Equilibrium and Non–equilibrium Structures in Electrodeposited Cu–Sn Alloys

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The differences between the structure of alloys, obtained by electrodeposition or metallurgical methods, is a fundamental aspect of significant practical relevance and long standing theoretical intricacy. The possibility of growing metastable phases by electrodeposition is well ascertained, and in many cases it is simply related to process irreversibility without deepening the understanding.

Electrocrystallization of alloys is certainly one of the most difficult topic in metal electrodeposition, because many different and related processes simultaneous occur and overlap at the reaction interface, under the influence of potential driven directional forces; surface phenomena, involving different and interacting species, are influencing crystallisation reactions under conditions of high supersaturation.

The crystallographic structure of electroplated Cu-Sn alloy films has been the subject of many investigations (1-4); but it is questionable if the published results are exhaustive and it is certain they are in relatively poor agreement, as long as the formation of metastable phases is concerned. On the other hand, there is a growing interest in the use of Cu-Sn or Cu-Sn(Zn) coatings not only for engineering applications, but also as decorative finishes, with the aim of substituting nickel in applications where allergy problems can arise (5).

The aim of this work is the determination of the crystallographic phase structure of electrodeposited Cu-Sn alloys, so as to provide a general understanding of this complex system as well as for the selection of suitable electrolytes and operating conditions for a feasible plating process.

Cu-Sn alloys were electrodeposited from acidic sulphate or metansulphonate electrolytes, with $[Cu^{2+}]$ 0.1M and $[Sn^{2+}]$ 0.1÷0.3M concentration, in the presence of complexing agents (gluconate, glycine and EDDS), at current densities in the range 5÷40mA/cm^2 and room temperature. Alloy films in the composition range from pure copper to CuSn55%at were deposited on steel substrate and characterised by X-ray diffraction analysis and microindentation measurements.

The ECD Cu-Sn alloy shows a well defined phase sequence:

1. a fcc solid solution, with a composition region enlarged with respect to the equilibrium phase diagram, up to Sn12%at;
2. an hexagonal close packed structure, in the composition range corresponding to the stoichiometric ratio Cu/Sn 5÷4 to 1, with c/a ratio in the range 1.60÷1.62;
3. a cubic structure, related to a simple bcc lattice with a small composition range, centred at about Sn22%at;
4. a pseudo-hexagonal NiAs type structure for Sn content in the range 40-50%at with c/a value near 1.21÷1.22.

Fig. 1 reports the X-ray patterns representative of all the observed structures: fcc, hcp, cubic bcc type and pseudo-hcp structure of alloy films obtained from the sulphate based electrolyte.

Mechanical properties of the alloy films were characterised by penetration curve recording during indentation load – displacement measurements, from which microhardness and elastic modulus data are derived. The plastic properties of the alloys are evaluated through measurement of the deformation work during a complete cycle of loading and unloading and measuring the indenter penetration depth under constant load. Microhardness measurements are matched to the results of phase structure analysis for a more precise assessment of the stability region of different phases.

The correlation between structure and electron concentration for ECD alloys is discussed, trying to account for the discrepancies between the expected sequence of phases according to Hume-Rothery rules and the experimental results.

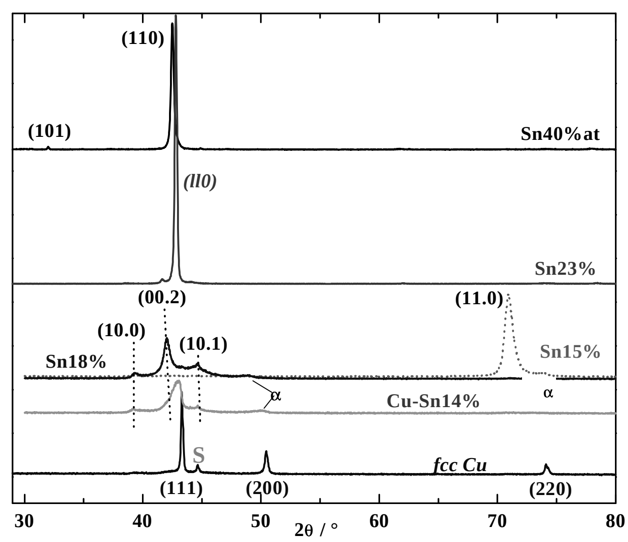

Fig. 1. XRD patterns of Cu-Sn coatings obtained from a tin-copper sulphate bath: from down up, pure copper; hcp Cu-Sn with Sn content from 14 to 18% at and different textures; cubic Cu-Sn23% and pseudo-hexagonal η Cu-Sn40%.

References

[1] E. Raub and F. Sautter, *Metalloberflaeche*, **11**, 249 (1957).

[2] K.M. Gorbunova and Yu.M. Polukarov, *Electrocrystallisation of alloys*, in Electrodeposition of alloys, V. A. Averkin Ed., Israel Program for Scientific Translation, Jerusalem (1964); p. 29.

[3] N. P. Fedot'ev and P. M. Vyacheslavov, *Plating*, **57**, 700 (1970).

[4] L. Haiying, M. Chikazawa and T. Watanabe, *J. Japan Inst. Met.*, **63**, 474 (1999).

[5] F. Simon, K. Leyendecker and F. Glaser, *Proceed. AESF 2000*, AESF Sur. & Fin. 2000, Chigaco, Illinois; p. 360.