Electrolysis of Converter Matte in Molten CaCl₂-NaCl

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Abstract

The electrolytic production of nickel-copper alloy by electrochemical reduction of converter matte in molten salt has been investigated. The sintered solid porous pellets of Ni_3S_2, Cu_2S and converter matte were electrolyzed at a voltage of 3.0 V in molten $CaCl_2$-NaCl under the protection of argon gas at 700°C, respectively. The electro-reduction processes were investigated and the products were characterized. The results show that the molten salt electro-reduction process can be used to produce nickel, copper and nickel-copper alloy directly from Ni_3S_2, Cu_2S and converter matte precursors in molten $CaCl_2$-NaCl, respectively. CaS would be formed as the intermediate compound during the electro-reduction process, and then the formed CaS can be gradually decomposed and removed with the increase of the electrolysis time. The experimental results show that the molten salt electro-reduction process has the potential to be used for the reduction of sulfide minerals in molten $CaCl_2$-NaCl.

Keywords

Converter Matte, Electro-Reduction, Nickel-Copper Alloy, Molten $CaCl_2$-NaCl, Solid-State Electrochemistry

1. Introduction

Nickel-copper alloy is a high-quality corrosion-resistant alloy with good corrosion resistance in seawater, acid, alkali and reducing gas atmosphere [1] [2] [3] [4] [5]. Nickel-copper alloy has high commercial value due to its excellent manufacturability and mechanical property. In the conventional smelting process for nickel-copper alloy production, pure nickel and copper metals should be

firstly produced from minerals and then alloyed together to form nickel-copper alloy. Generally, this conventional method needs complex and energy-intensive processes.

So far, over 90% of the world's primary copper on the earth's crust is present in the form of copper sulfide minerals, and about 50% of the world's primary nickel production starts from nickel sulfide ores [6] [7] [8]. Meanwhile, most of the nickel sulfide ores are inevitably associated with copper sulfides [9] [10] [11]. In the traditional pyrometallurgical process, the sulfide ores are mined, reduced in size, and floated to produce nickel- and copper-rich concentrates. Then, the concentrates are smelted in flash smelter or electric furnace to produce nickel-copper matte. Subsequently, the nickel-copper matte is smelted and converted into converter matte, the converter matte is commonly dominated by nickel and copper sulfides with a small amount of iron sulfide. After that, the converter matte is separated into nickel concentrate and copper concentrate by flotation. Then, the nickel and copper concentrates are fabricated into Ni_3S_2 and Cu_2S anodes for the electrolysis in aqueous electrolyte to produce Ni and Cu, respectively [12] [13] [14]. It is obvious that the traditional process is complex. In addition, this process may also be suffered from the limited electrochemical window of the aqueous electrolyte and the large ohmic polarisation caused by the non-conducting sulfur deposited on the anode [15].

In recent years, a generic process for producing metals and alloys by direct electrochemical reduction of metal oxides or their mixtures has attracted worldwide attention [16]. Many efforts have been devoted to the direct reduction of metal oxides [17]-[25]. Actually, many metal sulfides are thermodynamically less stable than their oxide compounds [26]. Recently, some researchers have investigated the electro-reduction of sulfides in molten salts [6] [15] [27] [28]. Li *et al.* [27] investigated the electrolysis of MoS_2 in molten $CaCl_2$. Chen *et al.* [28] examined the removal of S in liquid copper. Ge *et al.* [6] studied the electrochemical extraction of copper from copper sulfide in molten $CaCl_2$-NaCl. Wang *et al.* [15] investigated the electrolysis of WS_2 to metal W in molten NaCl-KCl. However, these previous work generally focused on pure metal sulfides, the direct electrochemical reduction of sulfide minerals in molten salts needs more investigation.

In the present work, the electro-reduction process has been used to directly extract nickel-copper alloy from converter matte in molten $CaCl_2$-NaCl at 700°C. This work will show that the converter matte can be reduced to nickel-copper alloy in molten salts. The results generally suggest that the molten salt electro-reduction process is a promising process for the facile reduction of sulfide minerals in molten $CaCl_2$-NaCl.

2. Experimental

Figure 1(a) shows the XRD pattern of the converter matte used in this experiment. Obviously, the converter matte is composed of Ni_3S_2 and Cu_2S. **Figure 1(b)** shows the SEM image of the cross section of the initial converter matte.
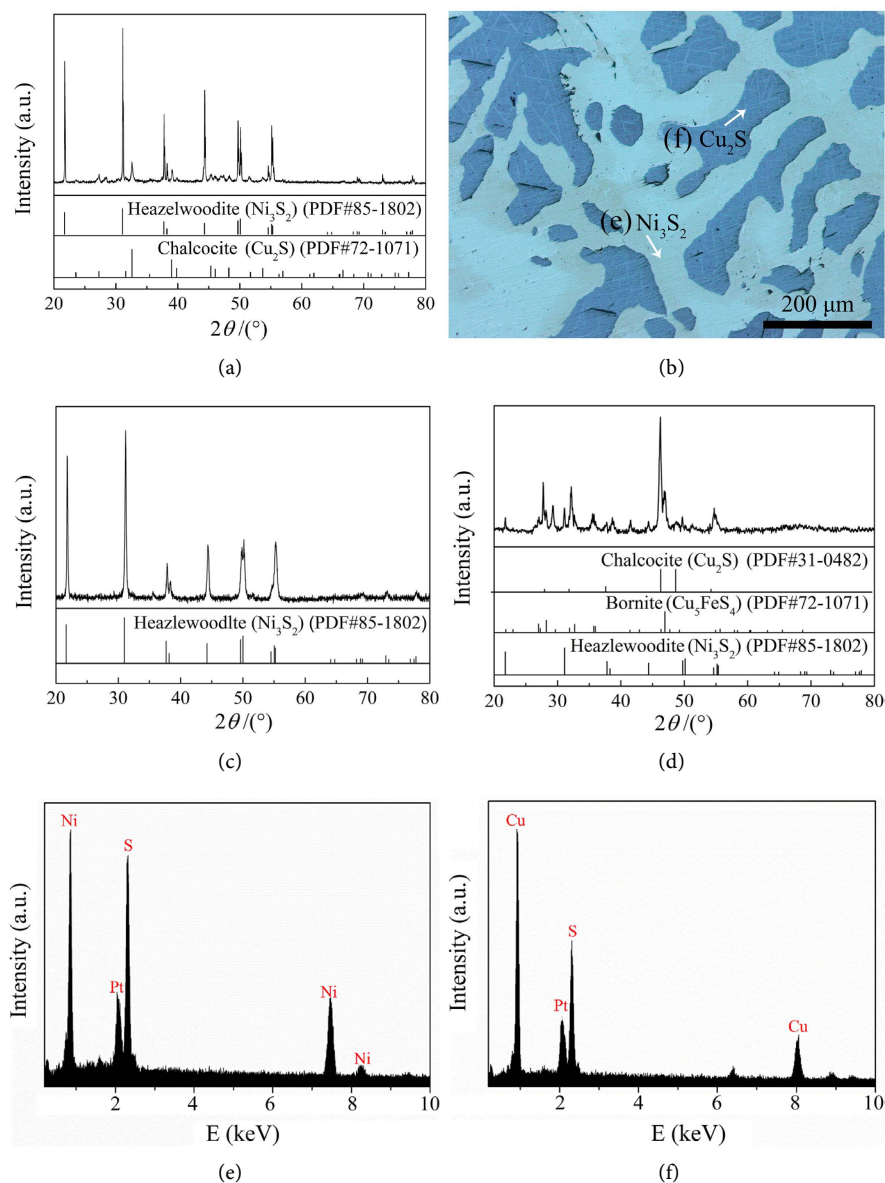
Figure 1. (a) XRD pattern and (b) SEM image of converter matte, (c) and (d) XRD patterns of Ni_3S_2 (c) and Cu_2S (d), (e) and (f) EDS results of watchet area (e) and mazarine area (f) in (b).

Two phases with different colors (mazarine and watchet) are observed, the EDS results ofwatchet area and mazarine areain **Figure 1(b)** are shown in **Figure 1(e)** and **Figure 1(f)**, respectively. It is observed that the phase with mazarine is determined as Cu_2S and the phase with watchet is confirmed to be Ni_3S_2. In addition, the Ni_3S_2 and Cu_2S separated from the converter matte were also used as the starting cathode materials for comparison. The phase compositions of the Ni_3S_2 and Cu_2S are shown in **Figure 1(c)** and **Figure 1(d)**, respectively. As shown in **Figure 1(d)**, the Cu_2S sample contains a small amount of Ni_3S_2 and Cu_5FeS_4. The chemical compositions of these initial samples (Ni_3S_2, Cu_2S and converter matte) used in the present study are listed in **Table 1**.

Table 1. Table type styles (Table caption is indispensable).

Component	Ni	Cu	S	Fe	O	other
Converter matte	43.77	31.83	18.54	3.24	1.88	0.74
Ni_3S_2	65.18	4.66	19.57	2.30	6.01	2.28
Cu_2S	5.09	67.74	16.66	6.51	3.75	0.25

The schematic diagram of the electrolytic cell used for the electro-reduction experiment is shown in Figure 2. The anhydrous $CaCl_2$ and NaCl were weighed and mixed at the molar ratio of 1:1. The $CaCl_2$-NaCl mixture was filled in an alumina crucible (55 mm in diameter, 120 mm in height) and served as electrolyte. The converter matte was firstly ball-milled and screened to obtain homogenous powders with particle size below 75 μm. Then, about 1.0 g of the converter matte powder was pressed into pellet with a diameter 8 mm under a pressure of 10 MPa, the pressed pellet was sintered in argon gas at 400°C for 2 h. Similar procedures were also used to fabricate the Ni_3S_2 and Cu_2S pellets. The sintered pellet was wrapped with thin stainless steel nets (pore size of 75 μm) and then attached to a Fe-Cr-Al wire (2 mm diameter) to form a cathode. A graphite rod (12 mm diameter) was used as an anode. The electrochemical experiments were controlled by using a BioLogic HCP-803 electrochemical workstation. Argon gas (99.99%) was used to maintain an inert atmosphere during electrolysis process.

During the electrolysis process, sulphur in cathode may get ionized and transport to the anode, which may cause the precipitation of CaS [6]. A high voltage of 3.0 V is adopted to promote the decomposition of CaS. After being electrolyzed at 3.0 V at 700°C in molten $CaCl_2$-NaCl for an appropriate time, the cathode was lifted and cooled in argon gas above the molten salt. Then, the cathode was taken out and washed by distilled water. The washed cathode product was dried and collected. The morphology of the obtained products was characterized by using a scanning electron microscope (SEM, JSM-6700F, JEOL Ltd., Japan) at an acceleration voltage of 15 kV. The elemental composition of the samples was analyzed by using an energy-dispersive X-ray spectroscopy (EDS, Oxford Inca, Oxfordshire, UK) attached to the SEM and also by an inductively coupled plasma optical emission spectrophotometer (ICP-OES, PerkinElmer Optima 7300 DV, Connecticut, USA). The phase composition of the samples was determined by a powder X-ray diffractometer (XRD, D8 Advance, Bruker, Germany) with Cu Kα radiation.

3. Results and Discussion

The typical current-time curve recorded during the electrolysis process of Cu_2S is presented in Figure 3(a). The current shows a drop within the first 1 h. Then, the current gradually decreases to about 0.2 A at about 2 h. In order to investigate the electro-reduction process of Cu_2S, the reduction products obtained at different electrolysis stages were characterized by XRD.
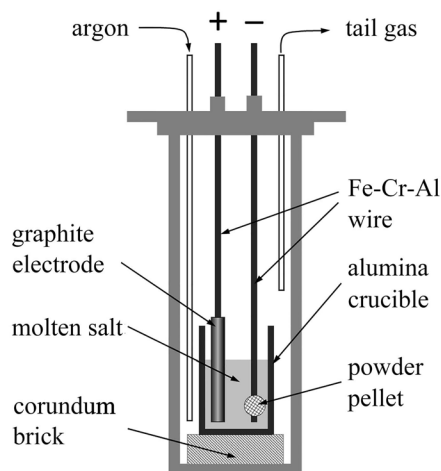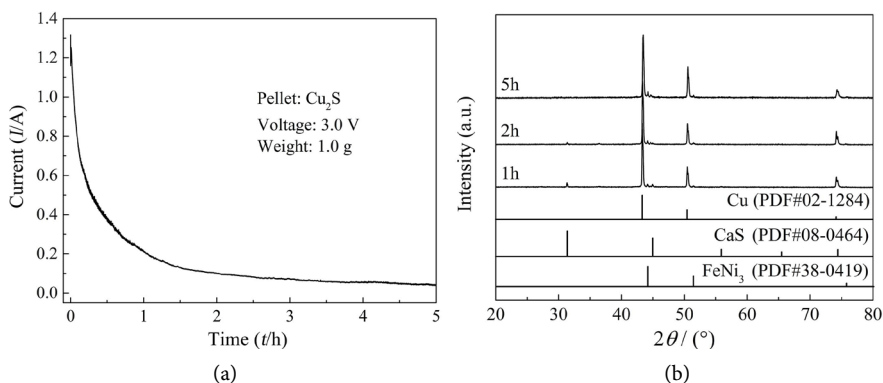
Figure 2. Schematic diagram of the electrolytic cell.

Figure 3. (a) Typical current-time curve of the electro-reduction of Cu_2S pellet at 3.0 V and 700°C in molten $CaCl_2$-NaCl; (b) XRD patterns of the products obtained from the electro-reduction of Cu_2S pellet at 3.0 V and 700°C for different times.

The XRD patterns of the Cu_2S pellets after being reduced at 3.0 V and 700°C for different times in molten $CaCl_2$-NaCl are shown in **Figure 3(b)**. It is seen that the phases of the sample obtained at 1 h include Cu, CaS and $FeNi_3$. Moreover, with the increase of electrolysis time, the peak intensity of CaS decreases evidently. According to the XRD patterns shown in **Figure 3(b)**, copper with a small amount of $FeNi_3$ obtained after being electrolyzed for more than 2 h at 3.0 V. According to the previous work [6], CaS has a low solubility in the salt melt and it will decompose into Ca^{2+} and S^{2-} as electrolysis proceeds further. S^{2-} will transport to the anode and then oxidize to form elemental sulphur. The electrode reactions for Cu_2S may be reasonably considered as:

$$\text{Anodic reaction: } S^{2-} \rightarrow 1/2S_2 \text{ (g) } + 2e^- \tag{1}$$

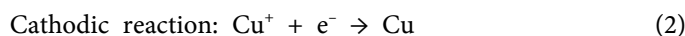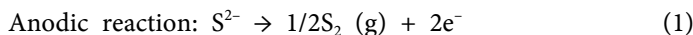$$\text{Cathodic reaction: } Cu^+ + e^- \rightarrow Cu \tag{2}$$

Figure 4 shows the SEM images of the Cu_2S pellets after being electrolyzed for 5 h. **Figure 4(b)** is the partial enlarged detail showing the particles corresponding to **Figure 4(a)**. After 5 h electrolysis, the pellet contains copper particles with
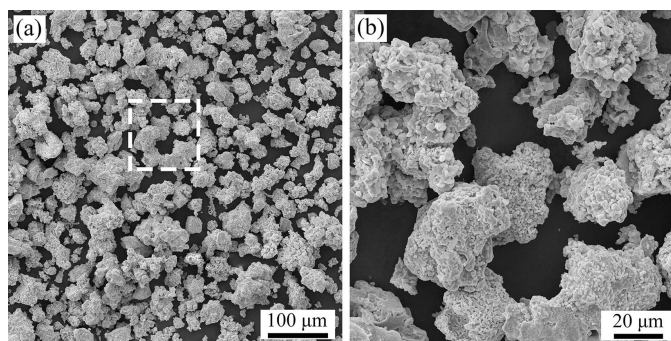
Figure 4. (a) SEM image of the Cu$_2$S pellet after being electro-reduced at 3.0 V and 700°C for 5 h in molten CaCl$_2$-NaCl, (b) the partial enlarged detail showing the particles in (a).

particle sizes of approximately 20 μm. Meanwhile, the obtained copper particles show rough surfaces and porous structures.

Figure 5(a) shows the typical current-time curve recorded during the electrolysis process of Ni$_3$S$_2$. As shown in **Figure 5(a)**, the current rapidly decreases within the first 30 min. Then, the current decreases to a steady value at 1.5 h. The products obtained at different electrolysis stages were characterized by using XRD. **Figure 5(b)** shows the XRD patterns of the Ni$_3$S$_2$ pellets after being reduced at 3.0 V and 700°C for different times in molten CaCl$_2$-NaCl. The phases of the sample obtained at 1 h include Ni and CaS. Moreover, with the increase of electrolysis time, the peak intensity of CaS decreases evidently. Based on the result of the XRD analysis (**Figure 5(b)**), it is suggested that the electrolysis process of Ni$_3$S$_2$ is similar to the electrolysis process of Cu$_2$S, and the reactions may be expressed as:

$$\text{Anodic reaction: } S^{2-} \rightarrow 1/2S_2 \text{ (g) } + 2e^- \tag{3}$$

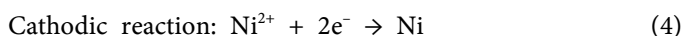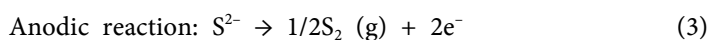$$\text{Cathodic reaction: } Ni^{2+} + 2e^- \rightarrow Ni \tag{4}$$

Figure 6 shows the SEM images of the Ni$_3$S$_2$ pellet after being electrolyzed for 5 h. **Figure 6(b)** is the partial enlarged detail showing the particles of **Figure 6(a)**. Obviously, after 5 h electrolysis, the particles presents a complicated structure. Although most of the particles are irregular strips, the dendritic crystals can also be found in **Figure 6**. The particle size of the obtained nickel is significantly larger than that of the copper obtained under the same electrolysis conditions.

The current-time curve of the electrolysis process of converter matte is shown in **Figure 7(a)**. Obviously, the current sharply drops within the first 20 min. Then, the current decreases and reaches to a steady value at 2 h. In comparison with the current-time curves shown in **Figure 3(a)** and **Figure 5(a)**, it can be seen that the current-time curve of the electrolysis of converter matte is different. In the initial reaction period, the shape of the current-time curve shown in **Figure 7(a)** is similar to that of the current-time curve shown in **Figure 5(a)**. The electrolysis process for the converter matte is mainly involved with the electro-reduction of Ni$_3$S$_2$ and Cu$_2$S. Therefore, after 1 h electrolysis, the shape of the
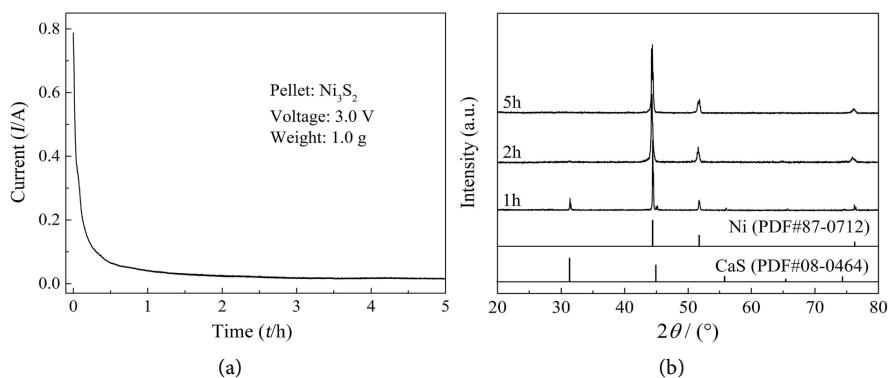
Figure 5. (a) Typical current-time curve of the electro-reduction of Ni_3S_2 pellet at 3.0 V and 700˚C in molten $CaCl_2$-NaCl, (b) XRD patterns of the products obtained from the electro-reduction of Ni_3S_2 pellets at 3.0 V and 700˚C in molten $CaCl_2$-NaCl.
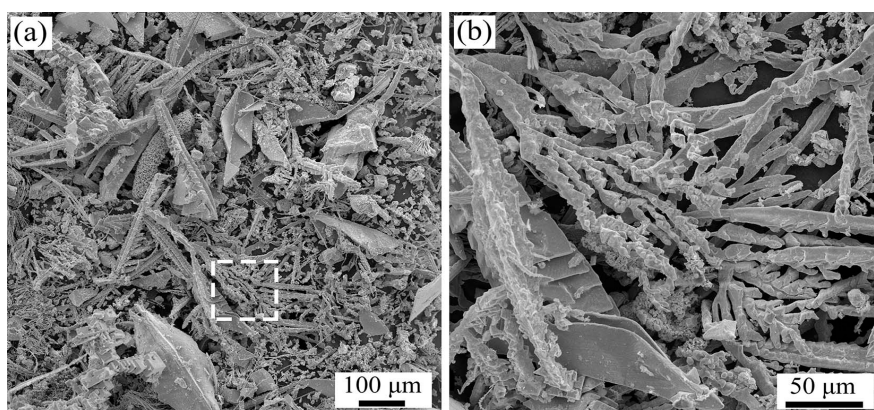

Figure 6. (a) SEM images of the Ni_3S_2 pellets reduced at 3.0 V and 700˚C in molten $CaCl_2$-NaCl for 5 h, (b) the partial enlarged detail showing the particles in (a).
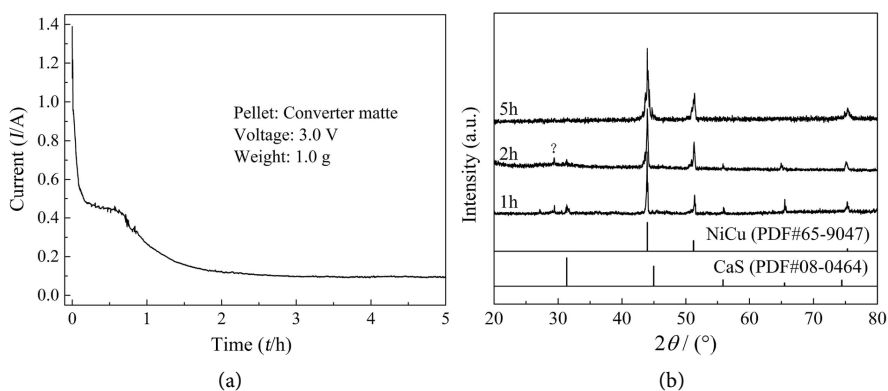

Figure 7. (a) Typical current-time curve of the electro-reduction of converter matte pellet at 3.0 V and 700˚C in molten $CaCl_2$-NaCl, (b) XRD patterns of the products obtained from the electro-reduction of converter mattepellets at 3.0 V and 700˚C in molten $CaCl_2$-NaCl.

current-time curve (**Figure 7(a)** from 1 h to 2 h) is similar to that of the current-time curve shown in **Figure 3(a)**. The XRD patterns of the converter matte pellets after being reduced at 3.0 V and 700˚C for different times in molten
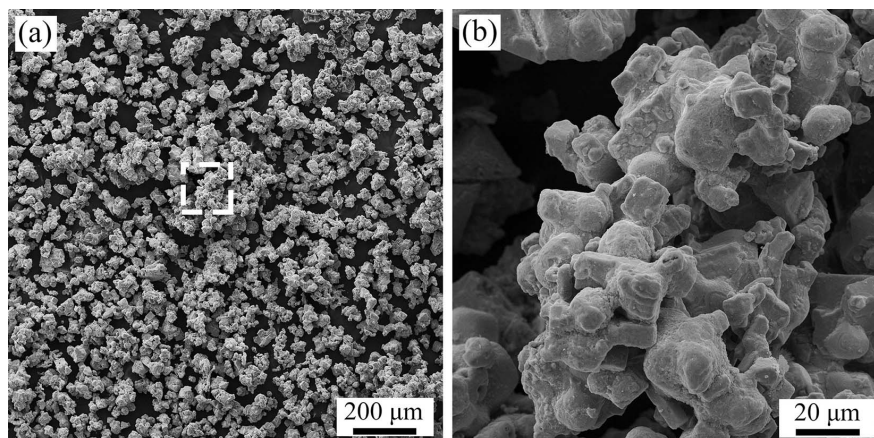
Figure 8. (a) SEM images of the converter matte pellet reduced at 3.0 V and 700°C in molten $CaCl_2$-NaCl for 5 h, (b) the partial enlarged detail showing the particles in (a).

$CaCl_2$-NaCl are shown in **Figure 7(b)**. Obviously, the CaS peaks gradually decrease with the increasing electrolysis time, and the phase of the product obtained at 5 h is cubic nickel-copper (NiCu) alloy. The reactions of the electro-reduction of converter matte can be expressed as:
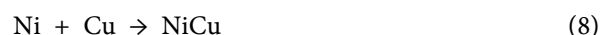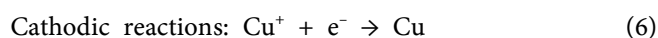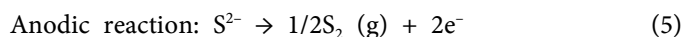
$$\text{Anodic reaction: } S^{2-} \rightarrow 1/2S_2 \text{ (g)} + 2e^- \tag{5}$$

$$\text{Cathodic reactions: } Cu^+ + e^- \rightarrow Cu \tag{6}$$

$$Ni^{2+} + 2e^- \rightarrow Ni \tag{7}$$

$$Ni + Cu \rightarrow NiCu \tag{8}$$

Figure 8 shows the SEM images of converter matte pellet after being electrolyzed at 3.0 V and 700°C for 5 h. **Figure 8(b)** is the partial enlarged detail showing the particles of **Figure 8(a)**. After 5 h electrolysis, the pellet contains large interconnected particles. In comparison with the pure nickel and copper particles produced from Ni_3S_2 and Cu_2S pellets, the NiCu alloy particles are more uniform and dense (**Figure 8**).

It should be noted that the electro-reduction process can produce sulphur element and NiCu alloy simultaneously. Considering there are several kinds of metals on the earth are present in the form of sulfides minerals, and the traditional extraction processes are complex. In addition, emission of SO_2 is also a difficult problem due to the increased environmental restrictions. Therefore, the molten salt electro-reduction process may provide a promising strategy for the sustainable reduction of sulfides minerals.

4. Conclusion

The molten salt electro-reduction process has been used to extract nickel-copper alloy from converter matte in molten $CaCl_2$-NaCl. The results show that the sintered solid porous Cu_2S, Ni_3S_2 and converter matte pellets can be electrolyzed to copper, nickel and nickel-copper alloy under a voltage of 3.0 V at low temperature (approximately 700°C), respectively. CaS would be formed as the intermediate product in the early electrolysis stage, and then CaS would be gradually

decomposed. It is suggested that the molten salt electro-reduction process is a promising process for the facile and sustainable reduction of sulfide minerals.

Acknowledgements

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