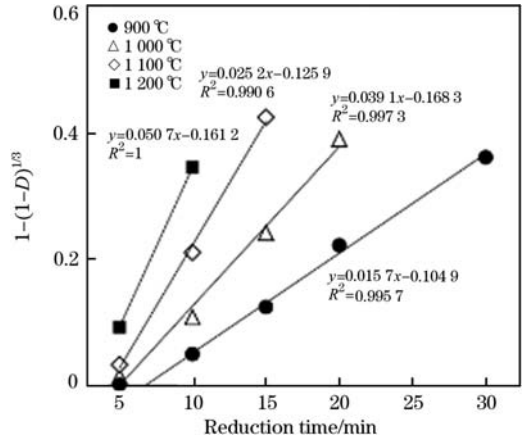


Fig. 6 Relationship of  $1 - (1 - D)^{1/3}$  and  $t$  with  $\text{Na}_2\text{CO}_3$

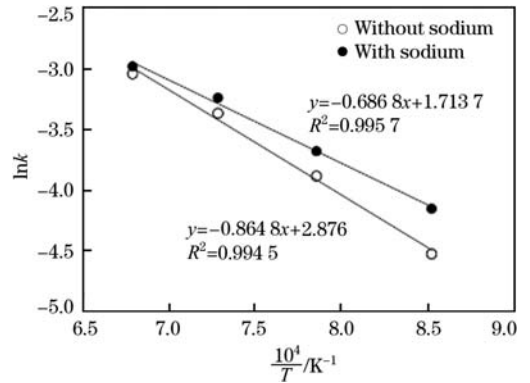


Fig. 7 Relationship of  $\ln k$  and  $10^4/T$

the activation energy decreased, which indicated that  $\text{Na}_2\text{CO}_3$  improved the reduction of boron-bearing magnetite.

### 2.3 Effect of $\text{Na}_2\text{CO}_3$ on metallization rate

Fig. 8 shows the metallization rate curve of boron-bearing magnetite concentrate at different time and different temperatures. From Fig. 8, it can be seen that the metallization rate of reduction products obtained without adding  $\text{Na}_2\text{CO}_3$  was continuously increased with prolonging the reaction time. After  $\text{Na}_2\text{CO}_3$  was added, the degree of metallization was improved at the early stage of the reduction. Kinetic analysis shows that the reduction of boron-bearing magnetite concentrate was controlled by chemical reaction, and the addition of  $\text{Na}_2\text{CO}_3$  reduced the activation energy. According to the study of Leder et al.<sup>[16]</sup>, the reduction of  $\text{FeO}$  into  $\text{Fe}$  was the rate-controlling step. Thus, the addition of  $\text{Na}_2\text{CO}_3$  improved the reduction of  $\text{FeO}$ , and more metallic iron was produced in a certain time. However, when the reduction time was too long, on the contrary, the metallization rate gradually dropped. This was be-

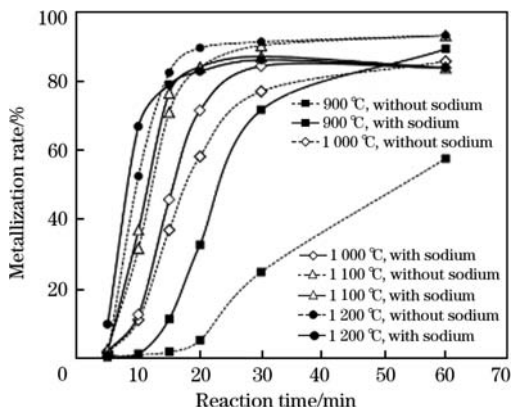


Fig. 8 Metallization rate curve of boron-bearing magnetite concentrate

cause the addition of  $\text{Na}_2\text{CO}_3$  released large amounts of  $\text{CO}_2$  which might consume some carbon. When the coal was insufficient, reduction atmosphere became weak at the late stage of the reduction, and part of metallic iron was re-oxidized.

#### 2.4 Effect of $\text{Na}_2\text{CO}_3$ on mineral composition of reduction product

The effect of  $\text{Na}_2\text{CO}_3$  on the mineral composition of the reduction product at 1100 °C for different reduction time was studied by XRD comparative analysis. The results are shown in Fig. 9.

From Fig. 9, it could be seen that apart from  $\text{Fe}_3\text{O}_4$ , most of the original mineral phase disappeared after roasting for 5 min, and new phase FeO was observed. It was obvious that  $\text{Fe}_3\text{O}_4$  was reduced to FeO, and most of other minerals were decomposed into amorphous. When the reduction time was extended to 10 min, metallic iron first appeared, and FeO became dominating in the products, with corresponding disappearance of  $\text{Fe}_3\text{O}_4$ , which indicated that the reduction of  $\text{Fe}_3\text{O}_4$  into FeO was completed within 10 min, and the reduction of FeO into Fe began before 10 min. Compared with the product obtained without  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_4\text{Mg}_2\text{Si}_3\text{O}_{10}$  was observed in the product with  $\text{Na}_2\text{CO}_3$ , which illustrated that  $\text{Na}_2\text{CO}_3$  changed the composition of non-ferrous phases. From the XRD results of 20 min reduction product, it can be seen that metallic iron dominated the sample, and no FeO was observed, which indicated that the reduction of FeO into Fe was completed within 20 min. Besides, MgO and  $\text{Na}_4\text{Mg}_2\text{Si}_3\text{O}_{10}$  were observed in the sample obtained at 20 min with  $\text{Na}_2\text{CO}_3$ . The XRD comparative analysis showed that the reduction pathway was  $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ , which was consistent with the results in

previous researches<sup>[17-20]</sup>, and the addition of  $\text{Na}_2\text{CO}_3$  has not changed the reduction pathway, but the composition of non-ferrous phases.

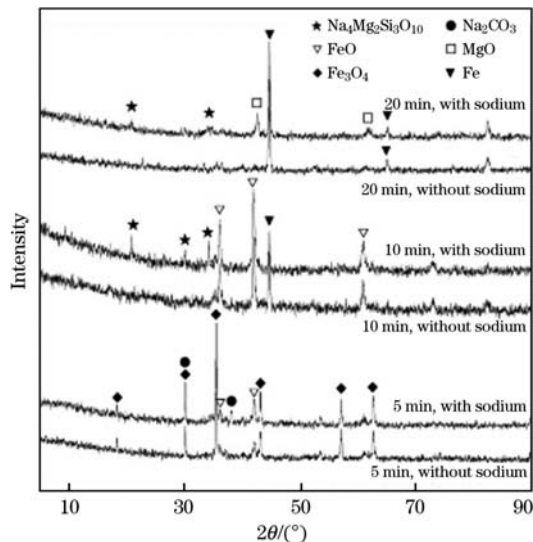
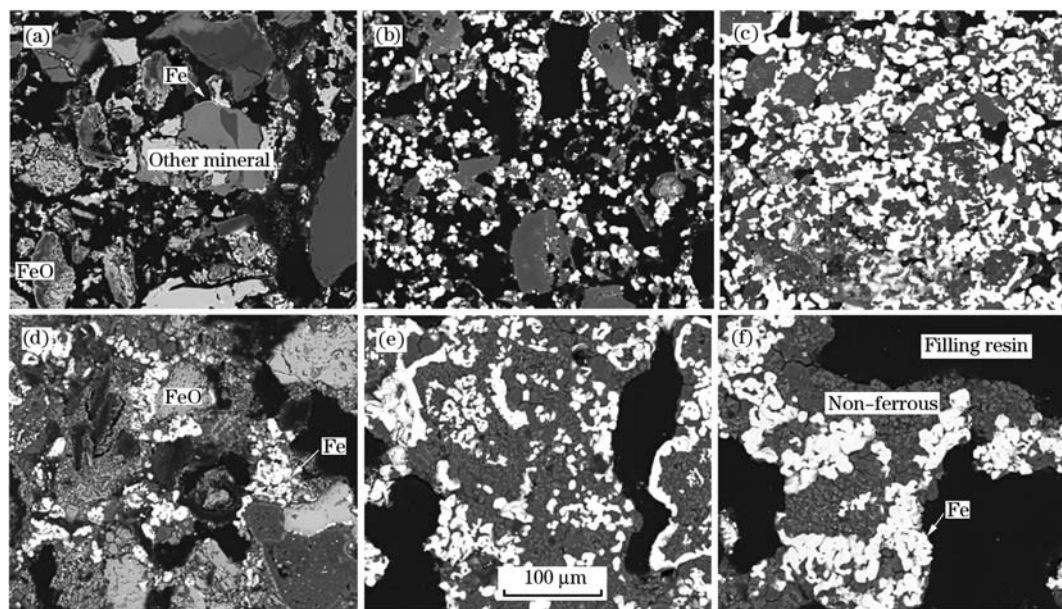


Fig. 9 XRD analysis with and without addition of  $\text{Na}_2\text{CO}_3$  at different time

#### 2.5 Effect of $\text{Na}_2\text{CO}_3$ on microstructure of reduction product

To investigate the effect of  $\text{Na}_2\text{CO}_3$  on the microstructure reduction product and metallic particles, SEM analysis were carried out at 1100 °C for different time with and without addition of  $\text{Na}_2\text{CO}_3$ . The results are shown in Fig. 10.

From Fig. 10, 10 min product photos without sodium shows that the contour of particles was substantially clear, and only a small amount of metallic iron was observed on the surface of the particles. However, when 30%  $\text{Na}_2\text{CO}_3$  was added, the contour of particles was almost unrecognizable, and many bigger metallic iron particles were observed at the peripheral of the particles. It illustrated that  $\text{Na}_2\text{CO}_3$  accelerated the generation of metallic iron, which was consistent with the results in previous kinetic analysis and metallization degree analysis. The SEM photo without sodium for 20 min shows that a large number of metallic iron particles appeared, and the contour of particles was almost unrecognizable. However, when 30%  $\text{Na}_2\text{CO}_3$  was added, the metallic iron particles obviously grew up, and no contour of particles could be recognized. This illustrated that the addition of  $\text{Na}_2\text{CO}_3$  reduced the melting point of non-ferrous phases, and then promoted the growth and aggregation of iron particles. After the reduction time was extended to 30 min, the role in promoting the growth and aggregation of iron parti-



(a) Without sodium, 10 min; (b) Without sodium, 20 min; (c) Without sodium, 30 min; (d) With sodium, 10 min; (e) With sodium, 20 min; (f) With sodium, 30 min.

**Fig. 10 SEM photos with and without addition of  $\text{Na}_2\text{CO}_3$  for different time**

cles is more obvious.

### 3 Conclusions

(1) The separation of iron and boron by coupling the direct reduction of iron oxides and the Na activation of boron minerals together was proved to be promising.

(2) The presence of additive  $\text{Na}_2\text{CO}_3$  during direct reduction reduced the activation energy of the reaction, and then promoted the reduction of iron oxides.

(3)  $\text{Na}_2\text{CO}_3$  did not change the process of iron oxides reduction, but the composition of non-ferrous phase, and then promoted the growth and aggregation of iron grains, which was conducive to the followed magnetic separation.

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