

## Recovery of cobalt from converter slag of Chambishi Copper Smelter using reduction smelting process

ZHAI Xiu-jing<sup>1</sup>, LI Nai-jun<sup>2</sup>, ZHANG Xu<sup>1</sup>, FU Yan<sup>1</sup>, JIANG Lan<sup>1</sup>

1. School of Materials and Metallurgy, Northeastern University, Shenyang 110819, China;

2. School of Science, Shenyang University, Shenyang 110044, China

Received 23 September 2010; accepted 5 May 2011

**Abstract:** The reduction smelting process for cobalt recovery from converter slag of the Chambishi Copper Smelter in Zambia was studied. The effects of reducing agent dosage, smelting temperature and time and the addition of slag modifiers (CaO and TiO<sub>2</sub>) were investigated. In addition, the depleted slag and cobalt-bearing alloy were characterized by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy. Under the determined conditions, 94.02% Co, 95.76% Cu and less than 18% Fe in the converter slag were recovered. It was found that the main phases of depleted slag were fayalite and hercynite; and the cobalt-bearing alloy mainly contained metallic copper, Fe-Co-Cu alloys and a small amount of sulfide.

**Key words:** converter slag; cobalt recovery; reduction smelting; slag modifier; cobalt-bearing alloy

### 1 Introduction

Cobalt is an important nonferrous metal and used mainly in high-temperature alloys, cemented carbides, magnetic alloys and catalysts for fossil oil refining [1]. So far, about 13 million tons of cobalt resources have been identified [2]. The vast majority of these resources are nickel laterite deposits in New Caledonia, Cuba, Indonesia and Philippines. And most of the rest occurs in copper deposits, including nickel-copper sulphide deposits in Australia, Canada, and Russia, and copper deposits in the Democratic Republic of the Congo (DRC) and Zambia [3–5]. Generally, cobalt is produced as by-products in the metallurgical processes of these deposits.

During the pyrometallurgy process of cobalt-bearing copper sulphide ore, cobalt is mainly accumulated in converter slag which is subsequently processed for cobalt recovery. Mineralogical studies showed that cobalt is present in oxidized form in converter slag and mainly in fayalite and magnetite as lattice substituents [6]. It is indicated that conventional techniques, such as slag cleaning, slow cooling of the slag followed by milling and flotation, are inappropriate

for cobalt recovery from converter slag [7–8]. Recently, hydrometallurgical processes for cobalt recovery from slag by selective leaching of metal values were reported [9–12]. For low content of cobalt in converter slag, however, plentiful slag is put through the entire process, resulting in high capital and operating costs for a practice process.

Reduction smelting is an efficient process for cobalt recovery from converter slag, which includes valuable metal oxides in molten slag reduction by the added solid carbon directly [13], gaseous carbon monoxide or metallic iron which is produced from the reduction of iron oxides, and the formation of cobalt-bearing alloy as reduced metal drops sinking to the bottom. Then the metal values are separated and recovered using a hydrometallurgical process. In this work, the reduction smelting process for cobalt recovery from converter slag is studied in laboratory scale. The converter slag is obtained from the Chambishi Copper Smelter in Zambia, in which copper concentrate with about 35% (mass fraction) Cu and 0.14% Co is smelted using Isasmelt's top-submerged lancing process followed by converting in Peirce-Smith converter. The effects of reducing agent dosage, melting temperature and time, addition of selected slag modifier on the reduction smelting process

are investigated.

## 2 Experimental

The converter slag from Chambishi Copper Smelter in Zambia was ground and analyzed by inductively coupled plasma-atomic emission spectrum (ICP-AES), infrared absorption carbon-sulfur analyzer and X-ray fluorescence (XRF), and the results are shown in Table 1. Its high copper content may contribute to the over-oxidation operation in converter to ensure cobalt beneficiation in the slag. X-ray diffraction (XRD) analyses showed that the main phases in the slag are fayalite ( $\text{Fe}_2\text{SiO}_4$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), metallic copper, chalcocite ( $\text{Cu}_2\text{S}$ ) and quartz ( $\text{SiO}_2$ ).

**Table 1** Chemical composition of converter slag sample (mass fraction, %)

Cu	Co	Ni	Fe	S	$\text{SiO}_2$
22.87	0.60	0.23	32.35	3.49	22.74

The reduction smelting of the converter slag was carried out under nitrogen atmosphere in a vertical  $\text{MoSi}_2$  tube furnace with the maximum operation temperature of 1 600 °C. And activated carbon was selected as reducing agent. As an experimental procedure, 100 g converter slag and 10 g alumina were mixed with the calculated amount of activated carbon and/or slag modifier ( $\text{CaO}$  or  $\text{TiO}_2$ ) in a corundum crucible which is then put in the tube furnace. The alumina addition is to avoid the corundum crucible damage by molten slag corrosion. The tube furnace temperature was raised to the desired value and hold for pre-set time. The crucible was naturally cooled to room temperature in the furnace and then taken out. The typical smelting parameters, except those with special mention, were activated carbon dosage of 5% (mass fraction), smelting temperature of 1 350 °C, smelting time of 2.5 h and without slag modifier addition.

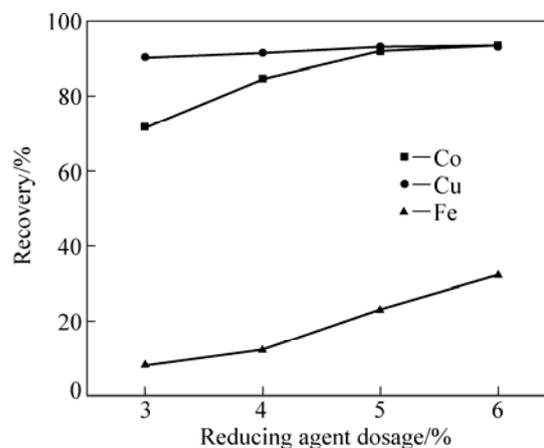
The depleted slag and cobalt-bearing alloy in the crucible were manually separated, weighed and ground in a vibrating mill for sampling. The contents of cobalt, copper and iron in the depleted slag and cobalt-bearing alloy were analyzed by ICP-AES. Based on the mass balance principle, the metal recoveries were calculated. In addition, the depleted slag and cobalt-bearing alloy were characterized by XRD, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

## 3 Results and discussion

### 3.1 Effect of reducing agent dosage

To determine the effect of reducing agent dosage,

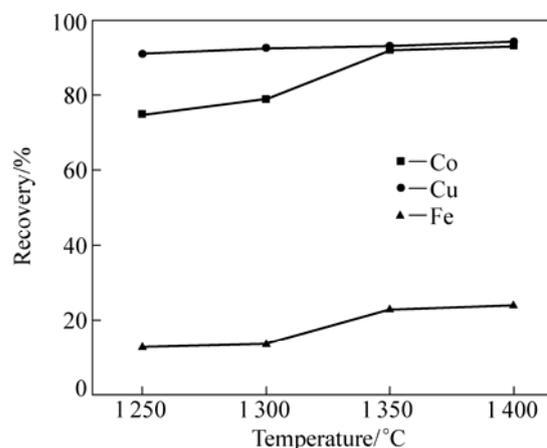
smelting experiments with activated carbon addition varying from 3% to 6% were conducted, and the results are shown in Fig. 1. The cobalt recovery increased as the reducing agent dosage increased from 3% to 5% and then increased slightly with the addition up to 6%. The reducing agent dosage had little influence on copper recovery, due to the fact that copper in the converter slag is mainly in the form of metallic copper and chalcocite. As the reducing agent dosage increased, iron recovery increased obviously. For the benefit of metal value recovery by subsequent hydrometallurgical process, a low iron recovery is preferred. Therefore, the optimum activated carbon addition is 5% and the recoveries of cobalt and copper reach 91.82% and 92.96%, respectively.



**Fig. 1** Effect of reducing agent dosage on metal recovery

### 3.2 Effect of smelting temperature

Smelting temperature is an important factor in the reduction process. With the temperature increasing, the viscosity of molten slag decreases, which can improve the diffusion of species and the delamination of depleted slag and cobalt-bearing alloy. Figure 2 shows the results of smelting tests at the temperature range of 1 250–1 400 °C. The recoveries of cobalt and iron increased as



**Fig. 2** Effect of smelting temperature on metal recovery

temperature increased from 1 250 °C to 1 350 °C but did not increase at higher temperature. In addition, copper recovery had a slight increase as temperature increased. At smelting temperature of 1 400 °C, the recoveries of cobalt and copper reached 93.08% and 94.09% respectively.

### 3.3 Effect of smelting time

Smelting experiments with various smelting time were carried out and the results are shown in Fig. 3. Prolonging smelting time was in favor of metal recovery but would cause higher energy consumption. With smelting time of 2.5 h, the recoveries of cobalt and copper were 91.82% and 92.96%, respectively, and reached 94.57% and 93.13% respectively as the time was prolonged to 3.0 h. From an economic point of view, the smelting time of 2.5 h was appropriate.

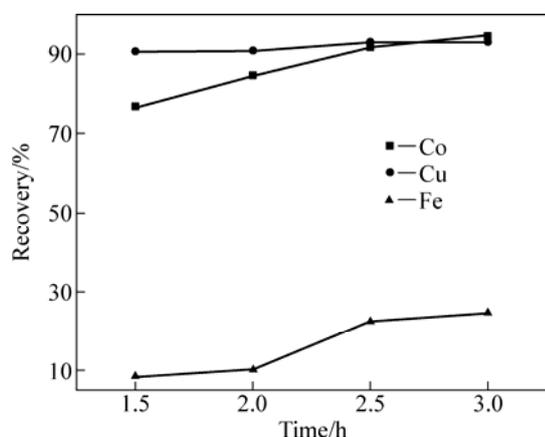


Fig. 3 Effect of smelting time on metal recovery

### 3.4 Effect of CaO addition

The addition of slag modifiers to molten slag affects the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio, the basicity, and the activity coefficients of iron oxide, silica, cobalt oxide, and other oxides [14]. In this work, the effects of slag modifier ( $\text{CaO}$  and  $\text{TiO}_2$ ) addition on metal recovery were investigated. Figure 4 shows the results of reduction

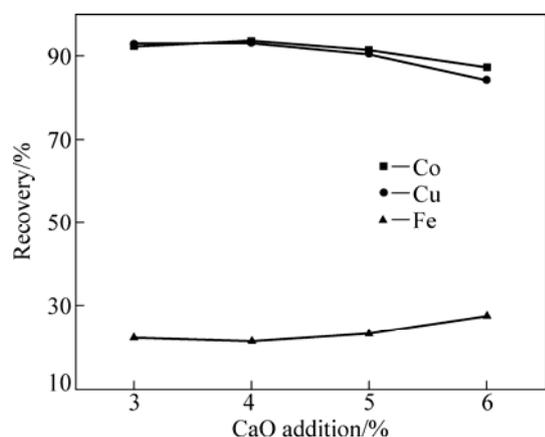


Fig. 4 Effect of CaO addition on metal recovery

smelting tests with various  $\text{CaO}$  additions. With calcium oxide addition, the metal recoveries were improved but the recoveries of cobalt and copper had a little decrease as the addition was more than 4%. The recoveries of cobalt and copper were 93.59% and 93.25% respectively with  $\text{CaO}$  addition of 4%.

Figure 5 shows the XRD pattern of depleted slag with  $\text{CaO}$  addition of 4%. It was found that the main phases of the depleted slag were fayalite, hercynite ( $\text{FeAl}_2\text{O}_4$ ), and calcium-iron oxide ( $\text{Ca}_2\text{Fe}_7\text{O}_{11}$ ). It was indicated that the added  $\text{CaO}$  and iron oxide can produce complex oxides of calcium and iron ( $\text{Ca}_2\text{Fe}_7\text{O}_{11}$ ). The  $\text{CaO}$  addition increased the activities of valuable metal oxides and led to higher metal recoveries. The diffraction peaks of alumina indicated that the added alumina was just dissolved partly in the molten slag.

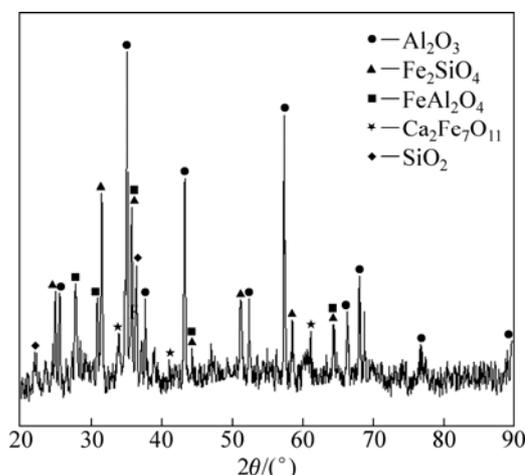


Fig. 5 XRD pattern of depleted slag with  $\text{CaO}$  addition of 4%

### 3.5 Effect of $\text{TiO}_2$ addition

To examine the effect of  $\text{TiO}_2$  addition on metal recovery, smelting experiments at  $\text{TiO}_2$  addition of 3%–6% were conducted, and the results are shown in Fig. 6. It was found that  $\text{TiO}_2$  addition was beneficial to the selective recovery of cobalt and copper. And 94.02%

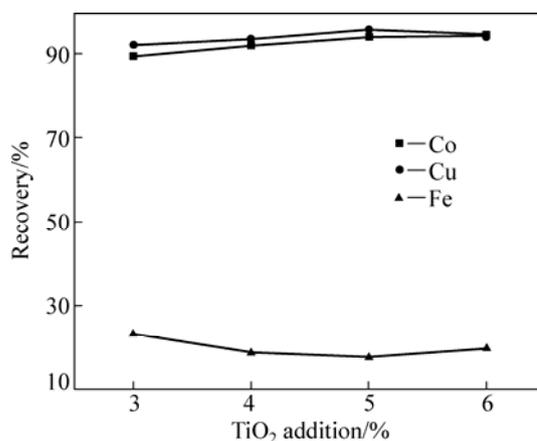


Fig. 6 Effect of  $\text{TiO}_2$  addition on metal recovery

Co, 95.76% Cu and less than 18% Fe in the converter slag were recovered with the optimum  $\text{TiO}_2$  addition of 5%. XRD analyses (Fig. 7) showed that the main phases in the corresponding depleted slag were fayalite ( $\text{Fe}_2\text{SiO}_4$ ), hercynite ( $\text{FeAl}_2\text{O}_4$ ) and ilmenite ( $\text{Fe}_5\text{TiO}_8$ ). These results showed that CaO and  $\text{TiO}_2$  can reduce the activity coefficient of FeO in the slag due to its strong affinity to FeO, and they produce the complex oxides as the slag was cooling.

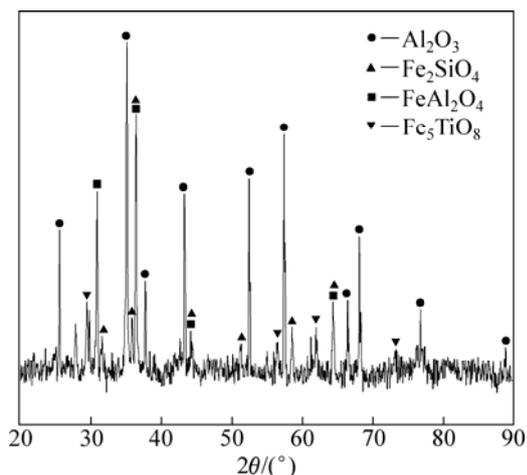


Fig. 7 XRD pattern of depleted slag with  $\text{TiO}_2$  addition of 5%

### 3.6 Characterization of reduction smelting products

With the  $\text{TiO}_2$  addition of 5%, the reduction smelting products, i.e. the depleted slag and the cobalt-bearing alloy, were characterized by XRD, SEM and EDS. Figure 8 and Table 2 show the SEM image of the depleted slag and the results of corresponding EDS point analysis. According to the analysis results of XRD and EDS, the major phase at point A was hercynite ( $\text{FeAl}_2\text{O}_4$ ); at point B, there was fayalite ( $\text{Fe}_2\text{SiO}_4$ ) with little hercynite; the main phase at point C was fayalite; and the particles specified by point D were ferrous sulfide (FeS) which was precipitated from the slag in the cooling process.

From the chemical analysis by ICP-AES, the

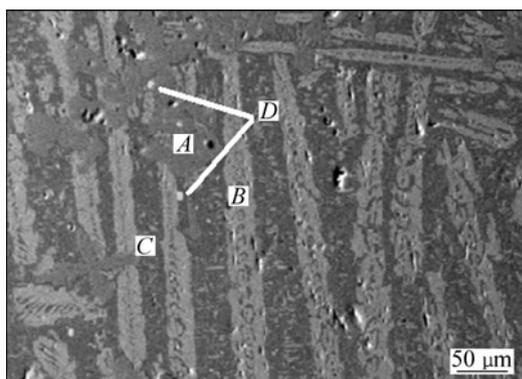


Fig. 8 SEM image of depleted slag

contents of cobalt, copper and iron in the cobalt-bearing alloy were 1.76%, 75.20% and 12.85%, respectively. XRD analysis showed that the main phases of cobalt-bearing alloy were metallic copper, iron alloy, and copper-iron sulfide (as shown in Fig. 9).

The SEM image of the cobalt-bearing alloy and the results of corresponding EDS point analysis are shown in Fig. 10 and Table 3. From the results of chemical analysis, XRD and EDS, the main phase point A was copper-iron sulfide ( $\text{Cu}_5\text{FeS}_4$ ); at point B, only metallic

Table 2 EDS point analysis results of depleted slag corresponding to Fig. 8

Location	w(O)/%	w(Fe)/%	w(Si)/%	w(Al)/%	w(S)/%
A	27.01	40.86	—	32.13	—
B	31.39	29.29	31.46	7.86	—
C	21.49	61.91	16.60	—	—
D	—	64.58	—	—	35.42

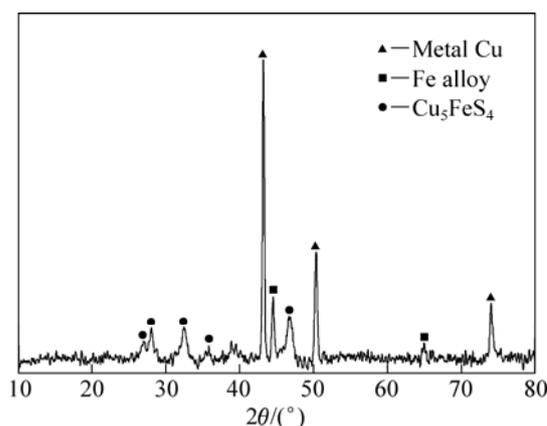


Fig. 9 XRD pattern of cobalt-bearing alloy

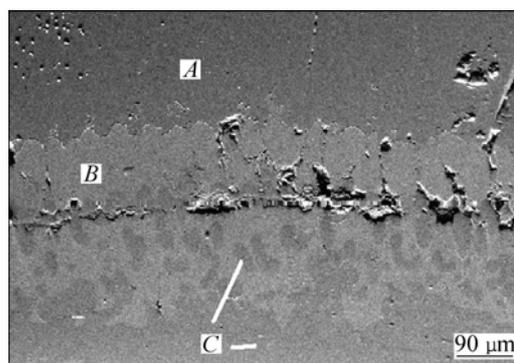


Fig. 10 SEM image of cobalt-bearing alloy

Table 3 EDS point analysis results of cobalt-bearing alloy sample corresponding to Fig. 10

Location	w(Cu)/%	w(Fe)/%	w(Co)/%	w(Ni)/%	w(S)/%
A	49.32	42.81	—	—	7.87
B	100.00	—	—	—	—
C	12.65	71.68	12.68	2.99	—

copper was found; the main phase at point C was iron alloy containing cobalt, copper and nickel. The metal values in the alloy could be separated and recovered using a leaching process in acid-oxygen or ammoniacal solutions [15–16].

#### 4 Conclusions

1) Under the optimum conditions: activated carbon dosage of 5%, TiO<sub>2</sub> addition of 5%, smelting temperature of 1 350 °C and smelting time of 2.5 h, 94.02% Co, 95.76% Cu and less than 18% Fe in the converter slag were recovered using the reduction smelting process.

2) The addition of CaO and TiO<sub>2</sub> can improve the selective recovery of cobalt from the converter slag, and the optimum additions were 4% and 5%, respectively.

3) The main phases of depleted slag were fayalite and hercynite. And the cobalt-bearing alloy mainly contained metallic copper, Fe-Co-Cu alloys and a small amount of sulfide, with the main chemical composition of 1.76% Co, 75.20% Cu and 12.85% Fe.

#### References

- [1] FENG Cheng-you, ZHANG De-quan, DANG Xing-yan. Cobalt resources of China and their exploitation and utilization [J]. Mineral Deposits, 2004, 23(1): 93–100. (in Chinese)
- [2] ZHAI Xiu-jing. Metallurgy on Heavy metals [M]. Beijing: Metallurgical Industry Press, 2011: 320–330. (in Chinese)
- [3] LUO Wei-ai. The cobalt resource and the marketplace [J]. Hunan Nonferrous Metals, 1998, 14(5): 17–20. (in Chinese)
- [4] JONES R T, DENTON G M, REYNOLDS Q G, PARKER A L, van TONDER G J J. Recovery of cobalt from slag in a DC arc furnace at Chambishi, Zambia [J]. The Journal of the South African Institute of Mining and Metallurgy, 2002, 102(1): 5–9.
- [5] JONES R T, DENEYS A C. Using a direct current arc furnace to recover cobalt from slags [J]. Journal of the Minerals, Metals and Materials Society, 1998, 50(10): 53–66.
- [6] DENG Tong, LING Yun-han. Process mineralogy of cobalt-bearing copper converter slag [J]. The Chinese Journal of Nonferrous Metal, 2001, 11(5): 881–885. (in Chinese)
- [7] WEI Ming-an. Study on mineral processing technology of copper converter cinder [J]. Mining & Metallurgy, 2004, 13(1): 38–41. (in Chinese)
- [8] SHEN H, FORSSBERG E. An overview of recovery of metals from slags [J]. Waste Management, 2003, 23(10): 933–949.
- [9] ARSLAN C, ARSLAN F. Recovery of copper, cobalt and zinc from copper smelter and converter slags [J]. Hydrometallurgy, 2002, 67(1–3): 1–7.
- [10] RUDNIK E, BURZYŃSKA L, GUMOWSKA W. Hydrometallurgical recovery of copper and cobalt from reduction-roasted copper converter slag [J]. Minerals Engineering, 2009, 22(1): 88–95.
- [11] LI Y, PAPANGELAKIS V G, PEREDERIY I. High pressure oxidative acid leaching of nickel smelter slag: Characterization of feed and residue [J]. Hydrometallurgy, 2009, 97(3–4): 185–193.
- [12] BAGHALHA M, PAPANGELAKIS V G, CURLOOK W. Factors affecting the leachability of Ni/Co/Cu slags at high temperature [J]. Hydrometallurgy, 2007, 85(1): 42–52.
- [13] HAYES P C, OKONGWU D A, TOGURI J M. Some observations of the reactions between molten oxides and solid carbon [J]. Canadian Metallurgical Quarterly, 1995, 34 (1): 27–36.
- [14] BANDA W, MORGAN N, EKSTEEN J J. The role of slag modifiers on the selective recovery of cobalt and copper from waste smelter slag [J]. Minerals Engineering, 2002, 15(11): 899–907.
- [15] ZHAO Zhong-wei, WANG Duo-dong, CHEN Ai-liang, HUO Guang-sheng, CHEN Xing-yu. Application and prospect of leaching processes of cobalt from Cu-Co alloy and slag [J]. Hydrometallurgy of China, 2008, 27(4): 195–199. (in Chinese)
- [16] BURZYŃSKA L, GUMOWSKA W, RUDNIK E. Influence of the composition of Cu-Co-Fe alloys on their dissolution in ammoniacal solutions [J]. Hydrometallurgy, 2004, 71(3–4): 447–455.

## 还原熔炼法从谦比希铜冶炼厂转炉渣中回收钴

翟秀静<sup>1</sup>, 李乃军<sup>2</sup>, 张旭<sup>1</sup>, 符岩<sup>1</sup>, 姜澜<sup>1</sup>

1. 东北大学 材料与冶金学院, 沈阳 110819;

2. 沈阳大学 理学院, 沈阳 110044

**摘要:** 研究从赞比亚谦比希铜冶炼厂转炉渣中回收钴的还原熔炼过程。实验考察还原剂用量、熔炼温度、保温时间及渣型改善剂 CaO 和 TiO<sub>2</sub> 的添加对还原熔炼金属回收率的影响。采用 X 射线衍射、扫描电子显微镜及能谱分析对所得贫化渣和含钴合金进行表征。结果表明, 在优化条件下, 转炉渣中钴、铜、铁的回收率分别为 94.02%, 95.76% 和小于 18%; 贫化渣的主要物相组成为铁橄榄石和铁尖晶石, 含钴合金中主要含有金属铜、含钴铜的铁合金和少量的硫化物。

**关键词:** 转炉渣; 回收钴; 还原熔炼; 渣型改善剂; 含钴合金

(Edited by YUAN Sai-qian)