

Generation process of FeS and its inhibition mechanism on iron mineral reduction in selective direct reduction of laterite nickel ore

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(Received: 16 December 2014; revised: 2 April 2015; accepted: 7 April 2015)

Abstract: Numerous studies have demonstrated that Na_2SO_4 can significantly inhibit the reduction of iron oxide in the selective reduction process of laterite nickel ore. FeS generated in the process plays an important role in selective reduction, but the generation process of FeS and its inhibition mechanism on iron reduction are not clear. To figure this out, X-ray diffraction and scanning electron microscopy analyses were conducted to study the roasted ore. The results show that when Na_2SO_4 is added in the roasting, the FeO content in the roasted ore increases accompanied by the emergence of FeS phase. Further analysis indicates that Na_2S formed by the reaction of Na_2SO_4 with CO reacts with SiO_2 at the FeO surface to generate FeS and $\text{Na}_2\text{Si}_2\text{O}_5$. As a result, a thin film forms on the surface of FeO, hindering the contact between reducing gas and FeO. Therefore, the reduction of iron is depressed, and the FeO content in the roasted ore increases.

Keywords: laterite nickel ore; direct reduction; sodium sulfate; iron sulfide

1. Introduction

According to geological genesis, nickel resources are mainly divided into nickel sulfide deposits and nickel laterite ore deposits. At present, more than 60% nickel production comes from nickel sulfide ore [1]. However, with increasing demand for nickel and the shortage of worldwide nickel sulfide resources available for exploitation, extracting nickel from abundant laterite ore has become a hot research topic [2–4]. Previous studies have demonstrated that direct reduction roasting followed by magnetic separation is an effective method for recovering nickel from laterite nickel ore [5–12].

To obtain nickalloy powder with high nickel grade, iron reduction needs to be controlled in the process of direct reduction roasting. Selective reduction can be achieved by controlling the reducing atmosphere [13–14] and the addition of additives [15–17]. Many results show that the reduction of iron oxide can be obviously depressed by adding Na_2SO_4 . Li *et al.* [5] found that FeS is formed by direct reduction with the addition of Na_2SO_4 . The formation of

Fe-FeS with a low melting point promotes the growing up of Ni-Fe particles; simultaneously, nonmagnetic FeS goes into tailings in the process of magnetic separation achieved the aim of selective reduction. Valix and Cheung [18] found that S added in the process of roasting can restrain the phase transition of serpentine to olivine, which can selectively increase the recovery rate of nickel and cobalt. Lu *et al.* [19] found that Na_2SO_4 added in the process of direct reduction can promote the lattice deformation of silicate minerals and enhance the utilization of H_2 . In addition, the formation of FeS promotes growing-up of metal particles. Jiang *et al.* [20] found that Na_2SO_4 can react with silicate to generate low-melting-point nepheline and depress FeO reduction by inhibiting the diffusion of reducing gas; it can also promote growing-up of nickel iron particles via the formation of FeS.

The above researchers take the view that Na_2SO_4 plays an important role in selective reduction through the following two pathways: (1) the generation of nonmagnetic FeS, which goes into tailings in the magnetic separation process, decreasing the iron content of the nickalloy; and (2) the formation of low-melting-point silicate minerals such as nepheline. The diffusion of reduction gas is inhibited along

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with the reduction of FeO due to the increased amount of liquid phase in the roasting system. All the above studies found that FeS plays an important role in the selective reduction process of laterite nickel ore. However, they only focused on the function of FeS in promoting gathering and growing-up of metal particles. The other functions of FeS may have been ignored. In addition, based on thermodynamic analysis, the generation process of FeS has been proposed to occur by the following processes: (1) $\text{Fe} + \text{SO}_2(\text{g}) + 2\text{H}_2(\text{g}) = \text{FeS} + 2\text{H}_2\text{O}(\text{g})$; (2) $\text{Fe} + \text{S} = \text{FeS}$; and (3) $\text{Na}_2\text{S} + \text{FeO} + 2\text{SiO}_2 = \text{FeS} + \text{Na}_2\text{Si}_2\text{O}_5$. However, these mechanisms were not confirmed experimentally.

In this paper, reaction Eq. (3) mentioned above is confirmed, and another function of FeS in the selective direct reduction of laterite nickel ore is identified. FeS is generated on the surface of FeO with a film formed which covers FeO. This thin film hinders the contact between reducing gas and FeO, depressing the reduction process.

2. Materials and experimental methods

The laterite nickel ore comes from southeast Asia, and the results of its main element analysis are shown in Table 1. The main elements in the sample are iron, magnesium, and silicon. The sample particle size is -2 mm.

Table 1. Chemical analysis result of major elements in laterite ore

								wt%
Ni	TFe	MgO	SiO ₂	Al ₂ O ₃	Cr ₂ O ₃	MnO	CO ₂ O ₃	
1.46	26.68	15.32	24.81	4.31	1.93	0.94	0.36	

The reductant used in the research was bituminous coal. The additive Na₂SO₄ was obtained as an analytical reagent. The reductant and additive dosages referred to the proportion of their mass relative to the ore mass and are expressed as percentages.

For the roasting process, laterite nickel ore, the reductant and Na₂SO₄ were blended in the proportion of 100:5:10 and loaded in a graphite crucible. The crucible was placed into a muffle furnace at a specified temperature. The roasted ore was ground to a particle size of -0.074 mm (100%). X-ray diffraction (XRD) analysis was then conducted on a diffractometer (Rigaku D/Max 2500, Japan) under the following conditions: Cu K_α radiation; tube current and voltage of 150 mA and 40 kV, respectively; scanning range of 10° to 90°; step size of 0.02°; and scanning speed of 5°/min.

Electron microscopy (EM) analysis was conducted in two ways. (1) Backscattering analysis. The roasted ore was fixed by resin and polished, and carbon was sprayed on the sec-

tion surface. (2) Secondary electron analysis. The roasted ore was broken into small particles of -1 mm and then sprayed by carbon without polishing. Scanning electron microscopy (SEM) and energy spectrum analysis were conducted on a German Carl Zeiss EVO18 scanning electron microscope and a Bruker XFlash Detector 5010 energy spectrum analyzer, respectively.

3. Experimental results and discussion

3.1. Effect of Na₂SO₄ on the reduction of iron

In the process of selective reduction, FeO content in the roasted ore can intuitively reflect the inhibition of iron reduction. To study the change in FeO content in the roasted ore due to the addition of Na₂SO₄, one group of laterite nickel ore blended with 5wt% reductant was roasted for 50 min at temperatures of 800, 1000, and 1200°C. A second group was roasted under the same conditions but with the addition of 10wt% Na₂SO₄. XRD was then conducted on the two groups of roasted ores, and the results are shown in Fig. 1.

As shown in Fig. 1, when roasted at 800°C without Na₂SO₄, the reduction of iron is not sufficient due to the low roasting temperature, and FeO still exists in the roasted ore. When Na₂SO₄ is added during the roasting process, kamacite disappears accompanied by the emergence of FeS and nepheline. At the same time, the diffraction peak intensity of FeO increases. Therefore, the depression of iron reduction may be related to the emergence of FeS and nepheline when Na₂SO₄ is added.

At a higher roasting temperature of 1000°C without the addition of Na₂SO₄, the diffraction peak intensity of kamacite increases obviously, and FeO disappears. Thus, it can be seen that the reduction of iron is enhanced with increasing roasting temperature. However, when Na₂SO₄ is added during the roasting process, the reduction of iron is noticeably depressed, as demonstrated by the obvious decrease in the diffraction peak intensity of kamacite and the appearance of FeO in the roasted ore.

When the ore is roasted at 1200°C, the diffraction peak intensity of kamacite continues to increase, a diffraction peak of pyroxene appears, and the structural formula of olivine is Mg_{1.2}Fe_{0.8}SiO₄. When Na₂SO₄ is added, the pyroxene diffraction peak disappears, the structure of olivine is transformed into (Mg_{0.5}Fe_{0.5})₂SiO₄, and the diffraction peak intensity of kamacite decreases obviously. Regardless of whether Na₂SO₄ is added, the diffraction peak of FeO is not observed in the XRD pattern of the roasted ore. However, more FeO is formed during the roasting process at 1200°C

with the addition of Na_2SO_4 . The FeO continues to react with pyroxene according to the equation $\text{MgSiO}_3 + \text{FeO} =$

MgFeSiO_4 ; it is then transformed into olivine, causing its diffraction peak to disappear.

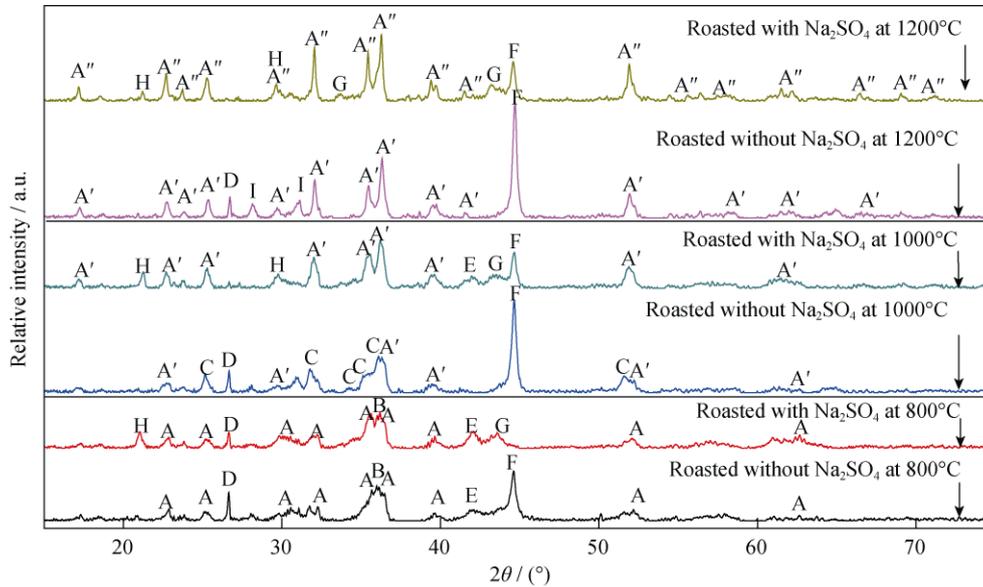


Fig. 1. Diffraction patterns of roasting ore obtained under different roasting conditions (A: (olivine) $\text{Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4$; A': (olivine) $\text{Mg}_{1.2}\text{Fe}_{0.8}\text{SiO}_4$; A'': (olivine) $(\text{Mg}_{0.5}\text{Fe}_{0.5})_2\text{SiO}_4$; B: (spinel) FeMgAlO_4 ; C: (fayalite) Fe_2SiO_4 ; D: (quartz) SiO_2 ; E: (wustite) FeO ; F: (kamacite) $[\text{Fe},\text{Ni}]$; G: FeS; H: (nepheline) $\text{NaAlSi}_3\text{O}_8$; I: (pyroxene) MgSiO_3).

3.2. Inhibition mechanism on iron reduction

According to XRD analysis results, the greatest change in the FeO content of the roasted ore is observed when Na_2SO_4 is added at 1000°C . Thus, the roasted ore obtained at 1000°C was chosen to study the mechanism of the inhibition of iron reduction using EM. The roasted ore was fixed by resin, polished, and subjected to backscattering analysis. The analysis results are shown in Fig. 2.

As shown in Fig. 2, many small metal particles are observed in the ore roasted without added Na_2SO_4 . Also, some of the mineral particles have clear outlines. When Na_2SO_4 is added during roasting, an obvious sintering phenomenon is observed, and a large amount of low-melting-point nepheline forms in the roasted ore (point 3 in Fig. 2). Due to the increased content of liquid phase, mineral particles have no obvious outline, and metal particles grow up significantly accompanied by a decrease in the number of metal particles. According to the results of energy-dispersive X-ray spectroscopy (EDS) of the metal particles in the two kinds of roasted ores, it is found that although the amount of metal particles decreases after the addition of Na_2SO_4 , the nickel content increases greatly. The most obvious difference between Figs. 2(b) and 2(d) is that after the addition of Na_2SO_4 , the content of FeO increases significantly, and FeO particles

grow up.

According to XRD and EM results, Na_2SO_4 obviously increases the FeO content of the ore. EDS analysis was conducted on the edges of FeO particles, and S element was identified (Fig. 2(i)). The XRD analysis shows that FeS is the only mineral containing S in the roasted ore. Thus, FeS forms at the surface of FeO, and this may be the key reason why FeO reduction is depressed after Na_2SO_4 is added in the roasting process. To study the substance on the FeO particle surface, secondary electron analysis was conducted on the roasted ore after it was crushed to -1 mm and sprayed with carbon. The results are shown in Fig. 3.

As shown in Fig. 3, when the ore is roasted without Na_2SO_4 , the surfaces of the particles are smooth (point 1 in Fig. 3(a)). When Na_2SO_4 is added during roasting, a film forms on the FeO surface (point 2 in Fig. 3(b)). According to the EDS analysis, the main elements in the film are Na, Si, O, Fe, and S. The film covers the FeO surface, hindering the contact between the reducing gas (CO) and FeO. The reduction of FeO is known to require a high CO concentration. Thus, a film covering the surface of FeO will undoubtedly make the reaction more difficult. This is one reason why the addition of Na_2SO_4 during roasting causes the FeO content in the roasted ore to increase significantly and the amount of metal particles to decrease.

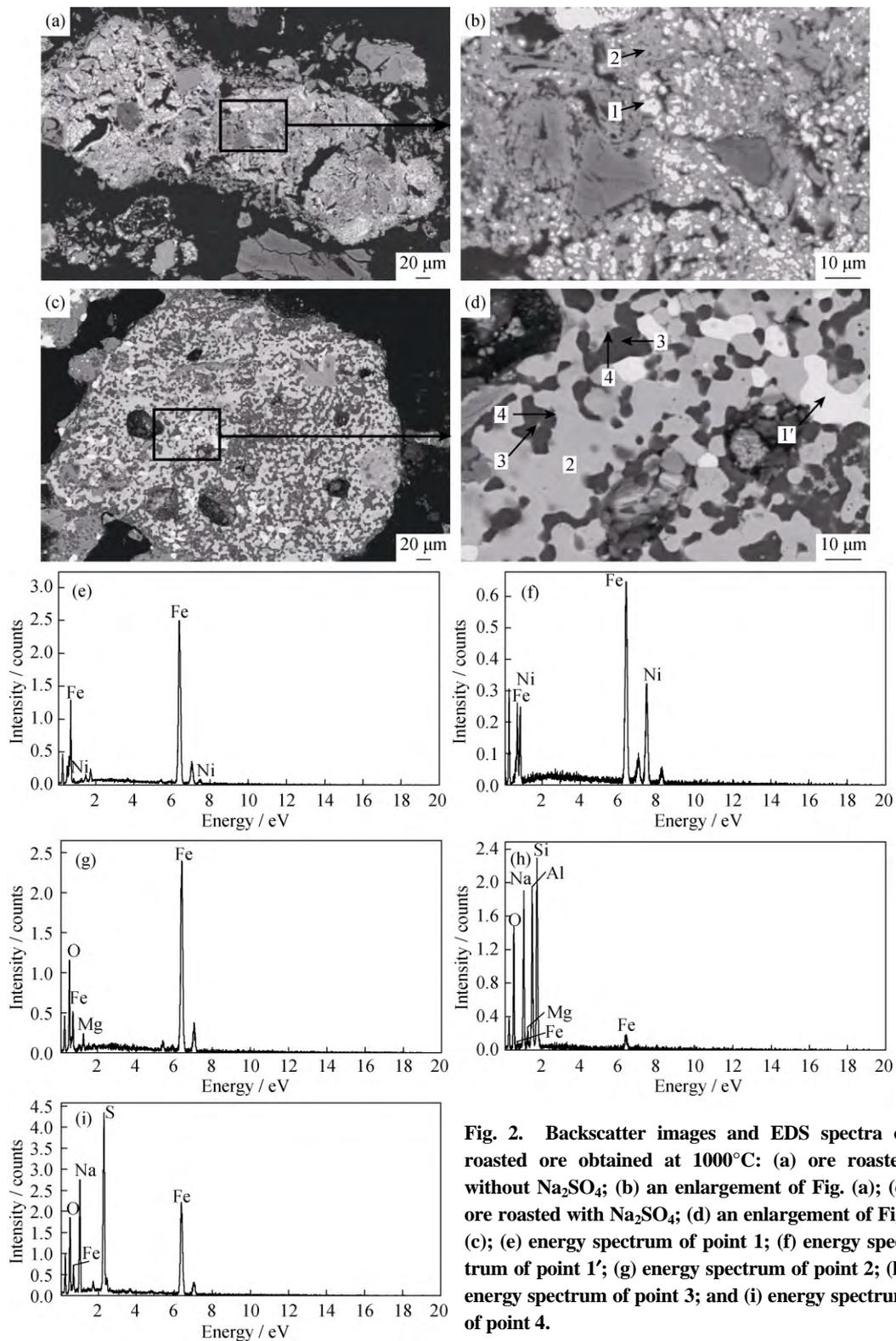


Fig. 2. Backscatter images and EDS spectra of roasted ore obtained at 1000°C: (a) ore roasted without Na_2SO_4 ; (b) an enlargement of Fig. (a); (c) ore roasted with Na_2SO_4 ; (d) an enlargement of Fig. (c); (e) energy spectrum of point 1; (f) energy spectrum of point 1'; (g) energy spectrum of point 2; (h) energy spectrum of point 3; and (i) energy spectrum of point 4.

3.3. FeS generation

According to above analysis, it is necessary to study the formation process of FeS and the film, which play important roles in the selective direct reduction roasting of laterite

nickel ore.

When Na_2SO_4 is roasted under a reducing atmosphere, the reactions (1) and (2) will occur, and FeS may then form by reactions (3) and (4). According to Fig. 4, reaction (1) proceeds more easily than reaction (2). Thus, it is easier to

form Na_2S than S in the reduction process. Thermogravimetric analysis was carried out to study the variation in the reduction process caused by the addition of Na_2SO_4 ; the re-

sults are shown in Fig. 5. The extremely high peak at 700°C is caused by the reaction of Na_2SO_4 with CO, and a peak corresponding to the reduction reaction appears later at

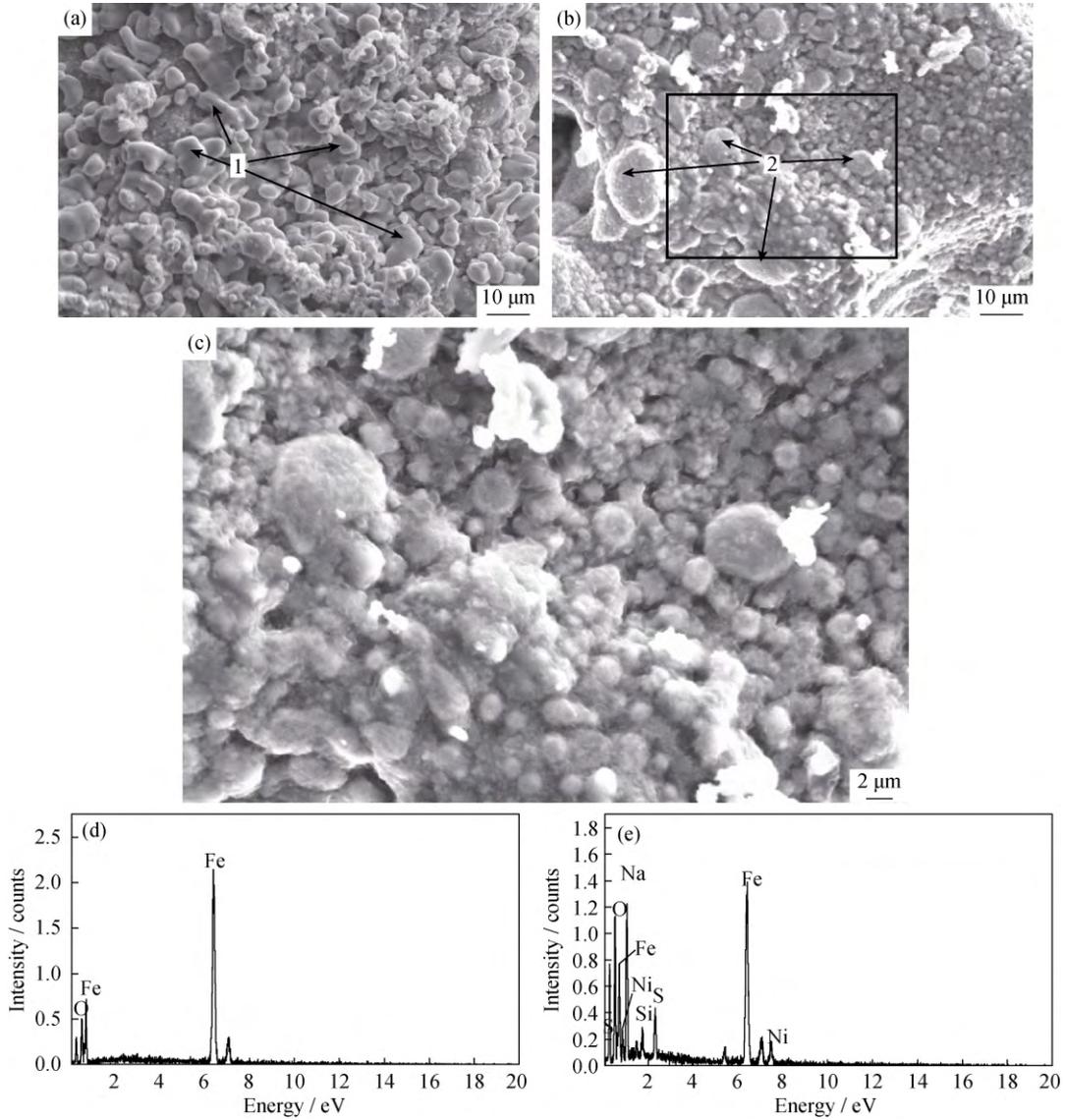


Fig. 3. Secondary electron images and EDS spectra of roasted ore obtained at 1000°C : (a) ore roasted without Na_2SO_4 ; (b) ore roasted with Na_2SO_4 ; (c) an enlargement of Fig. (b); (d) energy spectrum of point 1; and (e) energy spectrum of point 2.

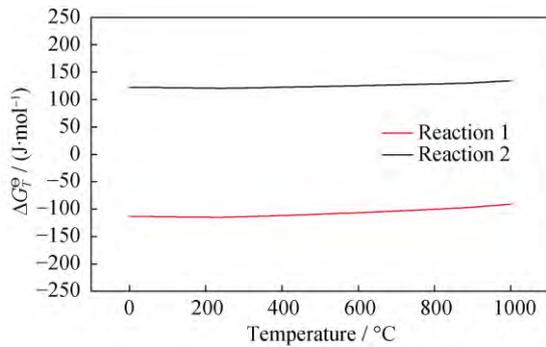


Fig. 4. Standard free energy change versus temperature for reactions (1) and (2). Data obtained by HSC 6.0.

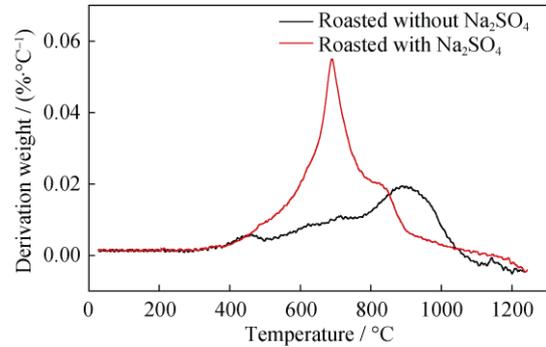
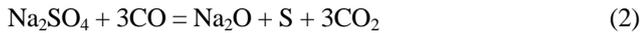
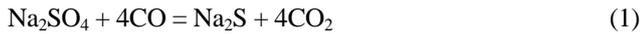


Fig. 5. Thermogravimetric curves of the direct reduction process.

800°C. Thus, the reaction of Na_2SO_4 with CO occurs before the reduction of iron, and Na_2S forms early, before FeO has been reduced. Subsequently, Na_2S reacts with FeO and SiO_2 at the FeO surface via reaction (3). The minerals in the thin film should be FeS and $\text{Na}_2\text{Si}_2\text{O}_5$ and contain the elements of Na, Si, O, Fe, and S. This is consistent with the EDS analysis results shown in Fig. 3(e). Thus, FeS is generated through reactions (1) and (3):



4. Conclusion

Unlike in the roasted ore obtained without the addition of Na_2SO_4 , FeS and nepheline appear in the roasted ore after Na_2SO_4 is added. The amount of metal particles decreases, while the nickel content of the metal particles is improved.

After Na_2SO_4 is added, Na_2S forms before FeO is reduced in the reduction process, and FeS then forms on the surface of FeO due to the reaction of Na_2S with FeO and SiO_2 . Thus, a film composed of FeS and $\text{Na}_2\text{Si}_2\text{O}_5$ covers FeO, inhibiting the contact between reduction gas and FeO. Thus, the reduction of FeO is depressed, achieving the goal of selective reduction. Finally, FeO that is not reduced reacts with pyroxene to generate olivine.

Acknowledgements

The authors wish to express their gratitude to the Specialized Research Fund for the Doctoral Program of Higher Education of China (No.20130006110017) for the financial support for this research.

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