

Distribution behavior of Copper and Tin between FeO-rich slag and iron solution^①

LI Chang-rong(李长荣)^{1,2}, HONG Xin(洪新)¹, ZHENG Shao-bo(郑少波)¹, JINANG Guo-chang(蒋国昌)¹

(1. School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China;

2. Department of Metallurgy, Guizhou University of Technology, Guiyang 550003, China)

Abstract: The distribution behavior of residual elements copper and tin between FeO-rich slag and iron solution was investigated under the condition of an induction furnace. The results indicate that a part of copper and tin is incidently oxidized when oxygen is blasted into bath to react with iron element. The distribution ratio of copper and tin between slag and metal is about 0.1. Phenomena of Cu and Sn elements segregation and accumulation in slag were observed by means of EPMA analysis. The distribution ratio of copper and tin between slag and metal may descend with increasing of CaO content in slag.

Key words: residual elements; distribution ratio; iron solution; FeO-rich slag

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1 INTRODUCTION

Copper has been widely used in various kinds of industrial fields due to its excellent electric property and heat conduction. But as alloy element, copper exists generally with the form of harmful element in steel products except in the atmosphere-resisting steel.

Copper and tin in molten steel are hard to be removed out in conventional refining process. So the reuse value of scrap steel containing copper or tin is greatly reduced^[1]. In Japan, for example, unrecyclable obsolete scrap has begun to be actualized since 2000, and 155 - 300 million tons of obsolete scrap will be heaped up throughout the land in 2015^[2]. Scrap steel, which is actually valuable material in industry, has been gradually regarded as rubbish. The typical scrap steel is discarded from vehicles and electric appliance. They must be recovered by its producer in many developed countries because they are not directly used as the raw materials of steelmaking.

In many developed countries, great attention has been paid to study the influence of residual elements on the properties of steel, which is becoming more and more serious^[3-7]. Many suggestions have been proposed and studied, such as mechanical separation, melting separation (molten Al or Pb), vaporous separation (Cl, HCl, NH₄Cl etc.), CaO-CaC₂ reaction separation, vacuum separation, sulfide flux (or matte) reaction, injecting metallurgical method and filtering method. Up to now, no economically feasible methods were industrialized yet. Furthermore these methods are difficult to further develop because the

efficiencies of removing are too low or the conditions are too strict. These studies were just aimed at the certain element or a few of elements. It cannot satisfy the requirement of clean steel to control residual elements in this situation. In Shanghai University^[8], a new technology has been proposed to separate residual elements from iron-base solution, that is, slagging-reduction process. The basic principle of this technology is selectively oxidized. Residual elements, like Cu, Sn, As, Sb and Bi, in the course of steelmaking, are not easy to be oxidized, Fe is oxidized into slag and other tramp elements are kept to stay and accumulate in the molten steel. Iron element would be successfully separated from residual elements. Pure FeO-rich slag was transferred into another container and reduced by means of hydrogen reduction and then further refined into clean steel. This technology is based on metallurgical principle of residual elements in steelmaking and is different from the approaches of all has been studied before. It is possible to exploit a new technology to remove many residual elements at the same time. The increasing tendency of residual elements in steel products will be largely reduced or disappear. Scrap recycle, finally, can be thoroughly achieved.

The distribution behaviors of elements between FeO-rich slag and iron solution involved in this technological route have rarely been reported. Under the condition of induction furnace melting, the distribution behavior of copper and tin elements between FeO-rich slag and iron solution are investigated.

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Correspondence: LI Chang-rong, Associate professor; Tel: + 86-21-56331176; E-mail: cr263@163.com

2 EXPERIMENTAL

2.1 Procedure

When the iron element is continuously oxidized into slag, copper and tin elements will be accumulated in the raffinate of steel if slagging process is used. In order to observe the distribution behavior of residual elements between FeO-rich slag and iron solution, the contents of residual elements in experiment is higher than in practical scrap. Experiments were conducted in an induction furnace of nominal capacity 10 kg and 2 500 Hz. After the charge was totally melted, Cu, Sn, As, Sb, and Bi were added into the molten bath in terms of its proportion to obtain the aimed composition. Sn and As elements were added in the state to prepare SnAs alloy in advance, the others were added in the state to get pure metal. After blowing oxygen to the molten bath for 5 min, the slag floating on the surface of the molten steel was moved with iron rod. The temperature of molten bath was measured with thermocouple and the sample was taken by silica tube. Seamless steel pipe of $d 12 \text{ mm} \times 2 \text{ mm}$ that lining quartz tube was used to blow oxygen. The purity of oxygen was 99.99% and blowing flow was 10 L/min. After continuously blowing oxygen for 5 min, sample Z_1 was taken by iron rod. At the same time, the bath temperature was measured. The temperature in the whole test was controlled within the range of 1 540–1 580 °C. After fetching the slag completely, 60 g lime was put into the molten bath. The same operation as mentioned above was repeated before sample Z_2 was taken. Another 120 g lime was put into the molten bath, the same operation was repeated and sample Z_3 was got.

2.2 Results

Table 1 and Table 2 show the chemical analyses results of samples.

Table 1 Composition of iron solution(%)

Element	Cu	Sn	As	Sb	Bi	Fe
Content	1.960	0.721	0.182	0.283	0.053	96.801

Table 2 Compositions of FeO-rich slags (%)

Sample No.	CaO	Cu	Sn	As	Sb	Bi
Z_1	1.80	0.22	0.15	< 0.01	0.01	0.03
Z_2	9.90	0.20	0.10	< 0.01	0.02	0.02
Z_3	19.6	0.18	0.10	< 0.01	0.01	< 0.01

The distribution ratio of the minor element X (X: Cu, Sn, As, Sb, and Bi) between the slag and molten metal was defined by the following equation:

$$L_X = (\text{mass \% X in slag}) /$$

(mass % X in molten metal)

They were determined from the results of chemical analysis of slag and iron solution, as shown in Table 3.

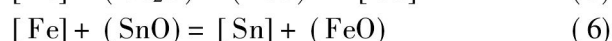
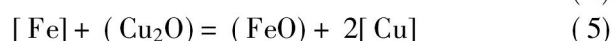
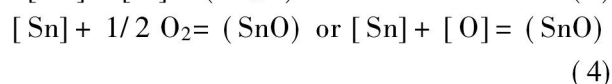
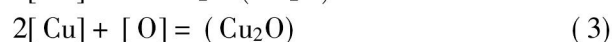
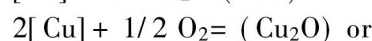
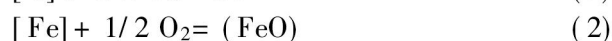
Table 3 Distribution ratios of elements in FeO-rich slag and molten metal

Number	L_{Cu}	L_{Sn}	L_{Sb}	L_{Bi}
1	0.112 2	0.208 0	0.035 3	0.569 2
2	0.102 0	0.138 7	0.070 5	0.379 5
3	0.091 8	0.138 7	0.035 3	

3 ANALYSES AND DISCUSSION

The practice of steelmaking showed that copper and tin remained almost entirely in molten steel whenever in LD furnace or EAF furnace. But the experimental results shown in Table 2 indicated that FeO-rich slag contains a certain amount of copper and tin. This meant that a part of copper and tin was incidentally oxidized as oxygen was blasted into bath to react with iron element.

As oxygen was blown into the molten bath, oxygen contacted directly with steel to create so called burning point. The pressure of blown oxygen was higher than 0.101 3 MPa and it was largely higher than partial pressure of balancing with pure FeO phase. The molten steel near the nozzle was over-oxidation. So iron, copper and tin can be oxidized in this burning point zone, then become high oxidation potential. Following reactions would occur:



In terms of the principle of selective oxidation, the composition of the slag would be controlled by reaction (5) and reaction (6). When reaction products formed in the high oxygen potential zone were floating, they would further react with molten steel. Copper oxide (tin oxide) would be reduced back into molten steel by iron element because of preferential potential. The reduction was determined by contacting with area of slag/iron, floating time and dynamic conditions of reaction in the slag. On the surface of bath, reaction (5) and reaction(6) would continue in

the interface of slag and molten steel.

It was not convenient to explore the influence of activity, activity coefficient and activity interaction coefficient on these reactions, because basic thermodynamics data of their oxides in the FeO-rich slag were lack. Discussions were carried out here in the condition of standard state. Within the range of steel-making temperature, the standard free energies of reaction (5) and reaction (6) are respectively as follows^[9, 10]:

$$\Delta G_5^\ominus / (\text{J} \cdot \text{mol}^{-1}) = -67\,425 - 68.73T \quad (7)$$

$$\Delta G_6^\ominus / (\text{J} \cdot \text{mol}^{-1}) = -246\,665 + 59.46T \quad (8)$$

Table 4 K_p of reaction (5) and reaction (6) under condition of standard state

Temperature/ K	K_p of reaction (5)	K_p of reaction (6)
1 673	4.94×10^5	3.93×10^4
1 773	3.77×10^5	1.45×10^3
1 873	2.96×10^5	5.94×10^3

The distribution ratios of Cu, Sn in the FeO-rich slag and metal would be on the level from 10^{-4} to 10^{-6} orders of magnitude if the reaction reached the equilibrium under the temperature of steelmaking.

But the actual distribution ratios appeared to be in 10^{-1} orders of magnitude. There were many possible reasons, some of which are as follows: 1) the reactions between slag and molten metal did not carry out completely because the floating distance of copper (tin) oxide formed in the burning point was very short and the temperature of slag in induction furnace was relatively lower, so the reduction of copper and tin oxide back to molten steel was restricted; 2) the separation of FeO-rich slag and molten steel was not perfect. Metallic bead was observed in the FeO-rich slag with microscope, as shown in Fig. 1(a). So the content of copper (tin) in slag appears higher than its actual content for the presence of metallic bead.

Elements are not well-distributed in the slag, where copper and tin are segregated and accumulated easily, as shown in Fig. 1.

Fig. 2 shows that the contents of Cu and Sn in the FeO-rich slag decrease with the increasing of CaO content of the slag. The reason seemed that the density and viscosity of CaO-FeO-Fe₂O₃ slag decreased with the increasing of CaO content, which caused the enhancement of Cu₂O activity in slag.

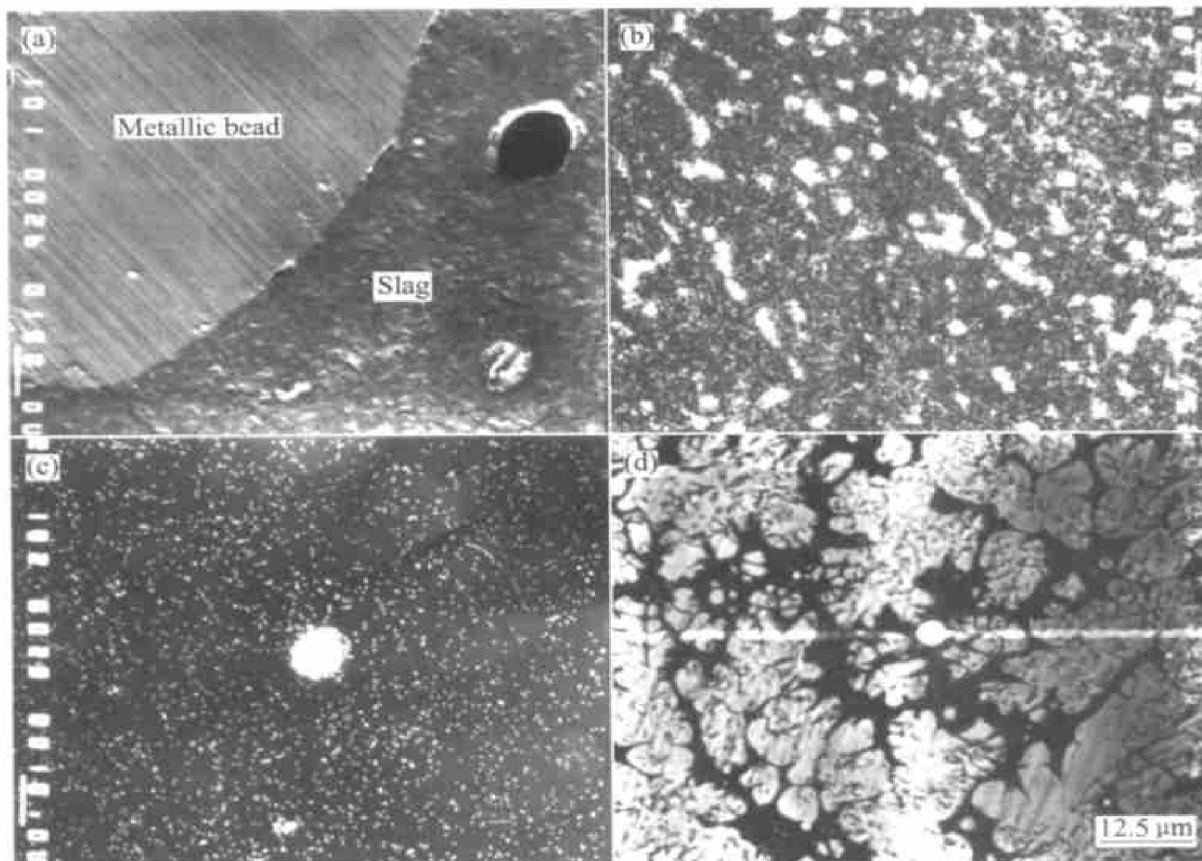
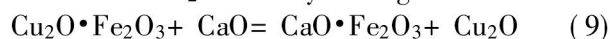


Fig. 1 EPMA photos of sample of FeO-rich slag

- (a) —Metallic bead + slag matrices; (b) —Cu element surface scan of metallic bead;
(c) —Cu element surface scan of segregation spot; (d) —Backscattered electron image of segregation spot

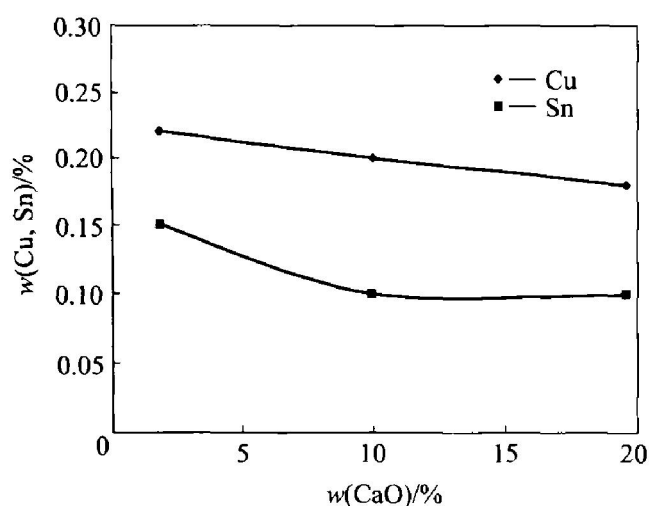


Fig. 2 Plots of Cu and Sn contents in FeO-CaO slag vs CaO content

4 CONCLUSIONS

1) Under the condition of induction furnace, parts of copper and tin in the iron solution were oxidized and remained in the FeO-rich slag when oxygen was blasted into bath to react with iron element. The distribution ratios of copper and tin in slag and molten metal were at 10^{-1} orders of magnitude.

2) The spread of copper and tin in the FeO-rich slag was not homogeneous. They were segregated and accumulated easily.

3) The distribution ratios of copper and tin in FeO-rich slag and iron solution may descend with the increasing of CaO content.

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