Tin-copper Alloys Electroplating from Thiourea Solutions

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Regulatory restrictions impose limitations on the use of lead containing materials for electronic applications. For this reason lead-free materials are extensively investigated and, in particular, Sn(Cu) alloys are evaluated as whisker free alternative to Sn(Pb) solderable coatings. Cu-Sn alloys can be electrodeposited from a novel electrolyte based on thiourea and copper(I) salt. In the presence of thiourea, copper forms Cu(I) aqueous complexes and such strong complexing action of thiourea can be used to electrodeposit copper together with tin. By adjusting the composition (that is, with low copper concentration and relatively high thiourea concentration) it is possible to produce Sn-Cu alloys with low copper content. In this paper we present experimental results on the electrodeposition of Sn(Cu) alloys from such electrolyte. A range of conditions was investigated. The electrolytes are relatively stable and reproducible results are obtained. Moreover, experimental results, after eighteen months ageing, suggest that these alloys are not prone to whiskers but only to nodules formation.

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Introduction

Tin-lead solder plating has been the common practice, however new environmental regulations enforce the use of other kind of alloys, and Sn(Cu) alloys are considered suitable whisker-free alternative to Sn(Pb).(1)

In this paper we present experimental results on the electrodeposition of Sn(Cu) alloys from acidic thiourea ($CS(NH_2)_2$) solutions. Even though the electrochemistry of thiourea ($CS(NH_2)_2$) solutions is quite complex and the electrochemical behaviour of thiourea oxidation products is not really well understood, thiourea is know as an effective complexing agent for Au(I), Ag(I) and Cu(I). Because of the high value of stability constants of copper(I) thiourea complexes (log K=11.1 for $Cu(CS(NH_2)_2)^+$ and log K=18.5 for $Cu_2(CS(NH_2)_2)_2^{2+}$ at 20°C(2)) it is possible to exploit the strong complexing action of thiourea to electrodeposit copper together, for example, with tin.

In the recent years the electrodeposition of copper-tin alloys from thiourea acid baths was investigated, and the phase structure of electrodeposited alloys over the entire range of composition was discussed. Baths for Cu-Sn, Ag-Sn, and Au-Sn alloys electroplating have been proposed.(3,4)

Figure 1 shows the equilibrium phase diagram for copper-tin alloys. In figure $2a_1$ (Raub 1950, ref.5) and $2a_2$ (Fedotev in 1970, ref.6) the stability regions of phases electrodeposited from copper cyanide and sodium stannate electrolytes are displayed. A partial agreement between them can be observed. Figure 2b represents the stability regions of Cu-Sn electrodeposited alloys from acid sulphate obtained recently by Watanabe et al..(7)

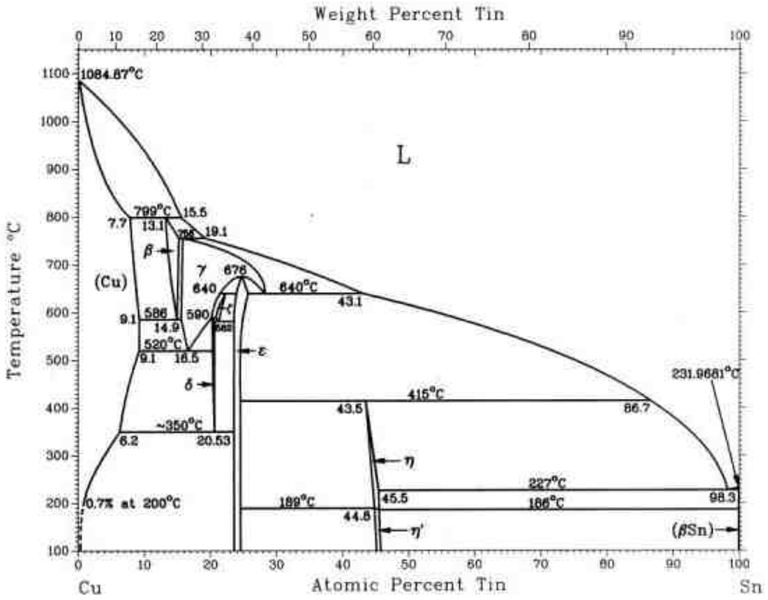

Figure 1. Cu-Sn phase diagram.

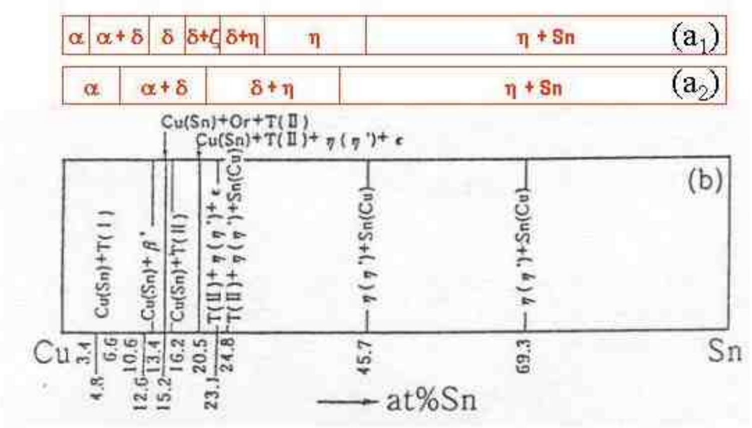

Figure 2. ECD Cu-Sn alloys stability: Cu-Sn electrodeposited phases: a_1: Fedotev', a_2: Raub; b: Watanabe (low).

We investigated the structure of electrodeposited phases, obtained by using cuprous acidic electrolytes and whose composition is given in Table 1. Operating conditions for deposition are reported.

Table 1. Electrolyte composition and operating conditions for ECD Cu-Sn.

Cu-Sn	
Component	Concentration
Cu_2O	0.005 ÷ 0.2 M
$CS(NH_2)_2$ (thiourea)	0.05 ÷ 0.2 M
$SnSO_4$	up to 0.2 M
H_2SO_4	1 M
$C_6H_2O_6$ (pyrocathecol)	Up to 0.2 M
Temperature	25 ÷ 60°C
Current density	5 ÷ 100 mA cm^{-2}
Stirring	

By XRD crystallographic investigation five main phases were identified. With increasing tin content, they were: face centered cubic, hexagonal close packed, body centered cubic, η phase (NiAs type), and orthorhombic tin copper solid solutions. Single phase regions were separated by two-phase region. Electrodeposits having a tin content comprised approximately in the range 7-25 at% showed presence of sulphur up to 8at%.

Copper coatings, deposited by addition of zinc salt to the electrolytes, were apparently characterised by anti-tarnishing properties. Copper-tin coatings with 22-25 at% of tin were semibright; while those with Sn 43-47 at% were satin-like. In the following the experimental results concerning the deposition of tin-copper coatings is discussed.

Experimental

Electrolytes were prepared by addition of thiourea to the sulfuric acid solution. Then, copper was added as cuprous oxide and dissolved at 50-60°C. Coatings with low amount of copper were obtained from electrolytes having low concentrations of copper. In this condition it was possible to use the bath at lower temperatures (30-40°C instead of 50-60°C, as usual for high copper baths of thiourea). Composition and operating conditions for Sn(Cu) electrodeposition are listed in Table 2.

Table 2. Sn(Cu) electrolyte composition and operating conditions.

Sn(Cu)	
Component	Concentration
Cu_2O	0.005 ÷ 0.01 M
$CS(NH_2)_2$ (thiourea)	0.05 ÷ 0.2 M
$SnSO_4$	Up to 0.2 M
H_2SO_4	1 M
$C_6H_2O_6$ (pyrocathecol)	Up to 0.2 M
Temperature	30 ÷ 44°C
Current density	10 ÷ 100 mA cm^{-2}
Stirring	

Electrodeposition was performed under temperature control. A magnetic stirrer was used during deposition. Before deposition, copper (or brass) substrates were degreased in acetone, rinsed with distilled water and activated in diluted sulfammic acid for few second. A pure copper specimen was used as counter electrode. Electrodeposition tests were carried out for 15÷60 minutes, at constant current density (AMEL). Coating composition was analyzed by EDS (Electron Dispersion Spectroscopy) and surface morphology by SEM (Cambridge Stereoscan 360). Structure was by assessed by XRD (X-ray Diffraction, Philips PW 1830, PW3020).

Results and discussion

Blue region in figure 3 corresponds to the alloys with high Sn content, that we were able to produce by electroplating. An eutectic point at 231°C and 98.3 at% of tin is present. Using the electrolyte and the conditions described in Table 2, copper-tin alloys with more than 95 at% of tin were obtained. Coatings electrodeposited at lower current densities (20-40-50 mA cm^{-2}), and lower temperatures (30°C) were mostly two-phase alloys (η - phase and supersaturated tin-copper solid solution).

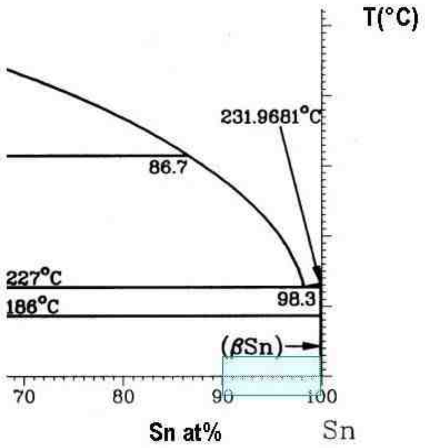

Figure 3. Sn(Cu) phase diagram region.

At high current density, copper deposition occurs at limiting current density. By using a tentative value for *k* (mass transfer coefficient $k = D/\delta$, that is the diffusion coefficient *D* divided by the thickness δ of the boundary layer) it is possible to make a sensitivity analysis on calculated values of copper deposition limiting current density (j_l).

Table 3. Sn(Cu) electrolyte composition and operating conditions.

Cu limiting current density		
k (10^{-5} m s^{-1})	[Cu] (M)	j_l (mA cm^{-2})
0.1	0.01	0.1
1	0.01	1
0.1	0.02	0.2
1	0.02	2

While intense parasitic hydrogen evolution corresponds to high *k* values, on the other side less intense hydrogen gas evolution corresponds to low *k* values. By assuming *k* values in the range $(0.1\div1)\cdot10^{-5}$ m s^{-1} and copper concentration in the range 0.01÷0.02 M, we are able to make an estimation of the limiting current density for copper deposition. The calculated values range approximately between 0.1 and 2 mA cm^{-2}. This confirms that the limiting current density for copper is attained during Sn(Cu) deposition.

Figure 4 shows the copper content in the deposits obtained at different current densities. The electrolyte is composed by 1M H_2SO_4, 0.2 M pyrocathecol, 0.2 M Sn, 0.01 M Cu(I), 0.1 M thiourea at 42-43°C. The curve is in agreement with the general behaviour that any increase of the current density favours tin deposition with respect to copper.

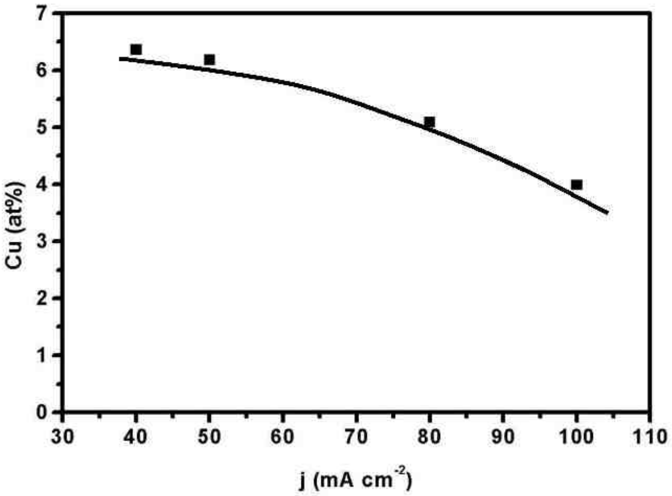

Figure 4. Cu content in ECD Sn(Cu) layer as a function of current density.

By increasing thiourea concentration (from 0.1 M to 0.2 M) the content of copper drops sharply, attaining values below 1 at%. On the other side, by decreasing thiourea to 0.05 M, the content of copper in the alloys can raise up to 13-14 at%.

Figure 5 shows a typical XRD pattern for a tin(copper) sample with a high tin content. Pattern refers to a sample containing 99.3 at% tin and 0.7 at% copper. Peaks marked with black arrows correspond to the orthorhombic structure of tin with some copper as alloying element. Other peaks are substrate peaks (brass). The lattice parameters calculated by least square method are a = 5.834 Å and c = 3.188 Å. Lattice parameters for pure tin are a = 5.832 Å and b = 3.1814 Å. The structure is that of a solid solution of copper in tin.

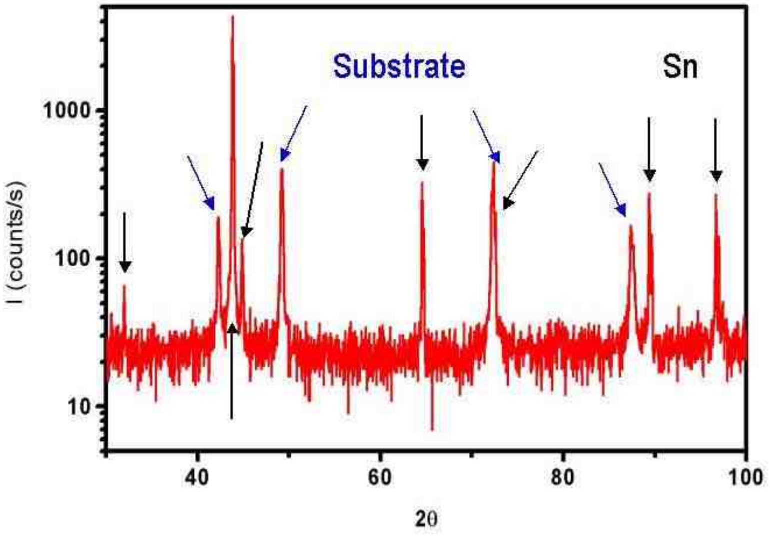

Figure 5. XRD pattern of a Sn(Cu) electrodeposited layer (tin rich phase is marked with black arrows).

Electronic devices manufacturers are particularly concerned with whisker growth on lead-free finishes. Tin-lead alloys (virtually immune from whiskers) must be replaced by other alloys with low or even zero whiskering. A series of tin(copper) samples were prepared and kept at room temperature for more that 18 months (Dec 2002 - May 2003). Immediately after deposition they were observed at the scanning electron microscope. After 18 months they were observed again in order to assess the formation of whiskers.

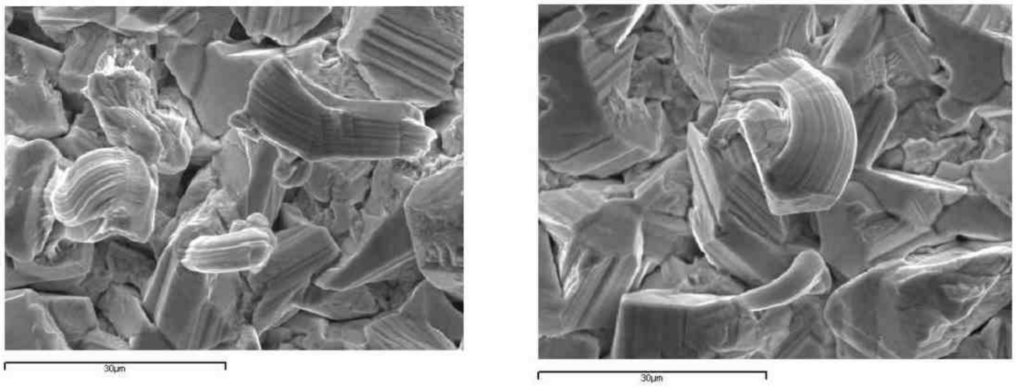

Figure 6. Sn(Cu) electrodeposited layer: Sn 96.01 at%; Cu 3.99 at% (1 M H_2SO_4; 0.2 M pyrocathecol; 0.2 M Sn(II); 0.01 M Cu(I); 0.1 M thiourea; 42°C; 100 mA cm^{-2}).

Micrographs show the presence of abnormal morphological features which are usually referred to as nodules rather than whiskers. In fact, whiskers are filamentary single crystals, commonly a few µm in diameter and often several millimetres in length. They can be solid, perforated or hollow. And external surfaces often have striations. In our case only few of these requirements are met. The micrographs in figure 6 refer to a sample electrodeposited at 44°C and 100 mA cm^{-2} from a solution containing 1M sulfuric acid, 0.2 M pyrocathecol, 0.2 M tin(II), 0.01 M copper(I) and 0.1 M thiourea. The sample was deposited at 42°C and 100 mA cm^{-2}. The content of tin is 96.01 at% and that of copper 3.99 at%.

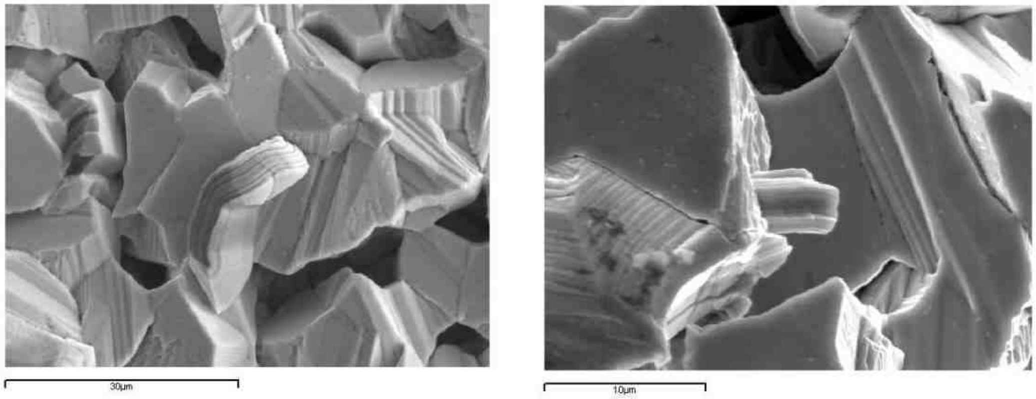

Figure 7. Sn(Cu) electrodeposited layer: Sn 99.73 at%; Cu 0.27 at% (1 M H_2SO_4;

0.2 M pyrocathecol; 0.2 M Sn(II); 0.02 M Cu(I); 0.2 M thiourea; 43°C; 60 mA cm^{-2}).

Micrographs in figure 7 shows similar morphology and very few columnar structures (in some case nodules) were found on the surface of the sample. The solution was similar to that utilised for sample of figure 6, but with twice the amount of copper (0.02 instead of 0.01 M). The composition of the sample was 99.73 at% Sn and 0.27 at% Cu.

Finally, Figure 8 shows surface morphology of a sample with higher copper content. This sample showed only presence of nodules and curved structures have been found. These structures of relatively large diameter and small length are typical of samples with high content of copper. The solution utilised was similar to that of sample of figure 7, but it was obtained at higher current density (80 instead of 60 mA cm^{-2}). The composition of the sample was 98.06 at% Sn and 1.94 at% Cu. Even in this case surface features do not resemble to whiskers.

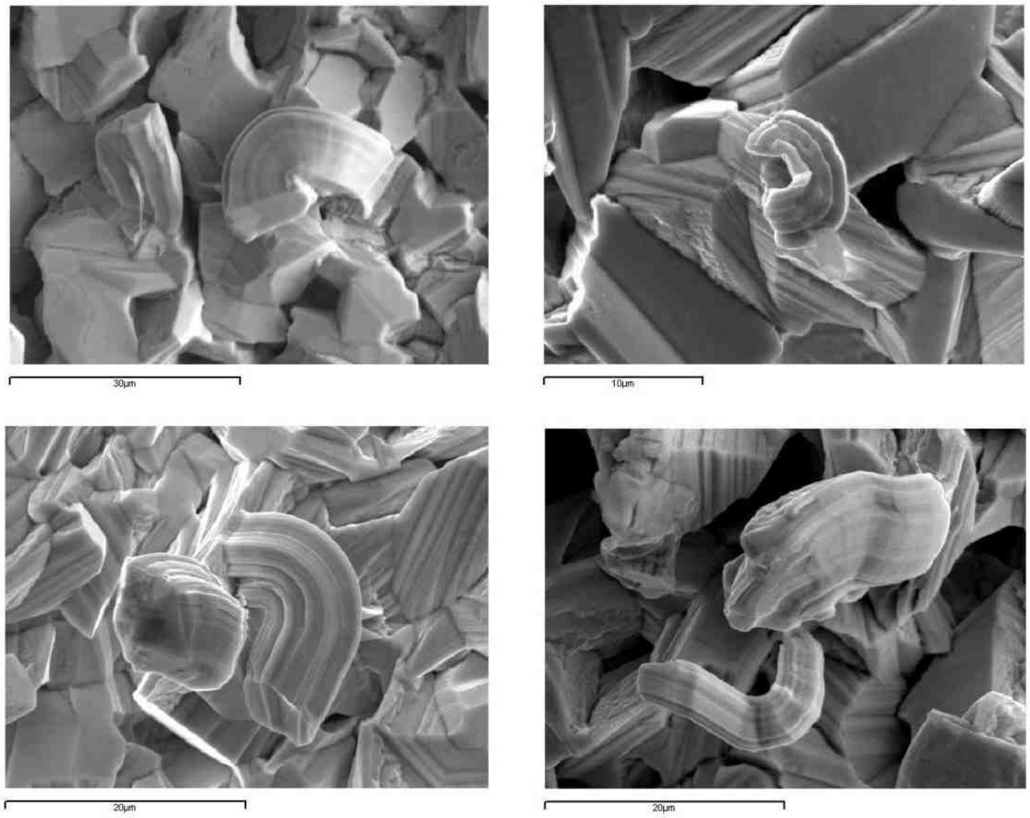

Figure 8. Sn(Cu) electrodeposited layer: Sn 98.06 at%; Cu 1.94 at% (1 M H_2SO_4; 0.2 M pyrocathecol; 0.2 M Sn(II); 0.02 M Cu(I); 0.2 M thiourea; 43°C; 80 mA cm^{-2}).

Conclusions

Composition and microstructure of electrodeposited Sn(Cu) alloys are strongly dependent on both thiourea concentration and deposition current density. Rich tin single orthorhombic phases can be obtained by using electrolytes containing copper(I)-thiourea and tin sulphate. Copper content in the deposits can be varied by controlling $[CS(NH_2)_2]/[Cu(I)]$ and $[Cu(I)]/[Sn(II)]$ ratios and current density as well. By adjusting the composition (that is at low concentrations of copper and relatively high concentrations of thiourea) it is possible to electrodeposit tin(copper) alloys with low content of copper. These electrolytes are relatively stable, and the results are quite reproducible. Electrolytic solutions were stables for prolonged periods of time. Finally, it appeared from the surface morphology of samples electrodeposited on brass and copper substrates that these alloys show only formation of nodules and similar features without whisker growth after several months ageing.

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