RECOVERY OF COPPER FROM BRONZE SCRAP

Morsi M. B., Rabah M. A. Central Metallurgical R&D Institute (CMRDI) P.O.Box 87 Helwan 11421 Cairo, Egypt. Fax 0202 5010 639 E-mail: rucmrdi @ rusys. eg.net

ZÍSKANIE MEDI Z BRONZOVÉHO ŠROTU

Morsi M. B., Rabah M. A. Central Metallurgical R&D Institute (CMRDI) P.O.Box 87 Helwan 11421 Cairo, Egypt. Fax 0202 5010 639 E-mail: rucmrdi @ rusys. eg.net

Abstrakt

Príspevok je venovaný získavaniu medi z bronzového šrotu obsahujúceho 9 hm. % Pb a 8-9 hm.% Sn tavením šrotu s prídavkom a bez prídavku aditív a periodického odstránenia trosky. Troska obsahujúca PbS, Cu, SnO₂ bola podrobená kyslému a alkalickému lúhovaniu za účelom získania čiernej medi pre zlepšenie celkovej výťažnosti medi. Experimentálne práce boli realizované za účelom určenia vplyvu parametrov ako sú čas, stechiometrický pomer sulfidického činidla, fúkanie kyslíka a teplota. Rafinácia medi bola vysvetlená na základe matematického modelu, za predpokladu, že separácia kovových inklúzií oxidáciou vyhovuje vzťahu Kuprowského, ktorý uvádza Wladyslaw.

Získané výsledky ukázali, že sulfid medi reagoval s olovom a vytvoril tepelne stabilný sulfid olova (galenit). Následný prívod kyslíka mal dvojitý účinok; aktivoval tvorbu sulfidu olova a súčasne došlo k oxidácii cínu na kyselinu cíničitú. Rýchlosť tvorby týchto zlúčenín sa zvyšuje s rastúcou teplotou reakcie až do 1250°C. Bolo zistené, že stupeň odstránenia olova a cínu z roztaveného bronzového šrotu je 92,5% pri použití 1.5 stechiometrického pomeru reagentov. Použitie alkalických tavív urýchľuje procesy sulfidácie a oxidácie znížením viskozity taveniny. Olovo bolo získané z trosky lúhovaním horúcim octanom amónnym, pričom oxid cíničitý zostal ako zvyšok. Okyslenie roztoku octanu spôsobilo vznik soli olova. Celkový stupeň získania medi a lúhovaním získaných solí dosiahol 86%, resp. 97,5%.

Abstract

This paper is concerned with the recovery of copper from bronze scrap containing 9-10 % by weight lead and 8-9wt % tin by melting of scrap with or without additives and periodic removal of slag. The slag including PbS, Cu, SnO₂ was leached with acid or alkali to recover black copper for improving the overall yield of copper. Experimental study was carried out to investigate the effect of parameters such as time, stoichiometric ratio of sulfide reagent, blowing with oxygen gas and temperature. Refining of copper was explained in the light of a mathematical model assuming that separation of metal inclusions by oxidation complied with the Kuprowski's formalism given by Wladyslaw.

Results obtained revealed that copper sulfide reagent reacted with lead to form thermally stable lead sulfide (galena). Subsequent lancing with oxygen gas caused dual effects; it activated formation of lead sulfide and simultaneously oxidized tin to stannic acid. The rate of formation of these compounds increases with increasing the reaction temperature up to 1250°C.

The extent of removal of lead and tin from the molten bronze scrap was found to be 92.5 % using 1.5 stoichiometric ratio of the reagent. The use of alkali flux promoted a rapid sulfidization and oxidation reactions by decreasing the molten viscosity of the metals concerned. Hot ammonium acetate leached lead from the slag leaving tin oxide as tailings. Acidification of the acetate solution produced the respective lead salt. The overall extent of recovery of copper and the leached salts attained 86% and 97.5%, respectively.

Key words: copper recovery, bronze scrap, slag, acid leaching

1. Introduction

Recovery of copper from secondary resources such as new scrap generated during the manufacturing process or old scrap-generated from the discard or demolition of copper producing units has been reported by Betterton et al (1995). Baranowski et al. (1993) studied the existence of different forms of copper in copper matte and slag taken from the copperworks in Glogow. Ludovicus et al. (1972) reported methods of recovering copper from copper scrap materials. The author melted the scrap at 1180°C and reduced it at 1300°C to form black copper. Blowing with oxygen gas oxidized the metallic impurities in the black copper and produced anode grade copper. Abdul Basir and Rabah (2001) showed that copper recovery from scrap was favoured with the use of some additives altogether with the chemical reagents. Yadavalli and Saha (1994) recovered pure electrolytic copper (99.98%) from leaded brass scrap containing 60.02 % copper, 39.3 % zinc and 0.53% lead. First, zinc was removed by distillation under vacuum at 1000°C, and then copper was recovered by electro-deposition from an acidified copper sulphate solution. Nelmes (1984) reported a process for recovering copper from copperbearing materials which comprised: (a) melting, (b) reduction of any combined metal to the elemental metallic state, (c) adding silica to form a refining bath and (d) blowing with oxygen. Allain and Gaballah (1994) and Gaballah et al (1995) described a new approach for the characterization and extraction of strategic metals such as Nb and Ta from an industrial slag. The method applied was a combined hydro- and pyrometallurgical process. The successive alkaline and acid leaching of such slag based on the "pseudo-structure" of these amorphous materials permitted selective dissolution of the economic metals, lower consumption of chemical reagents especially HF, less toxic residues and high % recovery $\geq 85\%$.

Bukhard et al. (1994) used thermal plasma as a heat source for recovering copper and nickel metals pyrometallurgically. The authors reviewed the recent developments and some future aspects of plasma metal recovery from scrap and wastes. Benerji et al (1994) showed that the structure of investment cast superalloys could be controlled by optimizing the process variables such as melt superheating temperature; time of homogenization and casting parameters such as mold preheat and pouring temperature. Gorushkina (1993) and Maker (1985) investigated variation of copper/gas content during melting and the effects of impurities during recycling of copper alloys. Boron-lithium fluxes were shown to have the most effective de-oxidizing and protective action. It was recommended to use a fluxing agent to reduce losses of copper went to slag. The charge when molten percolated as drops through a layer of flux and in the process oxygen content decreased.

The aim of this work was to remove lead and tin from bronze scrap and to recover copper by melting the scrap and removal of lead and tin rich slag applying pyrometallurgical treatment. Alkali/acid leaching conditions to recover copper, lead and tin from the slag were investigated. Parameters affecting the extent of copper recovery and the efficiency of the suggested method were studied such as temperature, stirring conditions, oxygen lancing, use of carbon and alkali fluxing materials.

2. Experimental

El-Maady Co. for Engineering Industries, Cairo, Egypt supplied the scrap material was used in this study. It was composed of bronze turnings, chips and pieces having various size (1-5 mm). A typical test sample weighing 100 kg and containing foreign contaminants such as wood pieces or cloth fine rags were visually inspected,. High-field magnetic treatment separated iron impurity. The chemicals used in this work were of technical BDH grade. Hydrochloric acid, hydrogen peroxide solution (30% volume) and ammonium hydroxide were used for leaching experiments. Doubly-distilled water was used for chemical analysis. Tap water from town network was used for washing. Commercial grades of alkali carbonate and borate were used for leaching, fluxing and de-oxidizing purposes respectively. Spent active carbon (from beverage industries) was used for reduction.

2.1 Treatment methods

The scrap material was classified, degreased with a detergent solution, rinsed with water and then left for natural drying. A sample weighing 5 kg was placed in 2 L Salamander (made of silicon carbide) crucible for melting in a computerized silicon carbide-heated muffle furnace at1600°C. In some experiments, fluxing or de-oxidizing chemicals having low melting points were used. These experiments were conducted under stirring conditions using 200 rpm. The slag so formed was frequently skimmed to prevent its joining to the molten copper. It was further leached using acid or alkali leachants to recover back the metals went to the slag phase. At the end of each experiment, molten copper was poured.

2.2 Hydrometallurgical acid/alkali leaching of the slag

Leaching experiments of slag was performed in 4 L round bottom glass reactor with four openings serving for the thermometer, a stirrer, a condenser assembly, and pH meter probe. Heating was performed with 2 kW Mantel heater connected to a digital thermostat. Copper was leached with ammonium hydroxide whereas tin and lead were leached with hot HCl or ammonium hydroxide. The required leachant was placed in the reactor and the leaching conditions were equilibrated. The slag weighing 250 g was then introduced. In each experiment, hydrogen peroxide was added in variable concentration to the leachant. At the end of the experiment, the leaching products were cooled to room temperature and filtered. Lead chloride was converted into carbonate with sodium carbonate solution.

2.3 Analytical methods:

Particle size measurement was carried out using SediGraph 5100 particle analyzer, Micromeritics, USA. Analysis of the scrap, intermediate and end products was carried out by a chemical method and with the help of an emission spectrophotometer type 3460-880 ARL, Seuces. Lead, was determined as chromate while tin and copper were determined titrimetrically with ~ 0.05 M iodine solution. A computerized Philips X-ray diffraction equipment model PW/1710 with Ni-filter, Cu radiation (λ = 1.5405 Å) at 40 kV, 30 mA, and scanning speed 2° in 2 θ min⁻¹ was used. The diffraction charts and relative intensities obtained were compared with JCPDS files.

3. Results and discussion

3.1 Chemical composition and particle size analyses of scrap

The scrap under investigation contains valuable metals such as copper, tin and lead. Chemical analysis shows that the input bronze scrap contains 9.95 % lead, 8.62 % tin and 81.43% copper (by weight). Particle size analysis using sieve analyzer type 246/M RK42 VEB Elektro Frankenhausen MLW revealed that 8% by weight has <1 mm in diameter, 80 % has 1-4 mm and 12% > 4 mm as shown in Fig.1.



Fig.2 Effect of temperature on tin and lead kontent in copper after melting for 15 and 30 minutes.

3.2 Melting of scrap

3.2.1 Melting without additives

Melting of the scrap in air produced copper alloy of low quality and the yield was rather poor. Formation of high amount of slag seems reasonable on the assumption that the scrap turnings oxidized before melting because of its high surface area. Figure 2 shows lead and tin contents in the obtained copper alloy after melting the scrap at temperatures up to 1300°C for periods up to 30 minutes. It is seen that tin content decreased gradually with increasing temperature and time of melting attaining its minimum value at 1300°C and after 30 minutes. On the other hand, lead content displayed an opposite trend. These results complied with the

high reactivity of tin towards oxidation compared to lead. Optimum conditions were 1250°C for 15 minutes.

Melting campaign (5 kg/batch) was conducted at temperatures of 1150, 1200, 1250 and 1300°C, for durations of 15 and 30 minutes. The results are shown in Fig.3. It can be seen that copper content in the alloy increases with increase in temperature. The extent of yield of the alloy decreased with increase in temperature and time. This finding demonstrates the regular loss of tin and lead metals going to slag.



Fig.3 Effect of temperature on copper (wt %) in the obtained copper alloy after heating for 15 and 30 minutes.



Fig.4 Effect of different stoichiometric ratio of copper sulfide on lead and tin content in obtained copper ($T= 1250^{\circ}C$ and stirring conditions).

3.2.2 Melting with additives and without blowing oxygen gas

Figure 4 shows the effect of using different stoichiometric ratio of copper sulfide to remove lead and tin from copper (T= 1250°C, stirring conditions without oxygen blowing and for 15 minutes). Lead and tin content in copper decreased gradually with increasing the amount of Cu₂S added. Fig.5 shows the Arrhenius plot of copper sulfide-lead reaction from which the activation energy of this reaction was calculated. It can be seen that Cu₂S was an effective reagent decreasing both lead and tin in copper.



Fig.5 The Arrhenius plot of copper sulfide-lead reaction.



Fig.6 Effect of temperature on lead content in copper using 10% and 20% by weight copper sulfide as decoppering agent.

3.2.3 Melting with additives and blowing of oxygen gas to remove tin and lead from the molten copper scrap

Figure 6 shows the effect of adding 10% and 20wt % copper sulfide on lead content in the obtained copper alloy by melting at temperatures up to 1300°C for 15 minutes. It can be seen that lead content decreased by increasing both the temperature and amount of copper sulfide added. Oxidation of these metals in the scrap may proceed in a multi steps sequence. However, direct oxidation of these metals with oxygen gas would not take place on basis of ΔG_o value of the M-O₂ reactions. Oxidation of tin, lead and copper metals in the scrap depends on the ΔH values given in Table 1.

ΔH value, kJ/mol										
Flow rate of oxygen, L/min with Lead				Flow rate of oxygen, L/min with Tin						
0	0.2	0.4	0.6	0	0.2	0.4	0.6			
65.6	79.12	72.85	69.36	119.22	145.29	114.1	95.4			

Table 1 The activation energy value obtained for the oxidation processes.

$\operatorname{Sn}^{2^+} + 2e^- \leftrightarrow \operatorname{Sn} - 0.136 v$	(1)
$Pb^{2+} + 2e^- \leftrightarrow Pb - 0.126 v$	(2)
$Cu^{2+} + 2e^{-} \leftrightarrow Cu + 0.3402 v$	(3)

Therefore, oxidation reaction takes place more readily with the metal having a more negative potential such as tin. The sequence of oxidation of these metals would be in the order Sn (-0.1364v), Pb (-0.126v) and copper (+0.3402v) that is nobler than Sn. However, oxygen

blowing at low pressure was insufficient to remove completely lead and tin from copper. This finding suggests that the extent of removal would be related to the equilibrium: $M \leftrightarrow MO$, which shifts to the right direction only at high oxygen partial pressure. Table 2 shows some physical properties of lead, tin and copper metals and their oxides. The formed oxides went to slag because they are thermo-chemical stable and

		Property						
	Chemical	Specific gravity, g/cm ³			Melting point, °C			
Material	formula	Metal	Oxide	Apparent	Metal	Oxide		
Copper	Cu	8.92			1083			
Copper oxide	CuO		6.3	5.94		1326		
Lead	Pb	11.34			327			
Lead oxide	PbO (yel.)		8	6.3		886		
Tin	Sn	7.28			231			
Tin oxide	SnO		0.44	0.41		1080		
Tin oxide	SnO ₂		0.95	0.88		1630		

 Table 2
 Some physical properties of lead, tin and copper metals and their oxides

have low-density values compared to free metals. Frequent skimming of the floating slag managed metals oxides re-entry into the molten copper at minimum.

Calculation of the free energy change, ΔG^{o} for copper oxidation :

$$\Delta G^{o} = -79.42 - 120.8T \text{ kJ/mol}$$
⁽⁴⁾

The equilibrium constant K for this reaction is;

$$K_{(Cu2S(I))} = \alpha_{(Cu2S(I))} / (\alpha_{Cu})^2 x(\alpha_S)$$
(5)

Golonka determined the activity of copper in copper-silver alloys and the activity coefficient data were fitted to the Kuprowski's formalism by Wladyslaw:

For copper:
$$Log \Upsilon_{Cu} = 700 [(1-X_{Cu})^{1.9}] / T$$
 (6)

For lead:Log $\Upsilon_{Pb} = 700 \left[(1X_{Pb})^{1.9} \right] / T$ (7)

Experimentally the weight % of Pb and Sn in the molten copper is relatively small, then:

$$X_{Pb} = \frac{(wt\%Pb)(63)}{(207)(100)}$$
(8)

The equation of equilibriUm of Pb content in copper::

$$Wt\%Pb = \frac{(\alpha_{Pb2+})_{(l)} \frac{1}{2}(207)(100)}{(\gamma_{Pb}^{o})(\alpha_{S})^{1/4} K \frac{1}{4}(63)}$$
(9)

and for Sn it becomes :

$$Wt\%Sn = \frac{(\alpha_{Pb2+})_{(l)} \frac{1}{2} (118.69)(100)}{(\gamma_{Pb}^{o})_{\alpha_{S}} \sqrt{4} K \frac{1}{4} (63)}$$
(10)

Figure 7 shows the effect of heating time and using different stoichiometric ratio of copper sulfide with subsequent blowing of oxygen gas on lead and tin content in the produced

copper alloy respectively. Experiments took place at 1300°C for periods up to 40 minutes. The content of tin and lead in the obtained copper alloy(s) decreased by increasing both the amount of copper sulfide added and time. This behavior can be summarized as follows:



Fig.7 Effect of heating time with blowing oxygen gas (10 L/min) on lead and tin (---) in obtained copper using 1, 1.25 and 1.5 stoichiometric ratio of copper sulfide

Copper sulfide decomposes to copper and sulfur:

$$Cu_2S_{(l)} \longrightarrow 2Cu_{(l)} + S_{(l)} \text{ (nascent)}$$
(11)

Sulfur then reacted with tin and lead to form the respective sulfides.

$$S_{(l)} + Pb_{(l)} \longrightarrow PbS_{(s)}$$
(12)

$$S_{(l)} + S_{n} \longrightarrow S_{n}S_{(l)}$$
(13)

$$\operatorname{SnS}_{(l)} \longrightarrow \operatorname{Sn}_{(l)} + \operatorname{S}_{(l)}$$
 (14)

The thermo-chemical stability of the formed sulfides follows the order PbS >SnS >Cu₂S.

Atmospheric oxygen gas then oxidizes tin or lead to form their oxide that goes to slag. In presence of Cu_2S in the molten scrap alloy, oxygen blowing enhanced the following oxidation reactions and helped removal of tin and lead from the molten copper.

$$SnS_{(1)} + \frac{1}{2}O_{2(g)} \longrightarrow SnO_{(+S)}$$
(15)

$$2Cu_{(1)} + \frac{1}{2}O_2 \longrightarrow Cu_2O_{(s)}$$
 (16)

Copper oxide decomposed at 1050°C to cuppric oxide:

$$Cu_2O_{(s)} \longrightarrow CuO_{(s)}+Cu_{(l)}$$
 (17)

Tin metal may reduce CuO according to:

$$CuO + Sn \longrightarrow Cu+SnO$$
 (18)

Therefore, increasing the stoichiometric ratio of Cu_2S reagent stimulated the removal of lead and tin in agreement with the law of mass action. Under stirring conditions, nearly all the alloying light metals oxidized and went to the slag. From the before said data, it can be concluded that copper sulfide followed by oxygen blowing has been found to be most suitable to remove lead and tin from molten copper. The optimum conditions to manifest adequate removal of tin and lead is to melt the scrap at 1250°C for 15 minutes using 1.25 stoichiometric ratio of copper sulfide reagent with subsequent blowing of oxygen gas at a rate of 10 L/min.



Fig.8 Effect of molarity of 1:1 HCl/HNO3 mixture on the extent of leaching tin, copper and lead from the slag.

3.3 Acid/Alkali leaching of the formed slag after removal of lead and tin

Figure 8 shows the effect of change in molarity of 1:1 HCl/HNO₃ mixture on the extent of leaching tin, copper and lead from the slag. Leached lead compounds dissolved in aqueous ammonium acetate solution whereas tin oxide did not. After filtration, lead acetate was treated with sodium carbonate solution according to:

$$Pb(C_2H_5O_2)_2 + Na_2CO_3 \longrightarrow PbCO_3 + 2 Na(C_2H_5O_2)$$
(19)

The carbonation process was carried out at room temperature for 3 h with a recovery percentage of 99.8%. Heating lead carbonate produced lead oxide whereas lead acetate decomposed to ammonia, acetic acid and lead oxide.

Hot HCl / HNO_3 acid mixture dissolved almost these metals to form soluble copper and lead chlorides whereas $SnCl_2$ deposits. Heating of the solution and filtration while hot helps separation of undissolved $SnCl_2$. Lead chloride on the other hand dissolved and can be filtered. It was precipitated upon cooling to room temperature and separated by filtration. Ammonia is selective for copper to form copper tetra-ammonium complex that dissolved in water (Fig.9). Similar reactions may take place in case of tin or lead failed. The reactions with ammonia were as follows:

$$4 \text{ NH}_4 \text{OH} \qquad \longrightarrow \quad 4 (\text{NH}_4)^+ + 4 \text{ OH}^- \tag{20}$$

$$M + 2 OH^{-} \longrightarrow MO^{-} + H_2O + 2e^{-}$$
(21)

$$MO + 4 (NH_4)^+ + 2e^- \longrightarrow M(NH_3)_4 (OH)_2 + 2H^+$$
 (22)

$$2H^{*} + 2OH \longrightarrow 2H_2O$$
(23)

and the overall reaction gives metal-tetrammonia $M(NH_3)_4.(OH)_2$ and water :

$$M + 4 (NH_4OH) \longrightarrow M(NH_3)_4.(OH)_2 + 3H_2O$$
 (24)

The leached copper, lead and tin compounds were then recovered separately.



Fig.9 Effect of molarity of NH4OH on the extent of leaching copper, tin and lead from the slag.



Fig.10 Effect of addition H₂O₂ to 6 M HCl on the extent of extraction of tin, copper and tin from the slag.



Fig.11 Effect of addition H₂O₂ to 6.8 M NH₄OH on the extent of extraction of tin, copper and tin from the slag.

Figures 10 and 11 show the obtained results after addition of hydrogen peroxide H_2O_2 to the acid or alkali leachants to enhance the leaching process. Peroxide decomposes to water

and nascent oxygen. Liberation of nascent oxygen explains the effect of peroxide enhancing the oxidation of tin and lead metals before the acid or alkali attack. It can be concluded that dissolution of the formed slag in acid solution dissolves almost all the metals in the slag. Ammonia is the only selective agent to dissolve copper. Ammonium acetate leached lead carbonate. Hydrogen gas reduced lead carbonate and stannous oxide at 900°C and 600°C to produce lead and tin metals respectively. The purity of copper, lead and tin was found to be 99.18, 99.8 and 98.67 respectively and the corresponding recovery figures were 96.2, 94.6 and 95.7 %.

Conclusions

- 1) Metallic copper was recovered from bronze scrap containing 80-83 % copper, 9-10% lead and 8-9 % tin by pyrometallurgical treatments like melting of scrap with removal of the slag.
- Addition of additives, CuS coupled with oxygen blowing during melting of the scrap at 1250°C for 15 minutes has been found best experimental condition to remove lead and tin from the bronze scrap.
- 3) Hot acid leaching dissolves almost all metals present in the slag. Ammonia was selective to leach copper only.
- 4) Addition of hydrogen peroxide to the leaching solutions enhanced dissolution of the metals of concern.

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