

The effect of slag composition on recycling of “OFHC” through the “ESCM” process

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Abstract

This paper reports the results of an investigation into the role of the slag composition in recycling Oxygen Free High Conductivity (OFHC) copper through a modified Electroslag Remelting Process (ESR) melting technique Electroslag Crucible Melting (ESCM). Materials used for the slag were alumina (Al_2O_3), cryolite (Na_3AlF_6), sodium fluoride (NaF), and fluorine (CaF_2) at different ratios. The results showed that in addition to purity of the slag and graphite used in the electrode and crucible, the percentage of alumina component in the slag composition was the main factor in the attainment of the purity. The best consequence was achieved when the content of alumina was in the range of 23–27%. Furthermore, in ternary compound systems with constant one component, the influence of the weight ratio of the other components was investigated, from a product purity viewpoint. Finally, in the optimized condition, copper with 99.988% purity was achieved, yielding an electrical conductivity of 100.1% IACS.

Keywords: OFHC copper, recycling processes, electro slag remelting, ESCM process

1 Introduction

Recent developments in electronic industries and energy fields have pushed the property requirements for oxygen free copper to the extreme. When recycling the OFHC copper, the main problem is to reduce oxygen contamination because it not only impairs the conductivity but also the mechanical properties of the material, possibly leading to high scrap losses [1–4]. Oxygen free copper is used in applications where the parts are going to be annealed in a hydrogen containing



atmosphere. The presence of oxygen in either its elemental state or as copper oxide, leads to the formation of water vapor, which means the brittleness of the material [5].

Two major techniques are used to reduce the oxygen content in copper. The first one involves casting in an inert atmosphere and fluxing the molten copper with an inert gas to prevent the oxygen involvement. The other approach which is a deoxidizing method consists of adding a reductive material to the melt to form selective oxide (instead of copper oxide). The reactive material must be chosen so that its oxide is stable and could not be reduced by hydrogen during annealing. Unfortunately, most of the reductive materials have highly deleterious effects on electrical conductivity if remain in the solid solution of copper. Because of the nature of these oxidants, it is difficult to accurately control the amount of reactive materials. So it's confronted with diminishing of conductivity. In conventional methods of producing OFHC copper, clean cathodes are melted in contact with carbon in an electrical furnace under a protected atmosphere or in vacuum. The protected atmosphere is a mixture of carbon monoxide and nitrogen gases [3, 6–11]. After charging clean cathodes in an induction melting furnace, providing the necessary vacuum or protected environment, the oxide removal agent is added to the completed melt without any intermission.

In this technique, the amount of this agent must be calculated as precisely as possible. It must first react with all the oxygen available in the composition and bring it into the slag and secondly, no residue of it remains as impurity in the melt [8].

Researches on the effect of vacuum on the other elements, also shows that Sb, As, and Bi reduces up to 90% and large fraction of S is removed as sulfur dioxides [8, 12]. Nesslage et al. produced OFHC copper with an electrical conductivity of 101% IACS just by adding approximately 30 ppm manganese [13]. Yurko and Peckens used a method to produce oxygen free copper from copper powders. The powders produced by hydrogen reduction from an aqueous ammoniac solution was formed into briquettes by cold compression and then heated in AC confined area at temperature of 1750°F for 1 h under reducing atmosphere of oxygen [14].

It is evident that, OFHC copper is nearly a precious material; therefore, recycling of the shavings produced in manufacturing processes is an interesting object. Because of a high surface to volume ratio of this kind of scraps, melting them in vacuum furnace is not possible and if so, it is not an economic solution. Consequently, they can not be recycled by ordinary techniques.

ESR or electroslag remelting is a process used for remelting and refining of special alloys which are used for critical applications in aircraft, thermal and nuclear power plants, defense hardware, etc. The principal set up of an electroslag remelting plant is shown in Figure 1. An electroslag remelting process (ESR) starts when the lower tip of a consumable electrode is immersed into a pool of molten slag. The pre-melted slag possessing electrical conductivity is located on the water-cooled mold base connected to a power supply. The electric current (commonly AC) passing through the slag keeps it at high temperature, which is about 360°F (200°C) higher than the melting point of the

metallic electrode. The electrode tip is heated by the hot slag and starts to melt forming droplets of liquid metal, which disconnect from the electrode and sink through the slag layer.

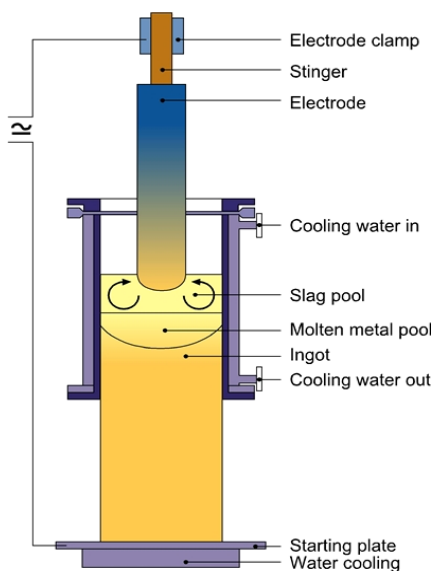


Figure 1: Schematic illustration of Electroslag Remelting (ESR) operation.

The ESCM (Electro Slag Crucible Melting) method was first invented by Borodin and co-workers in 1985 with inspiration from the ESR process [6, 16]. The main target was to design a system for remelting the scraps. The results of analysis showed the fact that applying this method results in decreasing the amount of Sn, Pb and S; although the Fe and Zn content may increase due to the contamination of the charged scraps [2, 16]. The produced ingots are free of impurities, voids, shrinkage and gas porosities. In addition, the problem of hydrogen embrittlement due to annealing (at high temperatures about 400°C) is reduced substantially [6, 16].

In ESCM method, the consumable electrode in ESR (made of the charge material) is replaced by a non-consumable graphite bar and a water-cooled copper mold is superseded by a graphite one. Schematic illustration of ESCM process is shown in Figure (2). This collection is set on a water-cooled base plate. Scrap is fed in small pieces after complete melting of the slag. These shavings are melted through passing the slag and form melt pool behind it. Finally, the molten metal covered by slag is cast into a permanent graphite mould [2].

Use of graphitic crucible and electrode makes it possible to reduce the oxygen content of the melt remarkably. In addition, the high deoxidizing capacity of graphite ceases the addition of deoxidizing agent, e.g. Lithium, copper phosphor, etc. which usually decrease the electrical conductivity of copper. Besides, for the reason of the very low solubility of carbon in copper (about 0.0025% in

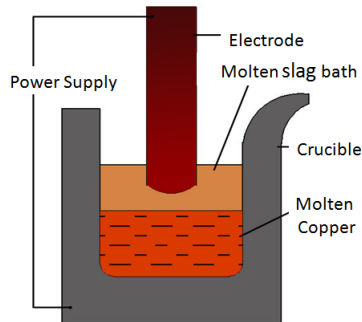


Figure 2: Schematic illustration of Electroslag Crucible Melting (ESCM) process.

25°C temperature), it can be used without the problem of carbon dissolution [6]. This method has several advantages such as simplicity of the equipment, the lower cost and possibility of recycling scraps of OFHC copper besides nearly uniform mechanical properties such as toughness in all directions [2, 6]. The results of Prasad et al. experiments have shown that while using cryolite, the content of oxygen decreases considerably. However, the harmful impurities such as Si, Fe, and S attract into the melt to a substantial extent so the melt doesn't have sufficient purity in this respect [17]. Therefore, in this research, it would be attempted to reduce the amount of impurity elements especially Fe and Si via altering slag composition. For this purpose, cryolite was replaced by mixtures of sodium fluoride and alumina, two effective components in preventing oxygen pick-up, with different ratios. An adequate fluidity of the slag as well as its ability of providing the desired temperature was considered in determining the slag composition.

1.1 Experimental procedure

An AC ESCM system with a capacity of 150 KVA, comprising a graphite electrode of 50 mm diameter and a graphite crucible with internal diameter of 105 mm was used to do the tests. Copper scrap was in the form of pieces with 5 mm diameters and the lengths of 2-3 cm. These particles were dipped in a 10% HCl solution for 20 min to remove the surface oxides and then dried in the air. The slag combination consisted of alumina, fluorine, cryolite and sodium fluoride in various ratios. The compositions are listed in table 1.

It can be seen from the table 1 that, various NaF to Al_2O_3 and CaF_2 to Al_2O_3 ratios were investigated in constant CaF_2 and NaF respectively. The effect of slag recycling was also studied by reusing a certain slag in the next melting. 4 kg of copper scrap and 2 kg of slag were used for each experiment. The slag materials were preheated in a resistance furnace up to 600°C for 2.5 h. The process started with an arc between the graphite crucible and the electrode.

Table 1: Chemical composition of the slag used in various testing conditions.

Sample No.	CaF ₂ (%)	Al ₂ O ₃ (%)	Na ₃ AlF ₆ (%)	NaF (%)
1	10.5	4.5	85	-
2	30	40	-	30
3	30	35	-	35
4	30	30	-	40
5	40	15	15	30
6	10.5	4.5	85	-
7	-	12.5	in addition to the recycled slag of test No 6	
8	30	40	-	30
9	30	35	-	35
10	30	30	-	40
11	23	17	-	60
12	35	20	-	45
13	40	15	-	45
14	33	27	-	40
15	35	15	25	25
16	35	25	-	40
17	37	23	-	40

Once the arc was stabilized, the slag was charged into the crucible. The heat required for the process was generated due to Ohmic resistance of the slag pool by the passage of electric current through it. When the slag was completely melted, the copper pieces were gradually added to the molten slag and melted. The molten slag covered the liquid copper and protected it from atmospheric contamination during the process. The slag composition was selected properly, so, passing the charge through, the oxide particles could be entrapped and the clean liquid metal was collected at the bottom of the crucible. During crucible melting, the melt and slag temperatures were measured using a thermometer. The temperature of the melt was maintained constant at about 1500°C by changing the voltage of the power supply and/or changing the distance between the electrode and the crucible bottom. After the copper was completely melted, the power was kept constant at about 28 KV for 7 min in order to complete the chemical reactions. Chemical analysis of the ingots was determined using an analyzer, and the oxygen content was also specified by LECO (ASTM B 170). The electrical conductivity was measured for some of the specimens by Ely chemical plant (DIN 48200, 48201). Tensile tests were performed by a MTS machine according to ASTM E 8M standard (D = 2.5 mm) and microstructural observations were carried out after preparation of the samples, polishing, and etching by a potassium dichromate solution for 10 sec.

2 Results

Chemical analysis of the primary OFHC scrap is presented in Table 2.

Table 3 shows the effect of the slag composition on the final analysis. The amount of oxygen content and electrical conductivity for some of the samples



was recorded. In all the samples, higher contents of impurity elements such as Si, Fe and P were observed as compared with the former analysis due to pick up from slag.

Table 2: Chemical analysis of primary OFHC copper (ppm).

Fe	S	Te	As	Se	Sb	Cd	Cr	Pb	Si	Bi	Ag	Zn	Ni	Co	Mn	Sn
<1	6.5	<1.2	<1	0.5	<1	3.5	<1	3.5	<1	<0.6	8.6	<3	1	<2	0.34	<1

Table 3: Amounts of different elements of impurity (ppm), the purity of Cu and the electrical conductivity for various testing conditions.

Sample No.	Fe	Si	S	P	Al	O	Other	Cu purity	Conductivity
1	2900	2500	260	750	700	15	Mn=40	99.200	
2	500	2500	110	1300	1700	-	Mg=700	99.150	
3	1500	2800	30	50	1000	-	Mn=40	99.390	
4	200	1700	20	790	100	-	Mg=800	99.550	
5	360	730	20	<1	360	-	Pb=230	99.680	
6	230	320	30	<1	450	-	Pb=60 Zn=240	99.850	
7	40	230	10	<1	<1	-	Pb=60 Sn=40	99.920	
8	330	410	70	<1	700	-	Pb=50		
9	290	420	30	<1	450	-	Sn=20 Zn=40		
10	200	300	20	<1	100	-	Pb=60 Mn=20		
11	200	570	10	<1	40	-	Pb=60 Sn=20 Zn=80	99.90	89.6
12	140	150	50	<1	90	-	Mn=20	99.950	91.7
13	40	80	20	<1	400	47	Pb=40	99.940	95.9
14	30	-	30	<1	130	42	Mn=10 Pb=30	99.980	100
15	11	101	29.4	<1	10	33	-	99.974	96.1
16	10	78	27.3	<1	-	12	-	99.985	100
17	32.6	<1	35.9	<1	-	18	-	99.988	100.1

As it is shown in Figure 3, it can be inferred from the comparison of samples 8 to 11 that the addition of NaF to Al₂O₃ weight ratio at constant CaF₂ percent results in a higher purity of the produced copper (Figure 3). Also, comparing samples 15 to 17 shows that increase of CaF₂ to Al₂O₃ weight ratio at constant NaF percent leads to production of higher purity ingot (Figure 4). It was reported that recycling of slag containing alumina resulted in diminishing pick up of oxygen [17]. Comparison of samples 6 and 7 shows that recycling of slag results in lower pick up of Fe, Si, S and Al into the copper ingots and therefore, the purity of the ingot is increased. The reason is attributed to the impurities that

transferred from the slag into the first melt and then the recycled slag is of lower contamination. Samples 8, 9 and 10 have the same production parameters as samples 2, 3 and 4 respectively, but the higher purity of graphite used for crucible and electrode; that leads to the higher purity of the final product.

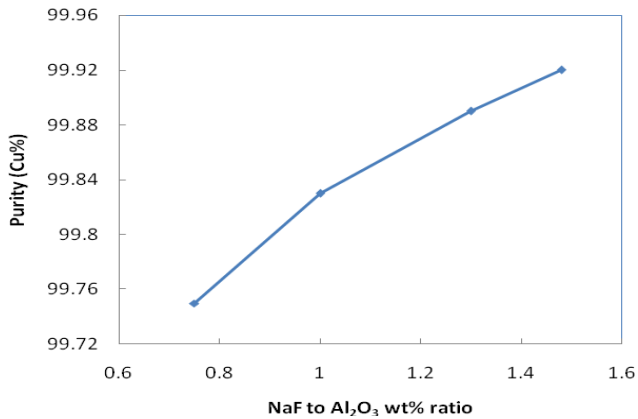


Figure 3: Influence of increase in the NaF to Al_2O_3 weight ratio in the slag on purity of the copper.

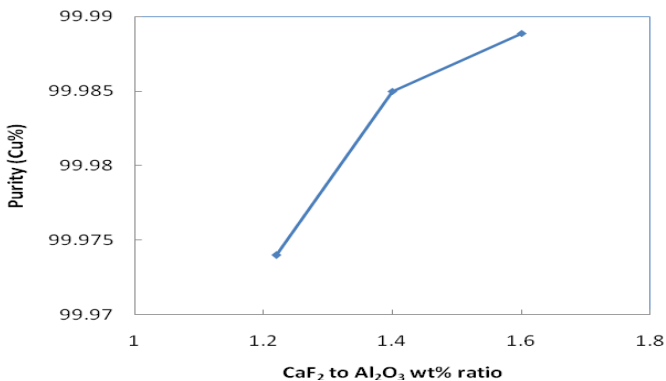


Figure 4: Influence of increasing the CaF_2 to Al_2O_3 weight ratio in the slag on purity of the copper.

3 Discussion

The aim of this research is the assessment of the capability of ESCM process in recycling of precious OFHC scrap with acceptable product purity. Introduction of oxygen into the melt leads to take place the oxide compounds. Since these kinds of inclusions have fragile natures, the presence of such particles in the microstructure, particularly on the grain boundaries results in lessening the

workability of the ingot. In addition, from the electrical conductivity point of view, it's necessary to avoid entering of any impurity in the melt. Microstructures of the sample no. 17, one having the highest purity in this work, are shown in figure 5. As can be seen, the grains and grain boundaries are thoroughly free of either oxides particles or other kinds of inclusions.

Besides, due to settlement of hot graphite crucible over the water-cooled copper base plate, directional heat flow exists during the solidification process. Furthermore, a thin slag skin is formed around the casting inside the mold and hot slag solidifies above the ingot which protects it from atmospheric contamination. Based on this reason, sound ingots without any shrinkage cavity or the other defects could be obtained in "ESCM" process.

It was also observed that, one of the most principal factors in ESCM process affecting on the product purity is the purity of the materials with which the molten copper is in contact (electrodes, crucible and slag components). The major impurities to be considered are iron, silicon, sulfur and oxygen. Entrance of iron to the melt was attributed to the reduction of iron oxide by graphite electrode or crucible by Prasad et al. [17]. In this research, it was also observed that iron content decreases in ingots using recycled slag of the other melts (Table 3, melt No. 7).

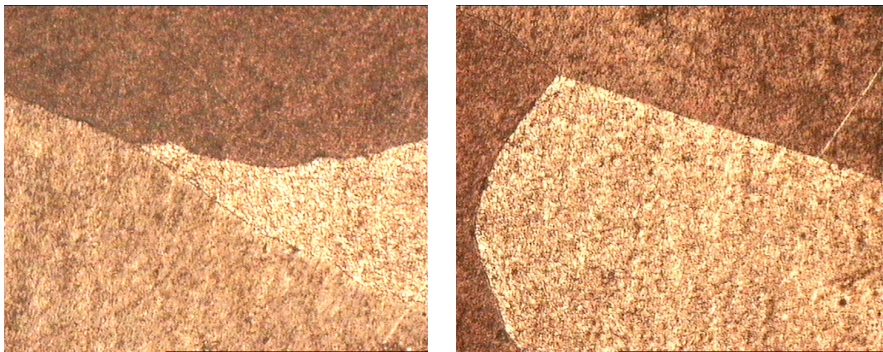


Figure 5: Microstructure of sample No. 17.

Also, increasing silicon and sulfur content in the melt can be attributed to reduction of their oxides in slag composition. These compositions are introduced via fluorine and sodium fluoride [17].

Previous researches have mentioned oxygen content reduction using cryolite as a slag component, but the results of this study determined that it's accompanied by silicon, iron and sulfur increase in the melt. As Table 3 represents, the best slag composition (40% sodium fluoride, 23% alumina, 37% fluorine) results in a product with a purity of 99.988% and electrical conductivity of 100.1% IACS.

4 Conclusions

1. ESCM is a successful and practical process for recycling of OFHC copper scrap.
2. Considering the results shown in figs 2 and 3, this shows that in these experiments the best results were achieved when the content of alumina in the slag is in the range of about 23-27%.
3. Using graphite with high purity in electrode and crucible has a very important role in obtaining higher quality product.
4. In ternary compound systems with constant NaF percent, when the weight ratio of CaF_2 to Al_2O_3 increases, the product purity increases too.
5. At ternary compound systems with constant CaF_2 percent, with increasing the weight ratio of NaF to Al_2O_3 , the product purity increases too.
6. The best combination of the slag which leads to the best result in this research is 40% sodium fluoride, 23% alumina, 37% fluorine.
7. Application of ESCM process in recycling of OFHC copper scraps, results in a copper with 15-33 ppm oxygen, purity of 99.988%, and electrical conductivity in excess of 100.1% IACS.

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