TECHNICAL PAPER

Study on Mechanism of Oxidation Modification of Copper Slag

Qiuju Li[1] · Fanxi Yang[1] · Ziyang Wang[2] · Songyan Liu[3]

Abstract The pyrometallurgical processing of copper concentrates generates large amounts of iron and copper-containing slag. It is an available way to separate and recover iron and copper by oxidative modification slag. The copper slag used in this experiment is water-quenched copper slag tailings. The method of the experiment is to separate copper and iron in the copper slag by oxidation-magnetic separation method, and the amount of copper and iron recovered in the later stage is also greatly reduced. Mineralogical phase transform of copper slag during oxidation modification process has been investigated with the goal to provide valuable information for the recovery of copper and iron. The influence of temperature and time on the mineral phase transformation has mainly been studied during the oxidation modification. XRD combined with FT-IR has been used to characterise the mineral phase change. The experimental results showed that the oxidation temperature and time were favorable for modification of copper slag under medium- and low-temperature conditions. When the oxidation temperature was 950 °C, fayalite was transformed to hematite and quartz, which provided the necessary conditions for separating iron and silicon, and copper embedded in fayalite was also released. In addition, the copper slag particles were significantly grown under the action of oxidation reaction which was also beneficial to subsequent selection and treatment.

1 Introduction

The copper output in the world has grown rapidly and has reached 23.50 million tons in 2017 [1]. At present, 80% of the world's copper production is produced by pyrometallurgical process. It will produce about 2.2 t [2] slag as product of one ton copper, and the yield of about 24.6 million tons of copper smelting slag is produced per year. The pyrometallurgical copper slag contains more than 0.5% of copper and 40% of iron which are mainly in the mineralogical compositions of fayalite and magnetite. It is critical for developing a method to recover the copper and iron resources from the copper slag with lower energy and the heavy metals in the residue slag. The knowledge of chemical composition and mineralogical phase transformation of slag are of industrial interest for recovery of copper and iron resources.

The fayalite and magnetite were directly reduced to metal iron by the addition of a co-reducing agent under high-temperature melting conditions [3, 4]. The flotation-magnetic separation method could effectively recover copper and iron in copper slag [5]. The content of magnetic iron oxide in copper slag was about 20–30%, while the main iron-containing phase of fayalite and other silicate phases entered the tailings during the magnetic separation process [6]. Some researchers [7] studied copper slag at temperature of 1250 °C by direct reduction-magnetic separation, and the recovery of iron was about 39.96 wt%.

✉ Qiuju Li
  liqj@t.shu.edu.cn

1   State Key Laboratory of Advanced Special Steels, Shanghai University, Shanghai 200444, China

2   Shanghai Key Laboratory of Modern Metallurgy and Materials Processing, Shanghai University, Shanghai 200444, China

3   School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China

Pang et al. [8] studied the enrichment of iron in high-temperature molten copper oxide slag, and the addition of CaO to roast copper slag under an oxygen atmosphere at high temperature would promote the decomposition of Fe_2SiO_4, and α-Fe_2O_3 increased in the later stage of the reaction. In our present work, the recovery iron resources from copper slag with oxidative modification at low temperatures were discussed in detail [9]. The reaction factors such as oxygen potential and temperature were the important influencing factor for converting the olivine to magnetic iron. The result showed that oxidative modification of copper slag was beneficial to improve the iron grade and recovery rate in the subsequent treatment.

The method of the experiment is to separate copper and iron in the copper slag by the oxidation-magnetic separation method, and the copper is concentrated in the non-magnetic residual slag, followed by leaching extraction. Iron enrichment is recovered in the magnetic slag. Not only can copper and iron be effectively separated, but the amount of copper and iron recovered can be greatly reduced. The aim of this paper is to research the mineralogical phase transform copper slag during process of oxidation modification, with the goal to provide valuable information for the recovery of copper and iron from copper slag. The possibility of fayalite decomposition reaction was estimated by the thermodynamics data. The distribution of species in copper slag was investigated. The structure variety during oxidation was detected. The mineralogical phases and morphology transformation during oxidation at different temperature were characterized. The transformation mechanism of iron-containing and copper-containing mineral during oxidation was explored in detail.

2 Experimental Equipment and Method

It was difficult to separate copper and iron from copper slag because of copper embedded into iron fayalite. It had to break fayalite phase and release copper to recover copper and iron. Iron fayalite phase in copper slag could be broken and oxidized and modified into a magnetic mineral phase at low temperature under oxidizing conditions on the basis of literature research and thermodynamic analysis. Oxidation modification of copper slag was affected by factors such as temperature, time, particle size and partial pressure of oxygen.

2.1 Experimental Equipment

The experimental tubular resistance furnace is schematically shown in Fig. 1. The reaction tube was made with stainless steel which was connected to the intake and outlet

ports at both ends. Copper slag put into corundum crucibles was placed into the stainless steel tube.

2.2 Experiment Method

Before the start of the experiment, the reactor was purged by nitrogen flow before oxidation reaction. Corundum crucible containing 10 g of copper slag particles was placed in a tube furnace. The samples were first heated in a nitrogen flow to the desired temperature, and then the nitrogen was switched to O_2–N_2 gas mixture. When the reaction finished, the samples were cooled down with cold water.

The cooled oxidized modification slags were crushed and ground, and separated with magnetic separation. The particle size was characterized with laser particle sizer. The composition of copper slag sample was analyzed by X-ray fluorescence spectrometry (XRF). The structure and composition of slag were detected with X-ray diffraction (XRD) and infrared spectroscopy (IR). The elemental composition and elemental distribution in the copper slag were determined by scanning electron microscopy–energy-dispersive spectrometer (SEM–EDS).

3 Results and Discussion

3.1 Characterization of Copper Slag

The copper slag used in this experiment is a secondary copper resource which has been crushed, ground and floated by a company in Gansu province. The size of the copper slag particle exceeding 70% of which is very fine with less than 10 μm in diameter are shown in Fig. 2.

The chemical composition of the copper slag is shown in Table 1. It shows that the main elements in the slag are Fe, O, Si and small amount of Cu and the content of Cu is 0.48 wt%, while the content of Fe is 38.5 wt%. In addition, there are many other elements such as Zn, Ca and Al in the slag. There are many kinds of trace metal elements such as Ni, Mn, Sr, Mo and P in the slag, and their contents are below 0.1%. These elements are mostly in the form of oxides.

The copper slag has been studied by an X-ray diffractometer, and the phase of the original slag has been found to contain fayalite (Fe_2SiO_4), magnetite, quartz and silicate, as shown in Fig. 3. Iron mainly exists in the form of fayalite and magnetite. Silicon is mainly in the form of combined and silicate; Ca and Al in slag are mainly in the form of complex aluminosilicate. Metal elements such as Mg and Zn in the slag are mainly in the form of oxide-fayalite. The average content of fayalite in copper slag is about 73 wt % with semiquantitative calculation, while
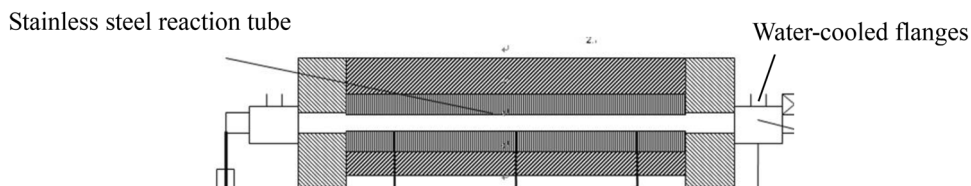
Fig. 1 Diagram of pipe electric furnace   Stainless steel reaction tube   Water-cooled flanges
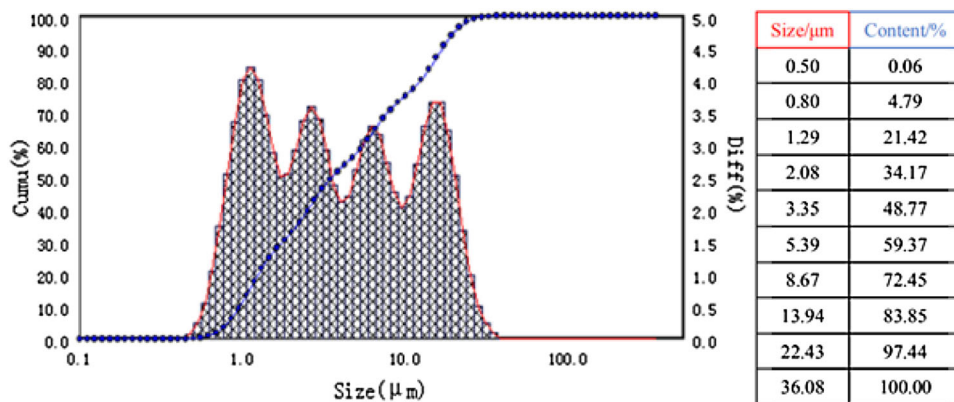

Fig. 2 Particle size of copper slag

Size/μm	Content/%
0.50	0.06
0.80	4.79
1.29	21.42
2.08	34.17
3.35	48.77
5.39	59.37
8.67	72.45
13.94	83.85
22.43	97.44
36.08	100.00

Table 1 The composition of copper slag (wt%)

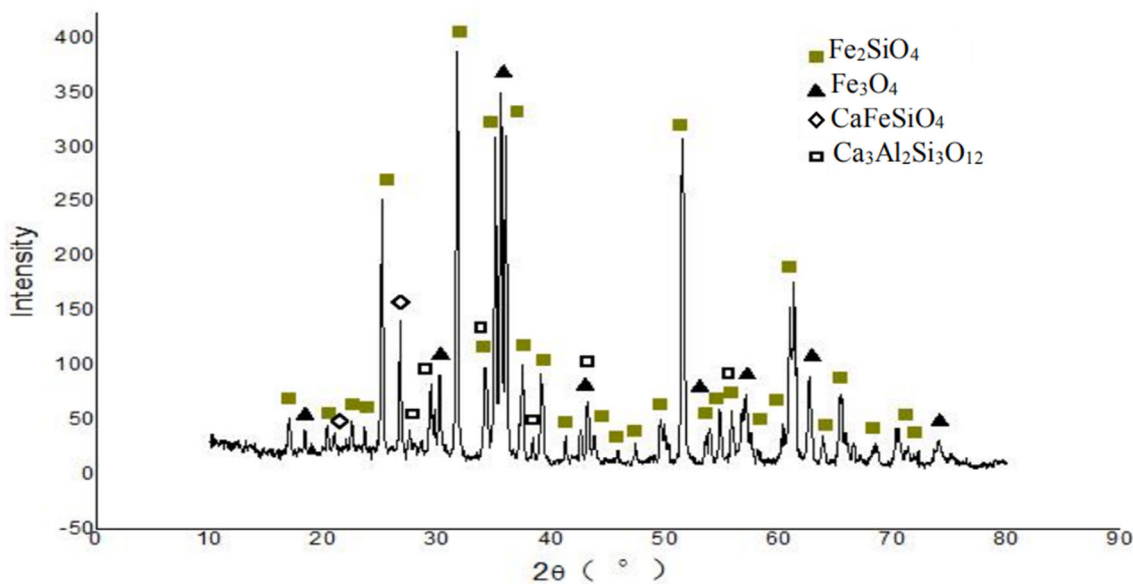| Composition	Fe	O	Si	Zn	Al	Ca	Mg	Cu	S
Content	38.51	33.00	18.72	2.66	1.55	1.27	0.91	0.48	0.38

Fig. 3 Phase structure analysis of copper slag

magnetite is only about 7 wt %, and the rest are other mineral phases.

The microscopy morphology of copper slag is observed by SEM combined with EDS shown in Fig. 4. From the results of Fig. 4a, the particle size of the copper slag particles is unevenly distributed from several micrometers to several tens of micrometers. The slag has apparently smooth and dense structure whether it is a large or small particle. The results of energy spectrum analysis of the original copper slag in Fig. 4a shows that Fe content in
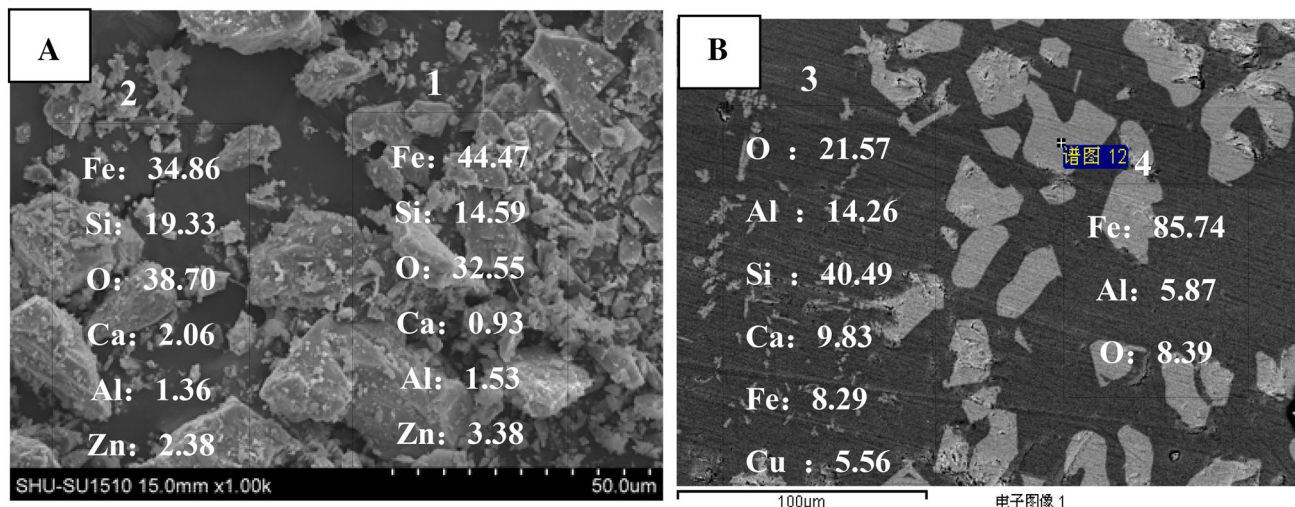
Fig. 4 Microscopy morphology of copper slag

the region 1 of larger particles is higher, while the content of Si, Ca and Al in the regions 2 of the small particles is relatively high. The EDS combined with XRD results show that the large particle copper slag is fayalite-magnetite phase. The larger particles are in the form of massive and short columns, and the angular angle looks obvious. The small particles are the fayalite-silicate phase coated with impurities such as calcium and aluminum. Cu is intercalated in the fayalite phase according to the energy spectrum analysis which make it difficult to recover copper from copper slag. Figure 4b shows the microprobe of backscattered imaging of copper slag. There are two phases in copper slag, region 3 and region 4. The composition and content of mineral phase about region 4 is rich Fe, Al and O which means magnetite phase. The composition of region 3 contains element of Fe, Al, Si, Ca and Cu which means copper is embedded into the fayalite phase.

3.2 Temperature Effect on Phase Transition

The purpose of this experiment is to completely oxidize and decompose the fayalite into magnetic iron oxides and silica under medium- and low-temperature conditions. Fayalite is beneficial to decomposition under oxidation at high ambient temperature according to reactive Gibbs free energy. The oxidation reaction is selected under the condition at the range of 800–1000 °C, with the oxidation time of about 60 min and the oxygen flow of 0.1 L/min. The mineral phase transformation of the copper slag during oxidation process with the temperature increasing is shown in Fig. 5.

The XRD patterns of copper slag exhibits more Fe_3O_4 and Fe_2O_3 characteristic peaks at 800 °C, indicating that the copper slag has undergone significant phase
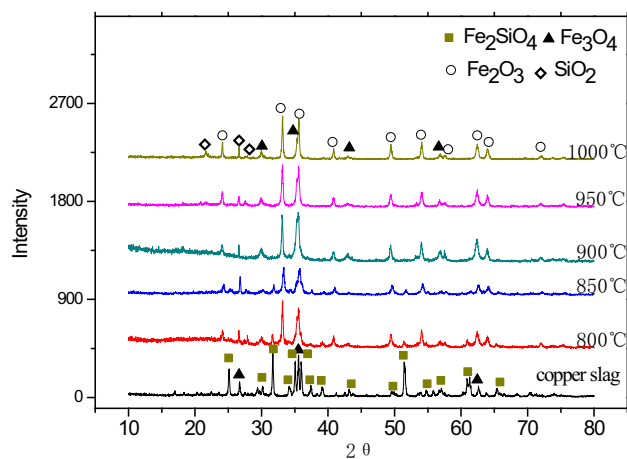

Fig. 5 XRD of copper slag at different oxidation temperatures

transformation at 800 °C. The fayalite in the copper slag transforms into magnetite and amorphous silica (Fe_2SiO_4 + $O_2 \rightarrow Fe_3O_4$ + SiO_2), and the magnetite is oxidized to form hematite (Fe_3O_4 + $O_2 \rightarrow Fe_2O_3$). The main phases of calcined copper slag at 800–850 °C are Fe_3O_4 and Fe_2O_3, but there is still a small amount of Fe_2SiO_4 phase, indicating that the oxidation of fayalite is not complete at temperature of 850 °C. With the increase in oxidation temperature, the intensity of Fe_2SiO_4 decreases, and the intensity of Fe_3O_4 and Fe_2O_3 increases. When the oxidation temperature rises to 900 °C, the characteristic peak of Fe_2SiO_4 disappears completely, and the characteristic peak intensity of Fe_3O_4 begin to decrease. The reason is that, Fe_2SiO_4 decomposes to Fe_3O_4 and SiO_2 completely. Magnetite continues to oxidize to form hematite ($Fe_3O_4 \rightarrow Fe_2O_3$), and the intensity of Fe_2O_3 peak increases. At 950 °C, the weaker SiO_2 characteristic peaks appear at 21.6°, 26.5°, 27.6° (2θ) (the characteristic peaks of

cristobalite at 21.6° and 27.6°, and the characteristic peaks of quartz at 26.5°). It has been indicated that a small amount of quartz crystal and cristobalite crystals begin to crystallize at 950 °C.

Figure 6 shows the FT-IR spectrum of copper slag's transformation at different oxidation temperatures. The FT-IR spectrum of the original slag mainly shows the vibration of the complex Si–O group in complex anion $[SiO_4]^{4-}$ of the Fe_2SiO_4. There are three absorption bands in the original slag in the wavenumber range of 1200–400 cm^{-1}. The absorption peaks with wave number of 951 cm^{-1} and 873 cm^{-1} in the first band between 1100 and 850 cm^{-1} are attributed to the asymmetric stretching vibration of Si–O bond. The absorption peak of the second wavelength band between 850 cm^{-1} and 600 cm^{-1} with a wave number of 825 cm^{-1} is attributed to the symmetric stretching vibration of the Si–O bond, and an absorption peak of the third band with a wave number of 474 cm^{-1} between 600 cm^{-1} and 400 cm^{-1} is attributed to the bending vibration of Si–O bond. The vibration at 562 cm^{-1} indicates Fe–O bond of magnetite.

The FT-IR spectrum of the copper slag transforms significantly with the increasing temperature. A new absorption peak appears at 1072 cm^{-1} at 800 °C which indicates that a new phase is formed at this temperature. The absorption peak with strong intensity and wide shape in the wavenumber range of 1100–1050 cm^{-1} is the characteristic of amorphous SiO_2 [10], which is caused by the asymmetric stretching vibration of Si–O bond in SiO_2. No quartz crystal can be detected in the copper slag in the XRD pattern at 800° which means the formed phase of amorphous SiO_2. Due to the different Si–O bonds of complex anion $[SiO_4]^{4-}$ strengths in the Fe_2SiO_4, copper slag has multi-peak splitting in the range of 1000–850 cm^{-1} calcined at 800 °C, and there appears two peaks, which are located at 902 and 875 cm^{-1}, respectively. The peaks of these two are not deep; the absorption peak at 825 cm^{-1} also split into two peaks at 835 and
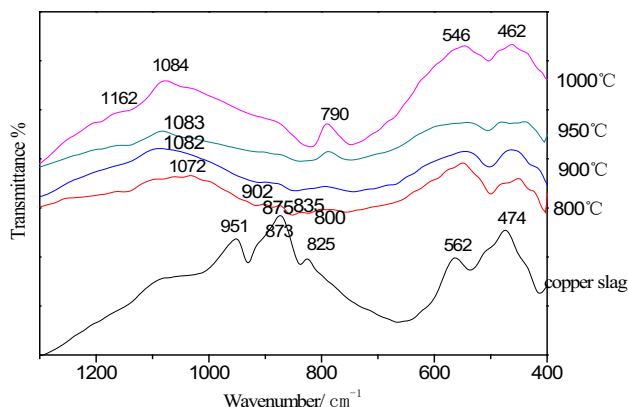
800 cm^{-1}, respectively. When the calcination temperature rises from 800 to 900 °C, the absorption peak intensity increased to around 1072 cm^{-1} and moves to a high wavenumber of 1082 cm^{-1}, indicating that the content of amorphous SiO_2 in the copper slag increases with the increase in calcination temperature. The absorption peaks around 902, 875, 835 and 800 cm^{-1} completely disappear, indicating that Fe_2SiO_4 completely decomposes into Fe_2O_3 and SiO_2 at 900 °C, and the content of SiO_2 in the copper oxide slag reaches a maximum at this temperature. At 950 °C, the intensity of the absorption peak near 474 cm^{-1} decreases and moves in the vicinity of 462 cm^{-1}. The weak shoulder peak appears at 1162 cm^{-1}, and the absorption peak appearing near 790 cm^{-1} is characterized as the absorption peak of quartz minerals [11] which indicates that a small amount of quartz crystal precipitates at this temperature, and it is consistent with the XRD analysis results in Fig. 5. When the oxidation temperature rises to 1000 °C, the intensity of absorption peak at 1162 cm^{-1}, 790 cm^{-1} and 462 cm^{-1} get enhanced, and the FT-IR spectrum of the calcined copper residue at 1000 °C shows obvious infrared absorption of quartz crystal. It has been indicated that the content of quartz crystal (quartz, cristobalite) in the calcined copper slag increases with the rising of temperature.

3.3 Oxidation Time Effect on Phase Transition

Figure 7 shows the XRD patterns of copper slag after different reaction times at a temperature of 950° C and an oxygen flow rate of 0.1 L/min. The characteristic peak of the fayalite disappears completely after 60 min, which indicates that the fayalite phase in the slag had been completely oxidized to a high-valent iron oxide. The main
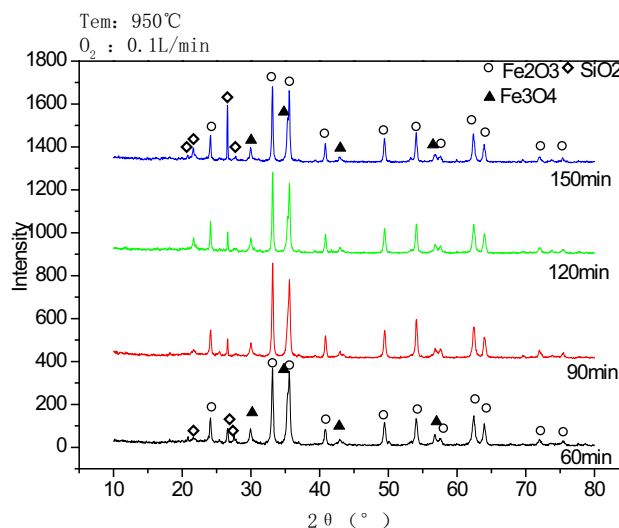

Fig. 6 FT-IR of copper slag at different oxidation temperatures

Fig. 7 XRD of copper slag at different oxidation times

phase of copper slag is Fe_2O_3 after oxidizing at 950 °C for 60 min, and the secondary phases are Fe_3O_4 and SiO_2. The difference between the diffraction peak intensities of two iron oxides is not large, and the characteristic peak of SiO_2 is weak. With the prolongation of oxidation time, the characteristic peak intensity of Fe_2O_3 increases slightly, the characteristic peak intensity of Fe_3O_4 decreases slightly, and the characteristic peak intensity of quartz increases obviously. The main phase of copper slag oxidized at 950 °C for 150 min is Fe_2O_3, and the secondary phase is Fe_3O_4. Quartz and cristobalite phases appear obvious, indicating that prolonged time is beneficial to the crystallization and growth of hematite phase and also beneficial to the precipitation and growth of cristobalite phase.

Figure 8 shows the FT-IR spectrum of copper slag at different reaction times at 950 °C. The FT-IR spectra of copper slag are characteristic absorption peaks of quartz, and the positions of the absorption peaks are basically the same, but the intensity of each absorption peak increases with the increase in oxidation temperature. It indicates prolonging of oxidation time is beneficial to increase the crystallinity of quartz.

3.4 Morphology Transformation During the Oxidation

The mineral phases transformed before and after the reaction are only judged qualitatively and semiquantitatively with XRD analysis, while the quantitative transformation of the mineral phase composition before and after the reaction is uncertain. Therefore, the scanning electron microscopy–energy-dispersive spectrometer (SEM–EDS) has been used to detect and analyze the copper slag composition before and after the reaction.

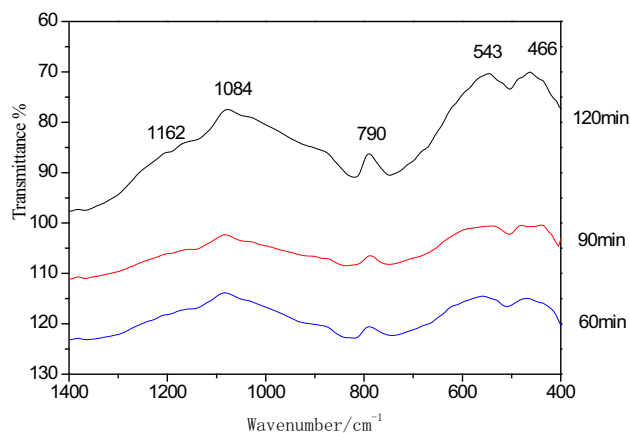Figure 9 shows SEM images of copper slag after oxidation under different temperature conditions. The

oxidation temperature and oxidation time have a great influence on the microscopic morphology of the copper slag. After oxidation, the surface of the original copper slag is smooth and the dense structure disappears, becoming a rough and loose porous structure caused by oxidation. The structure of Fe_2SiO_4 in the copper slag is broken and decomposes into iron oxide and SiO_2.

The morphology of copper slag transformed at different temperatures is characterized with SEM shown in Fig. 9 A–D. A–D show the copper slag morphology at temperature of 800°, 900°, 950° and 1000°, respectively. With the increase in oxidation temperature, the number of larger particles in copper slag increases, and the surface roughness of large granular mineral phase increases. The element content of the different particles transform greatly with the increase in the oxidation temperature. After oxidation, the larger particles contain more iron than the small ones and the silicon content is lower, which means that the main mineral phase of large particles is hematite and magnetite at temperature lower than 900 °C, and fine particle is silicate phase. The content of iron increases with temperature at 950 °C. The main iron-bearing mineral phase in the larger particle size are hematite phase, and magnetite phase in smaller particle size.

Figure 9 E and F shows SEM images of 1000 °C oxidation for 60 min and 120 min at high magnification amplification (5 K times). The results show that there are two mineral phases on the surface of the particles, namely the fayalite-oxidized decomposition products. A large number of fine and uniform dot-shaped Fe_2O_3 crystal particles are distributed on the surface with the particle's size less than 1 μm. There are also some embedded silicate phases on the surface of the particles with a particle size of 1–2 μm. When the oxidation time extends to 120 min, there is enrichment of Fe_2O_3 particles on the surface which has a quasi-spherical shape with an average particle size of about 3 μm. It can be indicated that the precipitation of Fe_2O_3 crystals has occurred with the prolongation of oxidation time. The "embedded" silicate phase with the particle size of 3 μm has been separated and have become the form of "adsorption." The silicon content in the hematite phase is less than 1 wt%, while other impurity elements such as Al and Ca decreases slightly. This is because element's diffused rate increases with improving temperature.

3.5 Oxidation Mechanism on Phase Transformation of Oxidation Copper Slag

During the oxidation reaction, the Fe_2O_3 "crystal nucleus" is first generated by oxidation reaction. The newly formed Fe_2O_3 "crystal nucleus" is connected to each other and they grow up. The interconnection process causes a

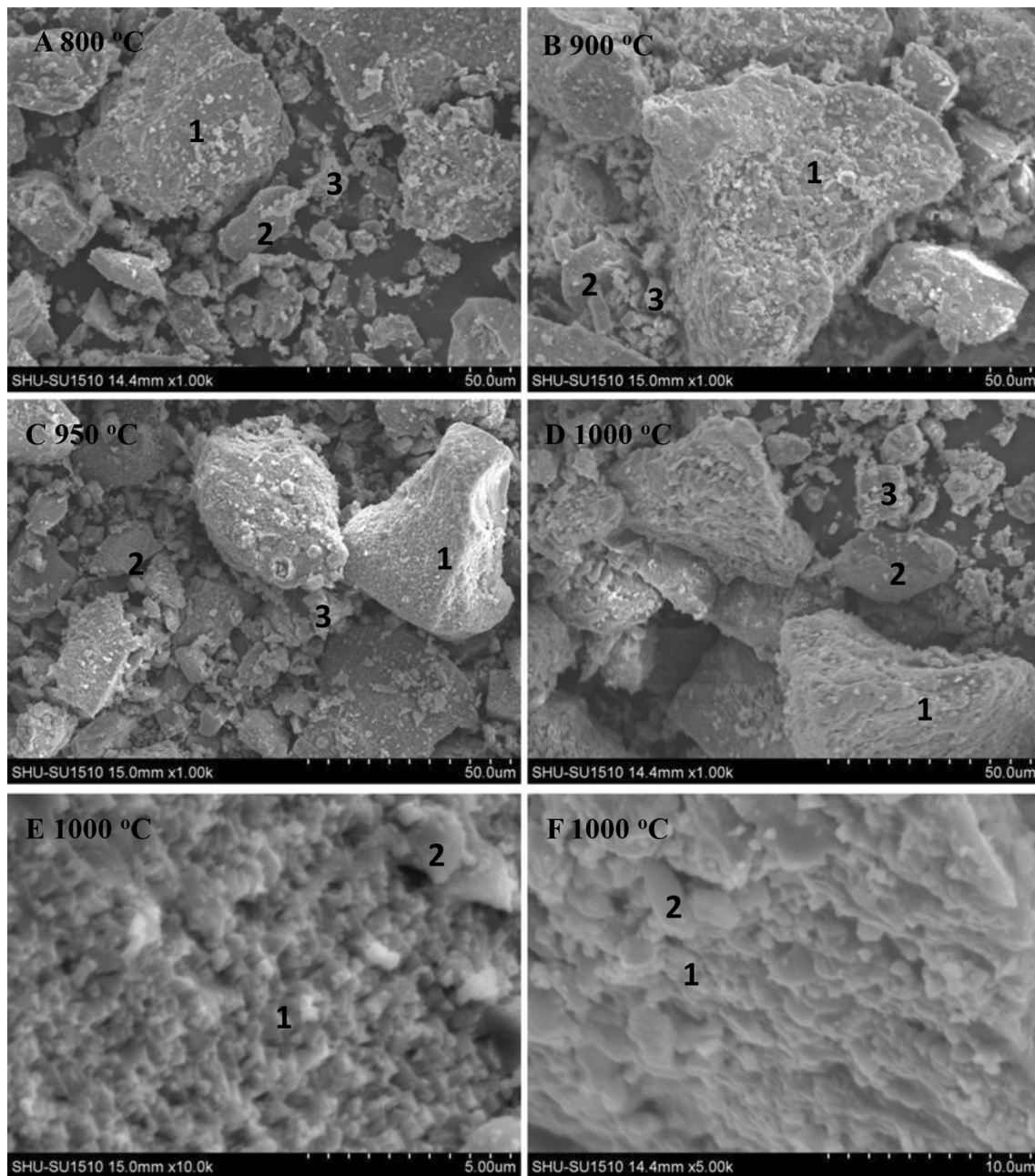**Fig. 8** FT-IR of copper slag in different oxidation times

Fig. 9 SEM image of copper slag after oxidation

decrease in surface energy, which make the elemental diffusion a spontaneous process. Fe migrate to the gas–solid reaction interface of slag through the newly formed iron oxide layer. With the oxidation temperature increasing and the oxidation time prolonging, small particles disappear and large particles are continued to form. The migration and diffusion of iron increases, and the original structure of the fayalite phase breaks. The silicon-oxygen bond in the fayalite get continuously saturated, forming a chain shape, and the silicate structure of the frame-shaped transforms into an island shape. The silicate structure

breaks and is thus peeled off from the whole magnetite in the form of small particles, and the final part get detached into small particles of iron silicate, and a part get adsorbed on the surface of the hematite phase.

The content of Fe_2SiO_4 in copper slag is accounted for more than 70% in the copper slag composition, and Fe_3O_4 is only accounted for about 7%. Therefore, the oxidation reaction of Fe_2SiO_4 occurrs mainly in the calcination process of copper slag. The results of XRD patterns show that Fe_3O_4 and Fe_2O_3 are the oxidation products of copper slag at 800 °C. At the same time, the wide and blunt
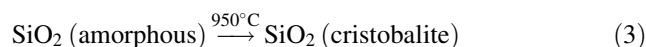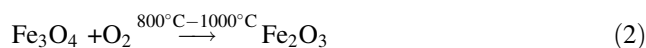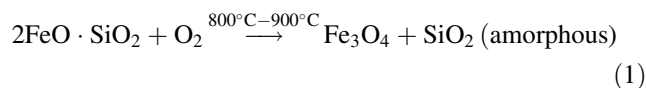
characteristic peak of amorphous SiO_2 appears. The fayalite get transferred to magnetite and amorphous silica ($Fe_2SiO_4 + O_2 \rightarrow Fe_3O_4 + SiO_2$) during oxidation at 800 °C, and the magnetite is oxidized to form hematite ($Fe_3O_4 + O_2 \rightarrow Fe_2O_3$). The characteristic peak of Fe_2SiO_4 disappear completely in the XRD pattern at 900 °C, indicating the transition of Fe_2SiO_4 to iron oxide completely. In the range of 800–900 °C, the transition from Fe_2SiO_4 to Fe_3O_4 and from Fe_3O_4 to Fe_2O_3 occurs simultaneously. The transition from Fe_3O_4 to Fe_2O_3 occurs with temperature increased to 900 °C.

The amorphous SiO_2 is glass phase formed from 950° C, and the glass phase products are quartz and cristobalite crystals. The cristobalite crystals are unstable in the range of 870–1270 °C on the basis of the literature [12]. The temperature range for transition to cristobalite is 1470–1670 °C according to thermodynamics. However, many non-metallic mineral materials also has metastable cristobalite formed during oxidation reaction. Cristobalite get precipitated [13] from different mineral phases at a wide range of temperature. Diatomite is converted into cristobalite at 900–1300 °C [13]; opal is converted into cristobalite at 1200 °C [14]; kaolinite also produces cristobalite at 1260 °C [15]; synthetic MCM-41 mesoporous SiO_2 molecular sieve transforms into cristobalite at 1000 °C [16]. Other processes such as ceramic sintering and mullite preparation also has metastable cristobalite formation. All the informations above indicate that the formation of cristobalite in the thermodynamic metastable state is a common phenomenon. The formation of metastable cristobalite is consistently considered to be a non-equilibrium thermodynamic process, which is mainly controlled by the reaction kinetic mechanism.

Amorphous SiO_2 ordered structure is similar to the disordered structure of cristobalite, and this similarity greatly increases the effective nucleation rate of cristobalite during the crystallization of amorphous SiO_2. The impurity element contained in the amorphous SiO_2 is advantageous for the formation of cristobalite at lower temperature and accelerating the progress of the reaction. Mollah et al. [17] found that lignite-burning ash had a cristobalite crystal formed during heat treatment at 1000 °C. The conclusion of the authors was that, alkali metal oxides (Na_2O and K_2O) and alkaline metal oxides (CaO and MgO) and Fe_2O_3 in ash led to the crystallization formation of cristobalite at lower temperature. Chen Meiyi et al. [18] also believed that impurity elements such as Mg, K and Ca were beneficial to decrease the cristobalite crystallization formation temperature. When the amorphous SiO_2 and quartz get converted to cristobalite, the Si–O–Si bond is broken and reconstructed. The metal ions can increase the number of Si–O–Si bond ruptures and form more lattice defects. These defects improve the free energy of the system and increases the reactivity of SiO_2, which is beneficial to the nucleation of cristobalite crystals at lower temperature.

According to the analysis above, the multiphase transformation reaction in the oxidation process of copper slag can be summarized as:

$$2FeO \cdot SiO_2 + O_2 \xrightarrow{800°C-900°C} Fe_3O_4 + SiO_2 \text{ (amorphous)} \tag{1}$$

$$Fe_3O_4 + O_2 \xrightarrow{800°C-1000°C} Fe_2O_3 \tag{2}$$

$$SiO_2 \text{ (amorphous)} \xrightarrow{950°C} SiO_2 \text{ (cristobalite)} \tag{3}$$

The copper slag oxidized at 950 °C from 60 min to 150 min mainly undergoes multiphase transformation from Fe_3O_4 to Fe_2O_3 and amorphous SiO_2 to quartz and cristobalite. The prolongation of oxidation time has a great influence on the size of Fe_2O_3 and quartz particles. The particle size of Fe_2O_3 and quartz become larger as the oxidation time get prolonged. The median particle size of the copper slag increases to 22.74 μm under the condition of 950 °C for 120 min. The proportion of the particles smaller than 10 μm is less than 30%. The proportion of particles larger than 35 μm increases to 60%.

4 Conclusion

The oxidation modification of copper slag mainly was investigated to provide the information about phase transformation which made it convenient for recovery of copper and iron from copper slag. The results of the experiment are shown as follows:

1. The study on process mineralogy showed that the particle size of copper slag was very fine. The median particle size was less than 10 μm. Si and Fe in copper slag mainly existed in the form of fayalite, and the content of Fe_2SiO_4 accounted for about 73% in copper slag which was much higher than that of Fe_3O_4. Therefore, the oxidation process of copper slag was mainly about the oxidation of Fe_2SiO_4.

2. The results of copper slag oxidation showed that the oxidization of the fayalite in the copper slag decomposed into iron oxide and silica by selecting suitable oxidation conditions. The phase transformation during the oxidation of copper slag is as follows: The phase transition of the origin slag at 800 °C had transformed from Fe_2SiO_4 to Fe_3O_4 and amorphous SiO_2, and the transition of Fe_2SiO_4 to Fe_3O_4 ended at 900 °C. The transition of Fe_3O_4 to Fe_2O_3 occured simultaneously at 800 °C, and the transition almost finished at 1000 °C. The transition from Fe_2SiO_4 to

Fe_3O_4 and Fe_3O_4 to Fe_2O_3 occured simultaneously at 800 ∼ 900 °C; after 900 °C, the main transition from Fe_3O_4 to Fe_2O_3 occured.

3. Quartz and cristobalite were formed by transformation of amorphous SiO_2, and the crystallization temperature of quartz and cristobalite was 950 °C. Prolongation of oxidation time was beneficial to both the crystallization and growth of the hematite phase and the growth precipitation of the quartz phase.

4. The median particle size of the copper slag was increased to 22.74 μm under the condition of 950 °C for 120 min. The proportion of particles smaller than 10 μm was less than 30%. The particle size larger than 35 μm was increased to 60%.

References

1. World Bureau of Metal Statistics. January to December 2017 Metals Balances.
2. Liu G, and Zhu R, *Min Metall* **17** (2008) 59.
3. Mackwell S J, *Phys Chem Miner* **19** (1992) 220.
4. Chen Y W, *World Nonferrous Met* 9 (2001) 53.
5. Kim B S, Jo S K, Shin D, Lee JC, and Jeong SB, *Int J Miner Process* **124** (2013) 124.
6. R.M.Manser, Li CG. Flotation selection of silicate minerals [J]. Foreign metal ore selection, 1979, 7: 8.
7. Finch C B, Clark G W, and Kopp O C, *Am Mineral* **65** (1980) 381.
8. Pang J M, Guo P M, and Zhao P, *Nonferrous Met (Extr Metall)* **3** (2013) 51.
9. Liao Z L, Tang P, Zhang B, Zhang H W, Shi X Y, Li Q J, and Hong X, *China Nonferrous Metall* **41** (2012) 74.
10. Dalby K N, and King P L, *Am Mineral* **91** (2006) 1783.
11. Chen M Y, and Li Z D, *Foundry* **4** (1993) 9.
12. Banza A N, Gock E, and Kongolo K, *Hydrometallurgy* **67** (2002) 63.
13. Cao H Y, Fu N X, Wang CG, Zhang L, Xia F S, Sui Z T, and Feng N X, *Multipurp Util Miner Resour* **2** (2009) 8.
14. Cao H Y, Fu N X, Zhang L, Xia F S, Sui Z T, Feng N X, *Chin J Process Eng* **9** (2009) 284.
15. Yang T, Hu J H, Wang H, and Li L, Chin J Process Eng **11** (2011) 613.
16. Deng Z Y, *Adv Ceram 20* (1999) 11.
17. Mollah M Y A, Promreuk S, Schennach R, Cocke D L, and Güler R, *Fuel* **78** (1999) 1277.
18. Xu C M, Wang S W, Huang X X, and Guo J K, *J Inorg Mater* **22** (2007) 577.