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Recovery of iron from copper tailings via low-temperature direct reduction and magnetic separation: process optimization and mineralogical study

Rui-min Jiao, Peng Xing, Cheng-yan Wang, Bao-zhong Ma, and Yong-Qiang Chen

School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

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Abstract: Currently, the majority of copper tailings are not effectively developed. Worldwide, large amounts of copper tailings generated from copper production are continuously dumped, posing a potential environmental threat. Herein, the recovery of iron from copper tailings via low-temperature direct reduction and magnetic separation was conducted; process optimization was carried out, and the corresponding mineralogy was investigated. The reduction time, reduction temperature, reducing agent (coal), calcium chloride additive, grinding time, and magnetic field intensity were examined for process optimization. Mineralogical analyses of the sample, reduced pellets, and magnetic concentrate under various conditions were performed by X-ray diffraction, optical microscopy, and scanning electron microscopy–energy-dispersive X-ray spectrometry to elucidate the iron reduction and growth mechanisms. The results indicated that the optimum parameters of iron recovery include a reduction temperature of 1150°C, a reduction time of 120 min, a coal dosage of 25%, a calcium chloride dosage of 2.5%, a magnetic field intensity of 100 mT, and a grinding time of 1 min. Under these conditions, the iron grade in the magnetic concentrate was greater than 90%, with an iron recovery ratio greater than 95%.

Keywords: copper tailings; iron; direct reduction; magnetic separation; recovery; process optimization

1. Introduction

Approximately 30 million tons of copper slag is annually produced worldwide [1], for China, the leading producer of copper, accounting for nearly one-third of the total [2]. Slag contains various valuable metals, e.g., copper, zinc, cobalt, and nickel, and a small amount of precious metals; in addition, the iron content in slag is significantly greater than the mining grade of several iron mines [3–4]. Currently, in addition to being a copper source, slag is directly used as an abrasive grit [5–6] in cement and concrete materials [7–9], most of which are discarded after the cleaning of copper. Copper, zinc, cobalt, and nickel are the primary metals recovered, and several cleaning methods (e.g., pyrometallurgical slag settling or reduction or reductive sulfidizing) and the processing of slag minerals have been used to recover copper and other valuable metals from copper slag [10–14]. However, currently, the bulk iron in copper slag is not effectively recovered on an industrial scale, leading to considerable waste of iron resources.

In recent years, considerable research efforts have been devoted to the recovery of iron from copper tailings. Because the iron in copper slag mainly exists as fayalite (Fe_2SiO_4) and extremely fine grains of magnetite (Fe_3O_4), it is difficult to effectively recover by conventional mineral processing technology [15–18]. Zhang *et al.* [19] have studied the conversion of the iron-bearing phases in copper slag into magnetite via the oxidation of molten slag with air or oxygen. The concentration of magnetite in the slag is increased from 22% to greater than 85% by this method, which is beneficial for the recovery of iron by magnetic separation. However, this process is complex, and the magnetic slag requires further treatment for recovering iron. Some studies [20–21] have reported the smelting reduction ironmaking of copper slag. Although a considerable recovery was achieved on the laboratory scale because of the high Si/Fe ratio, the feasibility of such processing on

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Corresponding author: Cheng-yan Wang, Yong-Qiang Chen E-mail: chywang@yeah.net, chyq0707@sina.com

the industrial scale requires further examination. Numerous laboratory-scale studies have focused on the reduction and magnetic separation of copper slags [22–24]. A high recovery ratio and grade of iron in the concentrate can typically be attained using this method, and the reduced iron concentrate can be used as a high-quality raw material for steelmaking. However, the high reduction temperature (1200–1300°C) adopted in these studies can easily lead to sintering, which would be detrimental during the processing of copper tailings in industrial facilities, e.g., in a rotary kiln. Furthermore, because most of these tests were conducted under nitrogen, oxidation of the reduced product under atmospheric conditions was not considered. In addition, the authors of previous studies did not thoroughly examine the mechanism of iron reduction. In this context, the low-temperature reduction of pellets of depleted copper tailings was proposed herein, and the process optimization and the reduction mechanism were investigated.

2. Experimental

2.1. Materials

In this study, the copper tailing sample was collected from a waste copper tailing stockpile of a dressing plant in a copper smelter. This sample was dried at 60°C for 12 h and subsequently analyzed by inductively coupled plasma–atomic emission spectroscopy (ICP–AES). The sulfur content was analyzed using an infrared absorption carbon–sulfur analyzer. Table 1 summarizes the chemical composition of the sample. The elemental composition was dominated by Fe, Ca, and SiO_2. The results obtained from the size analysis of the initial ore and the content analysis of Fe in different fractions (0.149–0.074, 0.074–0.048, and −0.048 mm) suggest that the primary particle size of the tailing sample was less than 0.048 mm, albeit with an almost equal iron content in each fraction. Lignite coal with 52.1wt% fixed carbon and 28.3wt% volatile matter was used in reduction experiments. Analytical reagent (AR)-grade calcium chloride was used as an additive.

2.2. Experimental method

First, the original sample (100 g) was mixed with various proportions of pulverized coal and calcium chloride. Second, 20 mL of water was added to the mixture, which was subsequently pelletized. Third, the pellets were placed in an oven at 110°C for drying. The pellets were then placed in a crucible with a sealed cover and reduced in a muffle furnace (TDW, Tianjin Zhonghuan Lab Furnace Co. Ltd., China) at a predefined temperature. Finally, the reduced samples were rapidly removed and quenched with water. The partially reduced pellets were wet-ground (5:1 liquid–solid ratio (v/w)) in a rod mill (XZM-100, Wuhan Exploring Machinery Factory, China) and then magnetically separated using a magnetic separator (DTCXG-ZN50, Tangshan Dongtang Electric Equipment Co. Ltd., China) to obtain the iron concentrate. The remaining pellets were dried for mineralogical analysis.

Table 1. Chemical composition of the copper tailing sample wt%

Fe	Ca	Zn	Al	Mg	Pb	Cu	Ti	Ba	S	P	Si
41.19	12.87	3.79	2.28	1.01	0.47	0.38	0.25	0.15	0.13	0.01	11.88

2.3. Experimental principle

The copper slag mainly contains ferrite (magnetite) and fayalite. Fayalite typically dissociates into FeO, followed by reduction to metallic iron [22], as shown in Eq. (1). Eqs. (2)–(4) show the reduction of iron oxides (FeO, Fe_2O_3, and Fe_3O_4, respectively) by carbon. Fig. 1 shows the standard Gibbs energy of these iron oxides vs. temperature. The initiation temperatures of the reactions shown in Eqs. (2)–(4) at atmospheric pressure were calculated as 718, 299, and 681°C, respectively.

$$Fe_2SiO_4(s) = 2FeO(s) + SiO_2(s) \tag{1}$$

$$FeO(s) + C(s) = Fe + CO(g) \tag{2}$$

$$3Fe_2O_3(s) + C(s) = 2Fe_3O_4(s) + CO(g) \tag{3}$$

$$Fe_3O_4(s) + C(s) = 3FeO(s) + CO(g) \tag{4}$$

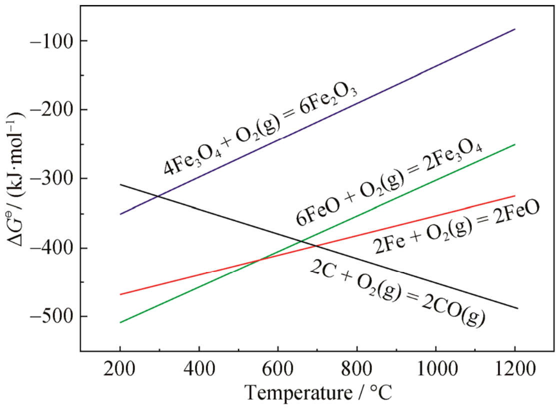

Fig. 1. Standard Gibbs free energy (ΔG°) of several oxides.

3. Results and discussion

3.1. Direct reduction and magnetic separation

Fig. 2(a) shows the effect of reduction temperature (800, 900, 1000, 1100, 1150, or 1200°C) on the recovery and grade of iron in the concentrate. The recovery ratio and iron grade in the concentrate increased with increasing reduction temperature (Fig. 2(a)). The recovery ratio reached a plateau at 1150°C, whereas the maximum iron grade was achieved at 1200°C.

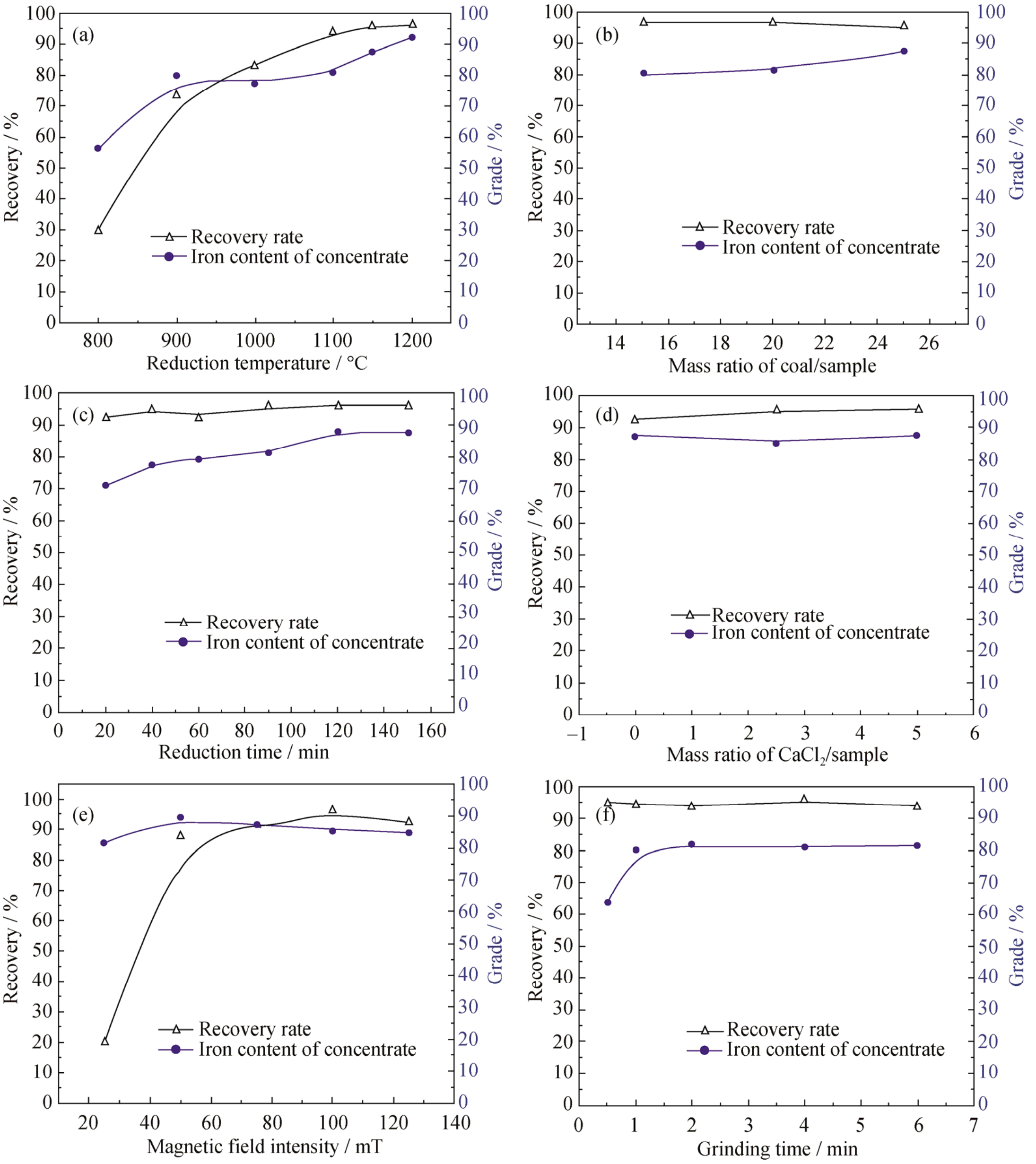

Fig. 2. Effects of reduction conditions on the recovery and grade of iron in the concentrate: (a) reduction temperature; (b) coal; (c) reduction time; (d) $CaCl_2$; (e) magnetic field intensity; (f) grinding time (In addition to the corresponding variables shown in the figures, other experimental conditions were as follows: reduction temperature, 1150°C; mass ratio of coal/sample, 25%; reduction time, 2 h; mass ratio of $CaCl_2$/sample, 2.5%; grinding time, 4 min; magnetic field intensity, 100 mT).

Fig. 3 shows the photographs of the samples reduced at different temperatures. The pellets reduced at 1150°C exhibited excellent physical and mechanical properties, e.g., a dense surface, good strength, and high antioxidant capacity (Fig. 3). However, with the further increase of temperature (1200°C), the reduced pellets were sintered and became semi-molten, which is detrimental to stable operation in industrial settings. For instance, in the case of a rotary kiln, which is a common piece of equipment for reduction of metals such as nickel and iron, the sintered material easily adhered to the rotary kiln wall, possibly leading to difficulty in the smooth passage of the reduced material. In addition to this issue, after the samples were quenched with water, the sample reduced at 1200°C was easily oxidized in the environment. On the basis of these findings, the optimum temperature for reduction was determined to be 1150°C.

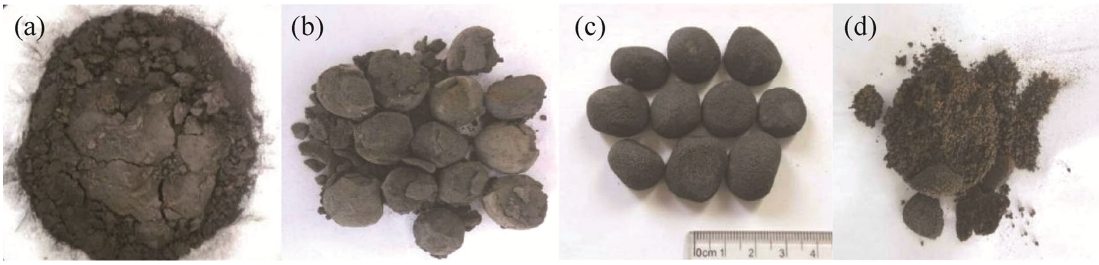

Fig. 3. Photographs of the pellets reduced at different temperatures: (a) 900°C; (b) 1000°C; (c) 1150°C; (d) 1200°C.

The effect of coal dosage on reduction was investigated at the mass ratios of coal:sample of 15%–25% (according to the carbon content of the coal and the reaction $FeO + C \rightleftharpoons Fe + CO$, 15% of the coal amount was 0.9 times the theoretical amount). The recovery ratio was slightly affected by the coal dosage; however, the concentration of iron grade increased with increasing reducing-agent dosage; hence, the optimum reducing-agent dosage was 25%.

Fig. 2(c) shows the effect of reduction time on the recovery and grade of iron. The grade of iron in the concentrate increased with increasing reduction time and reached a plateau at 120 min, whereas the recovery was barely affected. The appropriate reduction time to ensure a high concentrate grade was determined to be 120 min.

Chlorides have been reported to be beneficial for the extraction of certain metals, e.g., nickel and lithium, from minerals in the presence of silica because of the chloride segregation effect [25–26]. Hence, we introduced calcium chloride. Fig. 2(d) shows the effect of the mass ratio of $CaCl_2$:sample on the recovery and grade of iron. The calcium chloride was not found to affect the recovery and grade of iron. However, the addition of calcium chloride was beneficial to pelletization; hence, the optimum calcium chloride dosage was determined to be 2.5%.

Fig. 2(e) shows the effect of the magnetic field intensity on the recovery and grade of iron. The recovery of iron rapidly increased with increasing magnetic field intensity and reached a plateau at 100 mT. The magnetic field intensity marginally affected the grade of iron in the concentrate. A high magnetic field intensity (100 mT) was imperative for iron recovery.

Fig. 2(f) shows the effect of grinding time on the recovery and grade of iron. In only 1 min, the grade of iron in the concentrate reached a plateau, which was reasonable because the reduced pellet could be easily ground; all particle sizes were less than 300 mesh. When the grinding time was insufficient, iron was not easily dissociated, resulting in a low grade of iron in the concentrate; hence, the optimum grinding time was 1 min.

On the basis of the aforementioned single-factor experiments, an integrated experiment was conducted. The following optimized leaching conditions were selected: a reduction temperature of 1150°C, a reduction time of 2 h, a coal:sample mass ratio of 25%, a $CaCl_2$:sample mass ratio of 2.5%, a magnetic field intensity of 100 mT, and a grinding time of 1 min. Under such conditions, a recovery of 95.86% and an iron grade of 90.2% were obtained, with the content of iron in the tailing being only 4.78wt%.

3.2. Mineralogical study of reduction

3.2.1. Characterization of the raw material

X-ray diffraction (XRD), optical microscopy, and scanning electron microscopy–energy-dispersive X-ray spectrometry (SEM–EDS) were used to analyze the copper tailing. Figs. 4–7 show the corresponding results.

The XRD patterns indicate that the main phases in the copper tailing were ferrite (magnetite), fayalite, hedenbergite, and a small amount of calcite. In the representative optical microscopy image of the raw material, the multi-granularity of ferrite (Frr) and fayalite (Fa) phases varies from 10 to 100 μm.

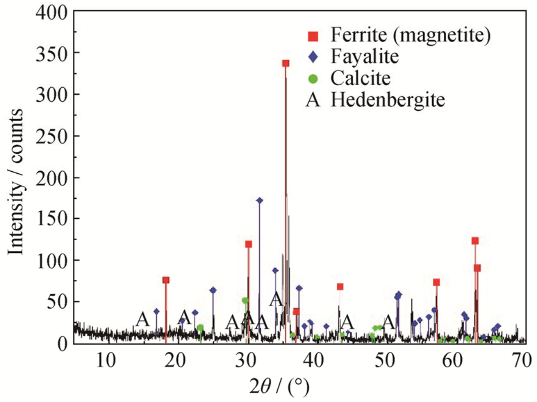

Fig. 4. XRD pattern of the copper tailing.

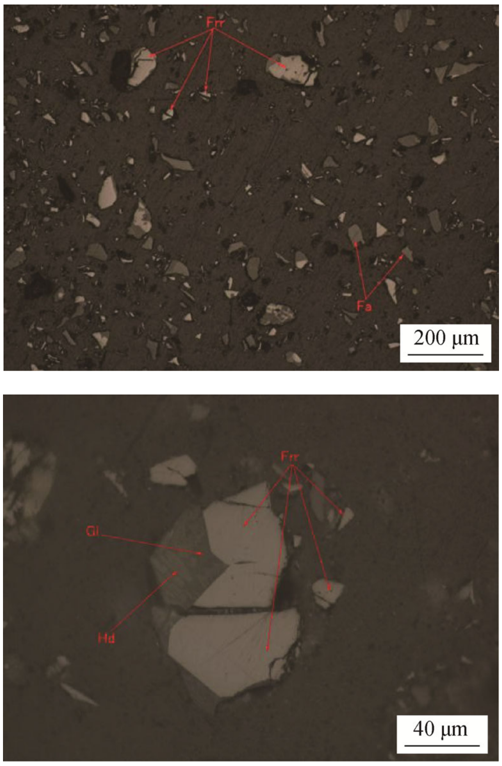

Fig. 5. Representative optical microscope image of the copper tailing. Frr—ferrite; Fa—fayalite; Hd—hedenbergite; Gl—glass.

The copper tailing contained ferrite, fayalite, hedenbergite, and silicate glass, with a marginal amount of matte particles (Fig. 4). The SEM–EDS results also indicate that the main phases of the copper tailing included ferrite and fayalite, which initially precipitated during slow cooling; hence, their crystal sizes are large. Later, hedenbergite precipitated as dendrites.

3.2.2. Characterization of the reduced pellet

Fig. 7 shows the optical microscopy images of the pellets reduced at different temperatures. Although the reduction of

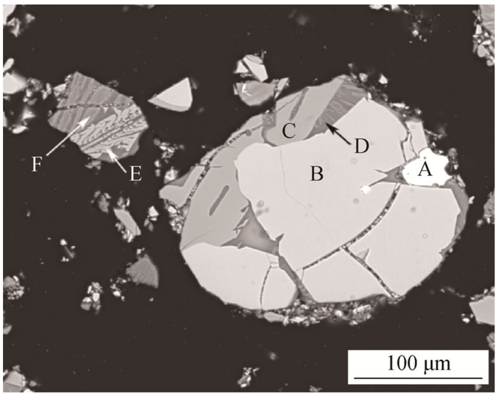

Fig. 6. Representative SEM–EDS patterns of the copper tailing. A—matte; B—ferrite; C—fayalite; D—glass; E—fayalite; F—hedenbergite.

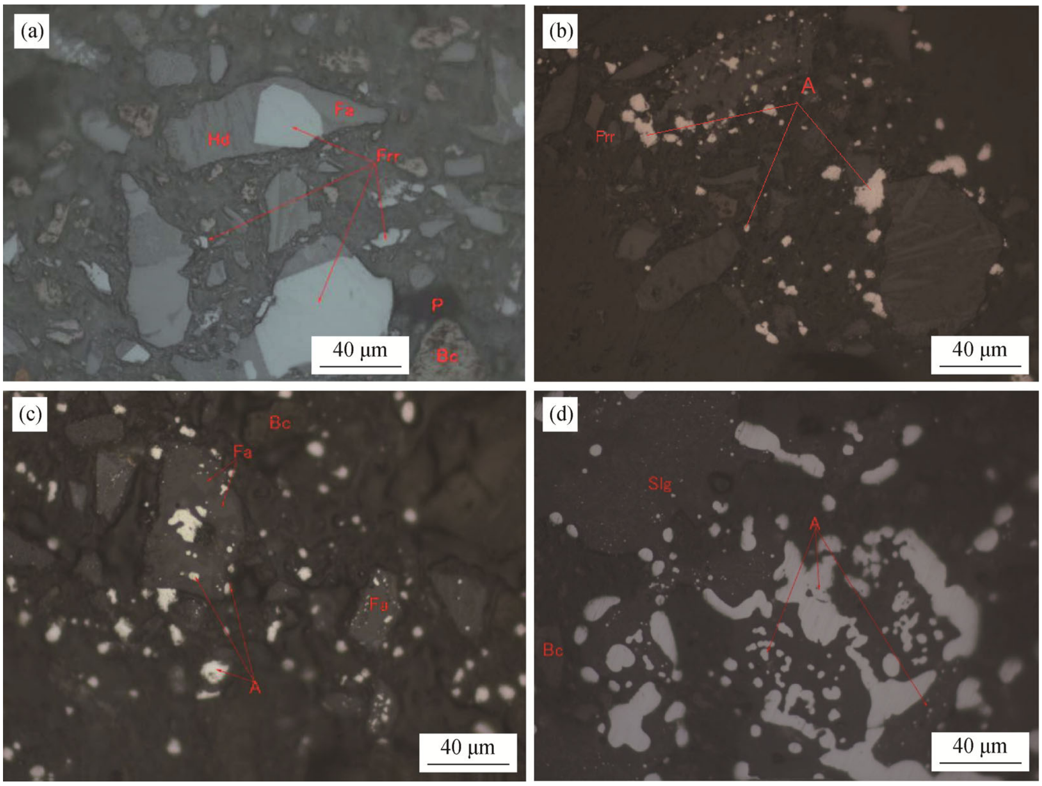

Fig. 7. Optical microscopy images of pellets reduced at different temperatures: (a) 800°C; (b) 900°C; (c) 1000°C; (d) 1150°C. A—metallic phase; Bc—black charcoal; Frr—ferrite; Fa—fayalite; P—pore; Slg—slag; Hd—hedenbergite.

FeO can theoretically occur at 800°C (Fig. 2), the ferrite and fayalite in the pellets were not reduced and the coal particle shape was also maintained at this temperature (Fig. 7) because carbon failed to react with oxygen to form a strong reducing atmosphere in the actual test environment even though carbon could theoretically react with oxygen. A small amount of metallic iron was observed in the pellet reduced at 900°C. Hence, the merging of metallic iron was not observed, and fine particles (<20 μm) of the metal phase were observed. Isolated ferrite with a small particle size is thought to be reduced to metal at this temperature; however, because the low-melting liquid and binding phases, which strongly affected pellet consolidation, were not formed, low pellet strength was observed and the metallic phase particles did not grow.

During reduction at 1150°C, a majority of the iron was reduced to the metal state, which merged as irregular granules and beads. The structure of the reduced pellet obtained at 1150°C differed substantially from that of the pellet reduced at 1000°C. Specifically, the pores of the pellet reduced at 1150°C were smaller, and the pellet exhibited a substantially increased density. The presence of residual coal particles in the pellet reduced at 1150°C indicates that the reducing-agent dosage was sufficient for iron reduction.

In addition, metal particles of the pellets reduced at high temperatures (900–1150°C) existed inside the ferrite and fayalite phases, indicating that the reduction of iron was initiated in the monomer and exposed silicate aggregates, subsequently proceeding via solid diffusion. Intuitively, Fe in the silicate gradually reduced and disappeared, and the products with a small amount of iron replaced the original ferrite and fayalite, with the simultaneous observation and merging of metal particles; thus, the size of the metal particles increased.

Fig. 8 shows the optical microscopy images of the pellet reduced at different coal dosages. The merging of the metallic phase particles in the pellets became more common at a coal dosage of 25%; under this condition, the size of the coarse particles was greater than 40 μm.

The optical microscopy images of the reduced pellet at different reduction times (Fig. 9) show that prolonging the reduction time promotes the merging of the metal particles and the reduction of iron silicate. This observation explains the results in Fig. 2(c).

The particle size of iron metal and the number and type of refractory silicate slag particles in the reduced pellets with or without calcium chloride differ (Fig. 10). Specifically, the particle size range of metallic iron was large, and some coarse metal particles were observed in the reduced pellet without the added calcium chloride; however, in the case where calcium chloride was added, a large amount of the liquid metal phase was generated and the particle size distribution of the metal phase was uniform, with a small number of coarse metal particles. In addition, hedenbergite was observed in the reduced pellet with calcium chloride. In summary, calcium chloride facilitated the diffusion and merging of metal iron particles. The mechanistic action of calcium chloride on the growth of metal particles is not clear and is beyond the scope of the present work.

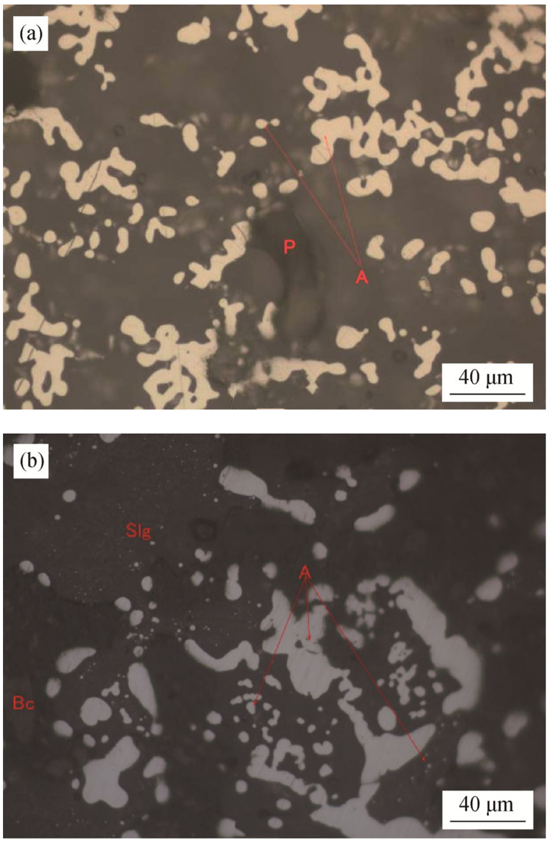

Fig. 8. Optical microscopy images of the reduced pellets at different coal dosages: (a) 15%; (b) 25%. A—metallic phase; Slg—slag; Bc—black charcoal; P—pore.

3.2.3. Characterization of magnetic concentrate and tailing

XRD and optical microscopic analyses were used to observe the magnetic concentrate generated under the optimum conditions, corresponding to the product obtained from magnetic separation. Figs. 11 and 12 show the corresponding results. The main phase of the concentrate is metallic iron (Fig. 11). In addition, small amounts of fayalite and magnesium aluminum silicate were observed in the concentrate.

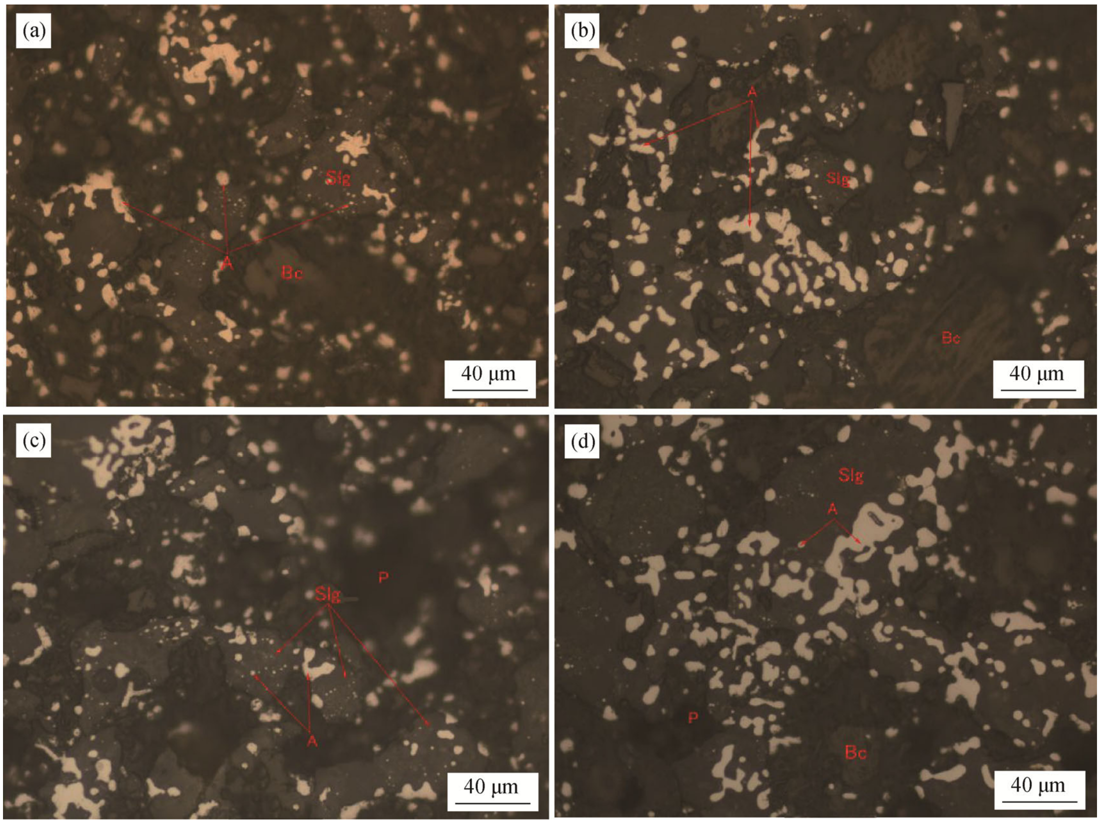

Fig. 9. Optical microscopy images of the reduced pellets at different reduction times: (a) 20 min; (b) 40 min; (c) 60 min; (d) 90 min. A—metallic phase; Slg—slag; Bc—black charcoal; P—pore.

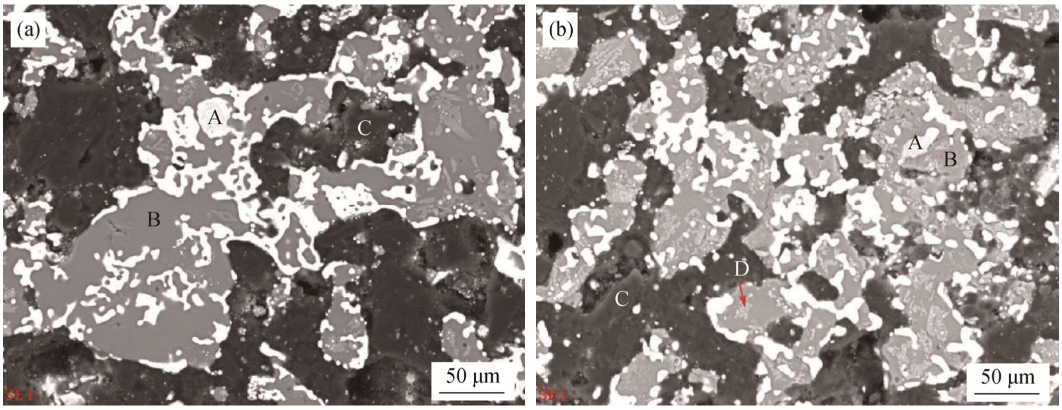

Fig. 10. SEM images of the reduced pellet at different calcium chloride dosages: (a) without calcium chloride; (b) 2.5% of calcium chloride. A—metallic phase; B—silicate with a low iron content; C—black charcoal; D—hedenbergite.

The optical microscopy image of the magnetic concentrate differed from that of the reduced pellet. Specifically, because of the crushing during grinding, the metal phase in the concentrate was flattened, with a length greater than 100 μm and a width of 3–40 μm. The presence of slag in the concentrate was mainly related to the fine metallic iron in the slag. Metallic iron was enriched during magnetic separation. Because the metallic iron and the slag were wrapped around each other and because of the inevitable entrainment during magnetic separation, a small amount of the slag still remained in the concentrate (Fig. 12).

The width of the XRD diffraction peak indicates poor crystallinity. In addition, a small amount of metallic iron was found in the slag (Fig. 12), which was unavoidable.

Clearly, the main loss of iron in the tailing was related to the incomplete reduction of fayalite.

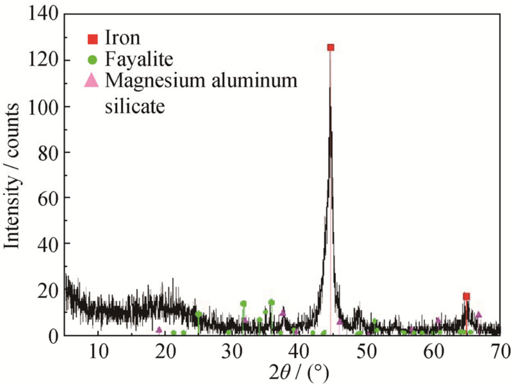

Fig. 11. XRD pattern of the magnetic concentrate.

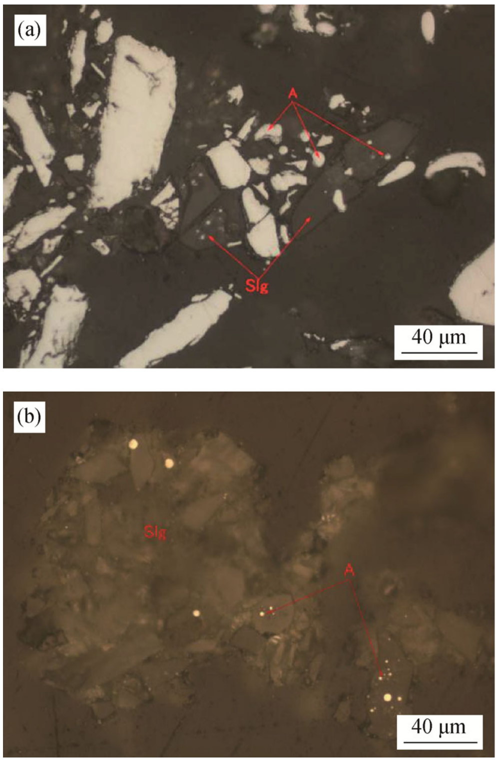

Fig. 12. Optical microscopy images: (a) magnetic concentrate; (b) tailing. A—metallic phase; Slg—slag.

4. Conclusions

(1) The optimal conditions for the recovery of iron included a reduction temperature of 1150°C, a duration of 2 h, a coal dosage of 25%, a calcium chloride dosage of 2.5%, a magnetic field intensity of 100 mT, and a grinding time of 1 min. Under such conditions, the iron grade of the magnetic concentrate was greater than 90%, and the recovery ratio of iron was greater than 95%.

(2) Mineralogical analysis suggested that ferrite and fayalite are the main constituent minerals in copper tailings and the main carriers of iron. A small amount of metallic iron was observed in the reduced pellet at 900°C. Increasing temperature is beneficial for the reduction, merging, and growth of iron. The merging of the metal phase particles in pellets becomes more common at a coal dosage of 25%. Prolonging the reduction time promotes the merging of metal particles and the reduction of iron silicate. Calcium chloride facilitates the diffusion and merging of metal iron particles. Fayalite and hedenbergite are the main phases in the tailing of the magnetic dressing. The main loss of iron in the tailing is related to the incomplete reduction of fayalite.

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