

Tin-copper alloys electroplating from thiourea solutions

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References

¹ M. Jordan, *Galvanotechnik* 92, 1225 (2001).
² M. Bestetti, A.Vicenzo and P.L. Cavallotti; *Proc. 200th ECS Meeting 2001* (San Francisco) Abs. 651.
³ P.L. Cavallotti, M. Bestetti, A.Vicenzo, L. Magagnin, M. Seregni. *Italian Patent Appl.* 2002.
⁴ I.V. Mironow and L.D. Tsvlodub, *J. Solution Chem.* 25(3), 315 (1996).

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.⁽¹⁾ The phase structure of Cu-Sn electrodeposited alloys was recently discussed ⁽²⁾, and thiourea (CS(NH₂)₂) based baths for Cu-Sn, Ag-Sn, and Au-Sn alloys electroplating have been proposed.⁽³⁾

In this paper we present experimental results on the electrodeposition of Sn(Cu) alloys from acidic thiourea solutions. In presence of thiourea, copper forms Cu(I) aqueous complexes (logK=11.1 for Cu(CS(NH₂)₂)⁺ and logK=18.5 for Cu₂(CS(NH₂)₂)₂²⁺ at 20°C)⁽⁴⁾ and such strong complexing action of thiourea can be used to electrodeposit copper together with tin. A range of conditions was investigated (see Table 1 for composition). Temperature was comprised between 30 and 60°C and current density was in the range 10 to 100 mA cm⁻².

Table 1. Composition of Sn-Cu Alloys plating solutions

Chemical	Concentration (mol dm ⁻³)
Cu ₂ O	0.01÷0.2
CS(NH ₂) ₂	0.05÷0.5
SnSO ₄	0.04÷0.2
H ₂ SO ₄	0.5÷1
Pyrocathecol	up to 0.2

Composition and microstructure of electrodeposited Sn(Cu) alloys are strongly dependent on both thiourea concentration and deposition current density. Tin content in the deposits can be varied by controlling the ratios [CS(NH₂)₂]/[Cu(I)] and [Cu(I)]/[Sn(II)].

Figure 1 shows, as example, the surface morphology of a Sn(Cu) layer deposited from a solutions containing Cu(I) 0.01M, CS(NH₂)₂ 0.1M, Sn(II) 0.2M, pyrocathecol 0.2M, H₂SO₄ 1M at 100 mA cm⁻² and 42°C, with gentle electrolyte stirring. Deposit composition was Sn 96at% and Cu 4at%.

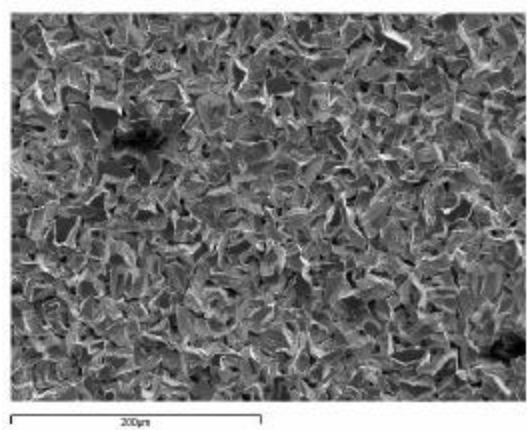


Fig.1. SEM surface morphology of a Sn(Cu) electrodeposited alloy (Sn 96at%, Cu 4 at%).