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STUDIES ON CEMENTATION OF TIN ON COPPER AND TIN STRIPPING FROM COPPER SUBSTRATE

Cementation of tin on copper in acid chloride-thiourea solutions leads to the formation of porous layers with a thickness dependent on the immersion time. The process occurs via Sn(II)-Cu(I) mechanism. Chemical stripping of tin was carried out in alkaline and acid solutions in the presence of oxidizing agents. It resulted in the dissolution of metallic tin, but refractory Cu_3Sn phase remained on the copper surface. Electrochemical tin stripping allows complete tin removal from the copper substrate, but porosity and complex phase composition of the tin coating do not allow monitoring the process in unambiguous way.

Keywords: tin; copper; cementation; stripping

1. Introduction

Copper and tin belong to the most valuable basic metals for EU (5,700 USD/t Cu and 14,700 USD/t Sn [1]), which are often obtained from waste materials and scraps. It is estimated, that about 15% of tin and up to 21% of copper produced worldwide originate from secondary sources [2]. Tin is used mainly for protective layers on steel packages for food products, as component of solders as well as coatings on copper wires, cables and tubes preventing oxidation of the substrate surface and formation of copper sulfides [3]. Tinned copper wires show beneficial anti-corrosion properties, which make them effective in marine usages as well as in high moisture and humidity environments. Tin coatings (0.5-5 μm) can significantly improve the lifespan of copper products, but recycling of tin coated copper scrap and obsolete electric cables is not a simply procedure. Direct casting of tinned copper results in an increase of tin content in the copper melt and its inability to re-use for production of new material with desired properties. To increase the purity of recycled copper, tin stripping from the copper scrap is needed before final copper treatment.

Removal of tin from copper surface is generally performed using hydrometallurgical methods (chemical or electrochemical). Table 1 shows exemplary solutions and conditions proposed for tin stripping. Baths contain oxidation agents and inhibitors of copper dissolution. However, it has to be mentioned that efficiency of tin dissolution depends on the method used previously for tin coating (hot dipping, electroless deposition, electroplating). Electroplated tin layers can be easy stripped completely from the substrate, since no Cu_xSn_y intermetallic compounds are formed between substrate and coat elements. Unfortunately, similar behavior may be not observed, when cementation (immersion process) or dipping of copper in melted tin are used for the tinning.

Therefore, the aim of this work was to investigate the influence of composition of the stripping baths and method (chemical, electrochemical) on the efficiency of removal of tin layers from copper surface produced formerly via immersion deposition.

TABLE 1

Exemplary solutions for tin stripping from copper substrate

No	Bath composition	Conditions	Reference
1	25wt% HNO_3 6.5 g/L $FeCl_3$ 0.03 g/L F127*	20-25 °C 1.5-2 min	[4]
2	20%(vol) CH_3HSO_3 (70wt%) 80 g/L $Fe(NO_3)3.9H_2O$	40-45 °C 3 min	[5]
3	Stage I: 100 g/L $C_6H_5NO_5SNa$ 400 g/L HNO_3 100 g/L $HOCH_2COOH$ 10 g/L NaCl Stage II: 3 g/L $FeCl_3$	Stage I: 40 °C 30 s Stage II: 25 °C 5 s	[6]
4	Stage I: 150 g/L $C_6H_5NO_5SNa$ 200 g/L HBF_4 50 g/L CH_3COOH Stage II: 100 g/L $NaClO_2$ 200 g/L NaOH	Stage I: 40 °C 10 min Stage II: 95 °C 6 min	[7]

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5	100 g/L HNO$_3$ (70wt %) 225 g/L H$_2$SO4 80 g/L Fe(NO$_3$)$_3$ (45wt %) 0.1 g/L inhibitor	30 °C 2 min	[8]
6	6% (vol) H$_2$SO$_4$ 50-100 g/L CuSO$_4$	80 °C	[9]
7	1 L HCl (1,17 g/L) 0.125 L H$_2$O 12 g Sb$_2$O$_3$		[10]
8	50 g/L Na$_2$SnO$_3$ 90 g/L NaOH	70-90 °C 1 A/dm^2	
9	5% NaOH	1 A/dm^2	
10	0.5 M C6H8O7 0.5 M C$_6$H$_7$O$_7$Na	Potentiostatic dissolution	[11]

* F127 - block copolymer of propylene oxide and ethylene oxide (M = 12,700 u, 70% ethylene oxide)

2. Experimental

Deposition of tin on copper substrate was performed using cementation method. Before coating, copper plates (2 cm x 2 cm) were grinded with sand papers, washed in water and acetone, then polished in a mixture of concentrated acids (HNO$_3$:H$_3$PO$_4$:CH$_3$COOH 1:3:1), washed in water and ethanol, then dried.

Copper plates were tinned in a solution containing: 0.1M SnCl$_2$, 0.4M SC(NH$_2$)$_2$ and 0.4M HCl. Deposition was carried out at the temperature of 80 °C for 2-45 min. All samples were weighted before and after cementation.

Chemical tin stripping was performed using solutions of various compositions. These were: 2M NaOH; 2M NaOH with addition of H$_2$O$_2$ (1-6%) or (NH$_4$)$_2$S$_2$O$_8$ (3%); 3M H$_2$SO$_4$ with 5.5% CuSO$_4$. Stripping was carried out usually at the temperature of 80 °C for 1-20 min. Before and after process samples were weighted.

Electrochemical tin stripping was performed galvanostatically using 0.1M NH$_4$Cl + 0.1 M CH$_3$COOH solution. Anodic current density was 10 mA/cm^2. Potential of the anode was registered versus saturated calomel electrode (SCE). Counter electrode was platinum plate. Electrolysis was carried out at room temperature.

Surface and cross-sections of the samples after tin deposition and tin stripping were observed using optical microscope (NIKON), while phase composition of the samples was determined using X-ray diffractometry (Rigaku).

3. Results and discussion

3.1. Cementation of tin

Electroless deposition is one of the simplest methods of formation of thin metallic layers on various substrates. Compared to other techniques (e.g. CVD, PVD, electrodeposition) process does not require cost and sophisticated equipment or special conditions. There are two hydrometallurgical electroless methods used for deposition of tin films: cementation (immersion process) [12-14] and autocatalytic deposition [15].

Cementation occurs via displacement of nobler metal ions from aqueous solution by the less noble metal. Cementation of tin on copper is typically carried out using acidic solutions of Sn(II) salts in the presence of thiourea SC(NH$_2$)$_2$ [12, 13]. Two mechanisms of the process are proposed in the literature:
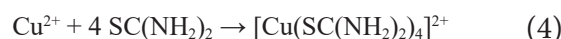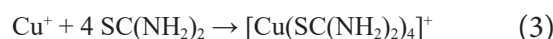
a)   reduction of Sn(II) ions with formation of Cu(I) ions [12]:

$$2\ Cu + Sn^{2+} \rightarrow Sn + 2\ Cu^+ \qquad (1)$$
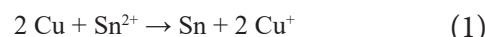
b)   reduction of ions Sn(II) ions with formation of Cu(II) ions [13]:

$$Cu + Sn^{2+} \rightarrow Sn + Cu^{2+} \qquad (2)$$
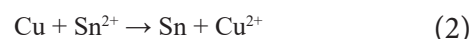
Despite that copper is more noble metal than tin, the presence of thiourea changes conditions for tin cementation. Large stability constants of copper-thiourea complexes (Table 2):

$$Cu^+ + 4\ SC(NH_2)_2 \rightarrow [Cu(SC(NH_2)_2)_4]^+ \qquad (3)$$

$$Cu^{2+} + 4\ SC(NH_2)_2 \rightarrow [Cu(SC(NH_2)_2)_4]^{2+} \qquad (4)$$

shift the electrode potentials of Cu/Cu(I) and Cu/Cu(II) systems to more electronegative values than the potential of the Sn/Sn(II) electrode [12]. This results in the spontaneous dissolution of copper with simultaneous tin deposition.

TABLE 2

Stability constants of copper ion-thiourea complexes (log values) at 25 °C [16]

Copper ion	β_2	β_3	β_4
Cu(I)	13.04	15.88	18.66
	12.30	14.30	15.53
Cu(II)	11.28	13.73	15.70
	13.0	15.9	18.1

Cementation of tin on copper can also occur in strongly alkaline solutions [14], where Sn(II) ions exist as hydroxy-complexes:

$$Cu + Sn(OH)_3^- \rightarrow Sn + Cu(OH)_3^- \qquad (5)$$

Regardless on pH of solutions used, tin plating can be hindered by the occurrence of side reactions. The most important are: oxidation of Sn(II) to Sn(IV) and hydrolysis of tin salts as well as secondary dissolution of metallic tin under action of acid solution [12]:

$$Sn + 2\ H^+ \rightarrow Sn^{2+} + H_2 \qquad (6)$$
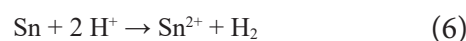
In the present study deposition of tin was carried out in acid chloride-thiourea solution. Fig.1 shows exemplary cross-sections of tinned copper samples. Obtained coatings were rather porous, but gray layer of metallic tin was clearly visible on the red copper surface. Microscopic observations enabled

to determine thickness of the coatings. Obtained average values are summarized in Table 3. It was found that increased deposition time from 2 min to 45 min favored formation of tin layers with the thickness from the range of 1-21 μm. Obtained values are higher than the data showed in the literature for the same temperature and similar plating times, where deposits of the thickness 1.2-1.6 μm (15 min) were reported. However, it has to be noted that the growth of the coatings is hindered by the reduction of metallic copper area due to covering the substrate by metallic tin.
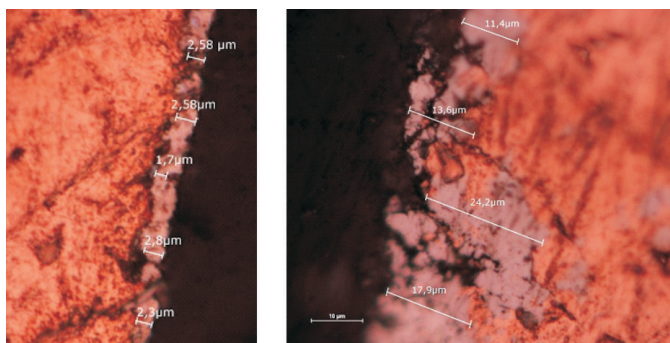
Fig.1. Cross-sections of tin coated copper samples. Deposition time: 5 min (left) and 15 min (right)

TABLE 3

Thickness of tin layers

Deposition time, min	Average thickness of coatings, μm	
	microscopic observations	mass change acc.to eq.(1)
2	1.4 ± 0.1	1.2
5	2.4 ± 0.2	2.3
15	11.2 ± 1.1	10.8
30	14.8 ± 1.4	15.6
45	21.0 ± 2.1	20.1

Gravimetric analysis showed decrement of the mass of the samples Δm after completed tin plating. Theoretical calculations of thicknesses of the coatings according to the equations (1) and (2) showed very good conformity of the results only for tin deposition according to Sn(II)-Cu(I) mechanism (Table 3). In the latter case thickness of the deposits l_{Sn} was calculated according to the following formula:

$$l_{Sn} = \frac{\Delta m \cdot M_{Sn}}{(M_{Sn} - 2M_{Cu}) \cdot S \cdot d_{Sn}} \qquad (7)$$

where: M_{Sn} and d_{Sn} – molar mass and density of tin, respectively; M_{Cu} – molar mass of copper; S – surface area of the sample.

Phase analysis of the tin coated substrates confirmed the presence of both metals in their pure forms (copper - cubic, tin - tetragonal), but additional Cu_xSn_y intermetallic compounds were not detected (Fig.2).
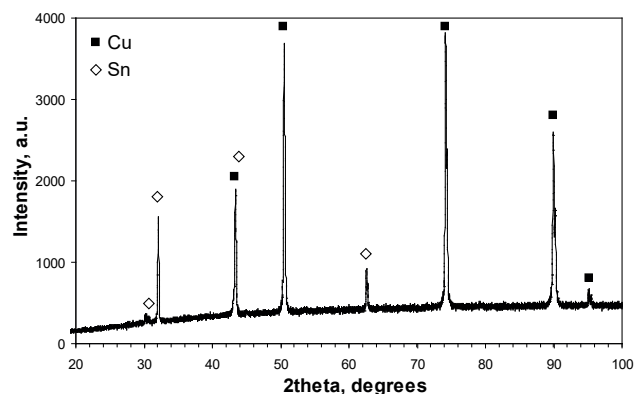

Fig. 2. Diffraction pattern of tin coated copper substrate

3.2. Stripping of tin

Metallic tin was stripped from the copper substrate in alkaline and acid solutions due to amphoteric properties of tin. Fig.3 shows exemplary results obtained for the samples coated with tin of a thickness of 4.5 ± 0.2 μm. The lowest stripping efficiency was observed in NaOH solution with no additives, while the most aggressive action of the bath was found in the H_2SO_4-$CuSO_4$ system. Ammonium persulfate proved to be high oxidation agent, since copper substrate was covered with thick black layer of copper(II) oxide, although tin(II) oxide was also detected (Fig.4b). Alkaline solution with hydrogen peroxide was the middle active solution for tin stripping, but tin was not dissolved completely and tin layer with a thickness of about 0.8 μm remained on the substrate. It was also identified that refractory soluble phase Cu_3Sn was formed during the cementation stage, since it was found in all samples after stripping treatment (Fig.5).

Fig.6 shows the influence of H_2O_2 concentration on the mass decrement of tin. It was observed that increased concentration of oxidizing agent was unfavorable for tin dissolution due to passivation of tin surface with SnO (Fig.4a).
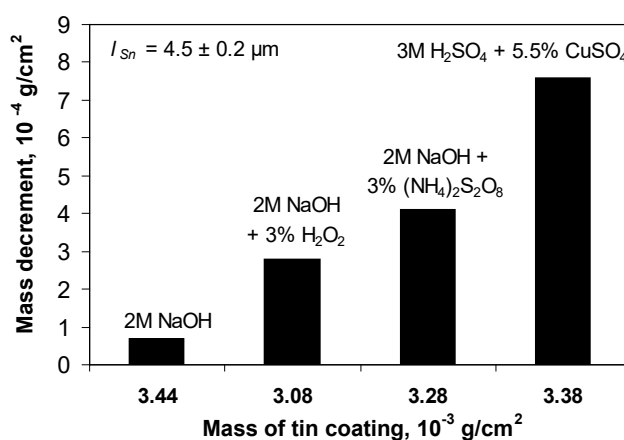

Fig. 3. Mass decrement of the samples during tin stripping for 20 min in various solutions (80°C)
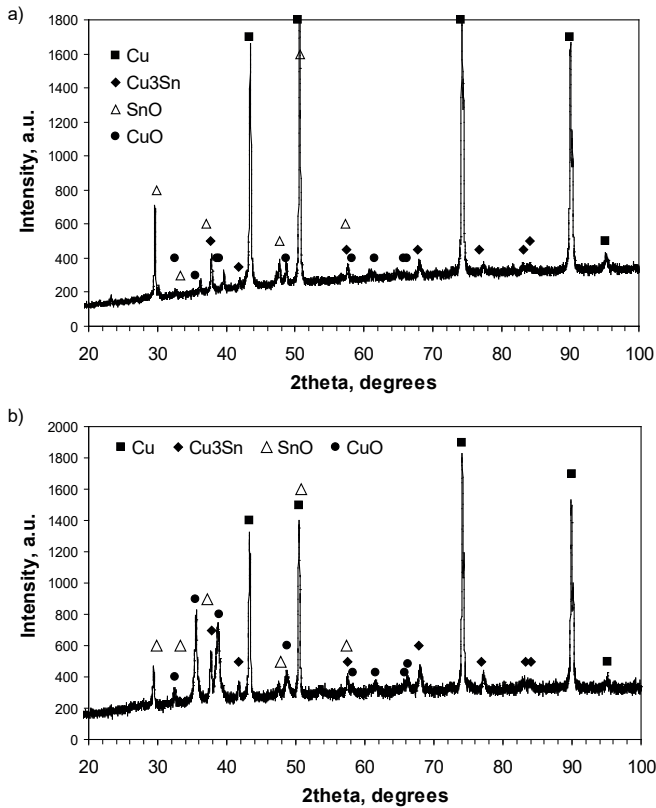
a)

b)

Fig.4. Diffraction pattern of tin stripped copper substrate in solutions: a) 2M NaOH + 3% H_2O_2,   b) 2M NaOH + 3% $(NH_4)_2S_2O_8$
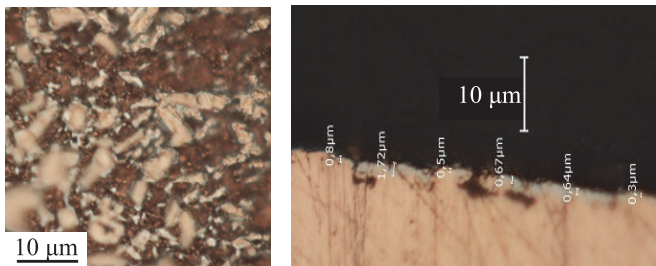

Fig.5. Surface and cross-section of the samples after tin stripping in 2M NaOH + 3% H_2O_2 solution for 20 min (80 °C)
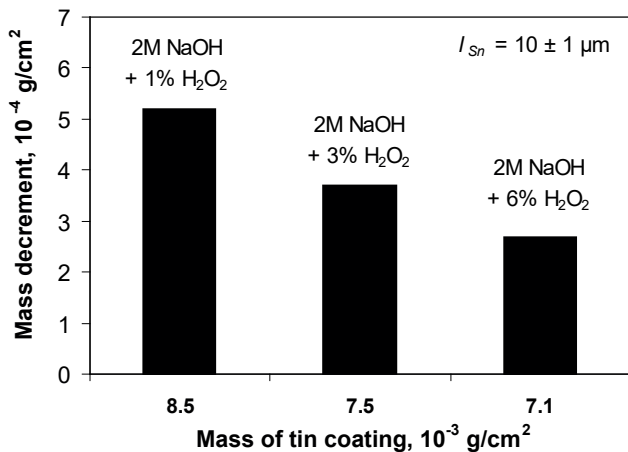

Fig.6. The influence of H_2O_2 concentration on tin mass decrement during stripping in NaOH solutions for 20 min (80°C)

Obtained results show that chemical dissolution of metallic tin cemented on the copper surface requires addition of oxidizing agent, but it is not enough for dissolution of refractory Cu_3Sn phase formed during plating. Moreover, the process is hindered by formation of passive films on the samples surface. Increased temperature (90 °C) or prolongated time of the stripping does not improve efficiency of the chemical dissolution (results not presented). Therefore electrochemical method was also tested.

Anodic dissolution of metallic coatings is used for determination of thickness of the layers by means of coulometric method [17]. In the present paper similar methodology was applied for removal if tin layer. It was observed that dissolution of tin starts at the anode potential of about 100 mV (VS. SCE), but then potential gradually increases due to anodic oxidation of metal, intermetallic phase and subsequently the copper substrate. Final anodic potential was maintained at about 800-1200 mV (SCE). However, porous structure of the coatings and their complex composition disturb changes of the potential, hence it could not be used for monitoring the progress the tin dissolution. Despite of that phase analysis of the samples after anodic oxidation did not show the presence of tin or tin-copper compounds (Fig.7). Only copper and copper(I) oxide as final products of the electrolysis were identified.
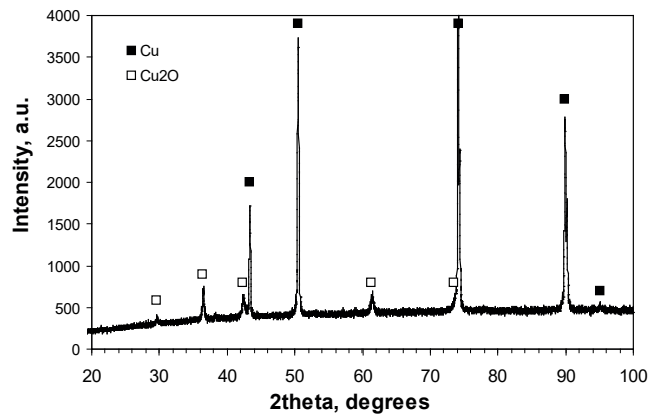

Fig.7. Diffraction pattern of electrochemically tin stripped copper substrate

4. Conclusions

Cementation of tin on copper in acid chloride-thiourea solutions allowed to obtain porous layers with a thickness from the range of 1-21 μm, depending in the immersion time. Studies confirmed that the process occurs via Sn(II)-Cu(I) mechanism.

Chemical stripping of tin carried out in various solutions (alkaline and acid in the presence of oxidizing agent) resulted in the dissolution of metallic tin, but refractory Cu_3Sn phase remained on the copper surface. Oxidation agents enabled dissolution of the metals, but too high concentration of the additives resulted in the passivation of tin and copper.

Electrochemical dissolution of tin resulted in complete tin removal from the copper substrate, but porosity and complex phase composition of the coatings do not allow monitoring the process in unambiguous way. It seems that the anodic

oxidation can be finished when the sample potential reaches values above 600 mV (SCE).

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