# Electrodeposition of Intermetallics of Ag, Cu and Au with Sn

P. L. Cavallotti, M. Bestetti, L. Magagnin, L .Nobili, A. Vicenzo Dip. Chimica Fisica Applicata – Politecnico Milano Via Mancinelli,7 – 20131 Milano, Italy

Intermetallic phases obtained by electrodeposition can be different from those obtained by metallurgical methods. A typical case regards IB metals with tin.

We studied the electrodeposition of silver, copper and gold alloys with tin from different baths, in order to understand the rules under which the different intermediate phases crystallize.

In the case of the Ag-Sn system only one intermetallic phase is obtained from different baths, of approximate composition  $Ag_3Sn$ , interpreted as an hexagonal close packed structure with c/a different from the metallurgical stable phase.

For Cu and Au with Sn more intermediate phases are obtained: of these one is rich in Cu or Au, and may be attributed to an HCP phase; near equiatomic composition, a phase of the NiAs type is obtained, similar to the well known NiSn intermetallic phase; in the case of gold more intermetallics rich in tin are also obtained.

The different behavior of these system is simply related to the sign of the enthalpy change for alloy formation.

The differences from metallurgical system are related to the disappearing influence of long range order and to the vanishing effect of atomic size factor for electrochemical systems, giving as a result phases of higher symmetry.

## For more information, contact:

P. L. Cavallotti Dip. Chimica Fisica Applicata – Politecnico di Milano Via Mancinelli,7 - 20131 Milano, Italy

Phone:	+39-02-23993149
FAX:	+39-02-23993180
E-mail:	pietro.cavallotti@polimi.it

#### Introduction

Electrodeposited silver and copper alloys with tin show peculiar properties, making them of great interest for both technical and theoretical reasons.

Copper and silver display low tarnishing resistance under exposure to sulfide containing environments. Silver forms a dark sulfide coating, under ordinary atmospheric conditions, in the presence of sulfur oxide even in small quantities. This film grows in a short time and its removal is not easy nor rapid <sup>1</sup>. This is a point of major concern when single metals are used for electronic applications, where contact reliability and solderability are mandatory. Silver-tin alloys show substantially higher tarnish resistance than pure silver<sup>2</sup>. Furthermore, silver shows poor mechanical properties, which make it unsuitable for applications where hardness and wear-resistance are required.

Both electrodeposited silver and copper alloys are attractive materials for decorative finishing. Besides, tin-silver is very interesting as a possible alternative to lead based soldering materials. Gold-tin electroplated alloys, of near eutectic composition, could find straightforward use as hard solder for chip bonding. Furthermore, the improved mechanical properties of these alloys, compared to the single metals, could make them eligible materials for applications were hardness and wear resistance are properties of concern.

The theoretical interest in these electrodeposited alloys arises from their structural properties. The observed crystal structures are often metastable, being supersaturated solid solutions or phases out of their stability field, at ordinary temperature, or possibly unknown phases, which do not compare at all in the equilibrium diagram.

In this work, which is a preliminary investigation into the structural properties of this class of pseudo-ordered electrodeposited alloys, IB group metals with tin, with special emphasis on silver -tin deposition, new evidence is found for the intrinsic irreversible behavior during alloys electrodeposition, which does not make it possible to obtain equilibrium phases such intermetallics and superlattices; in addition, the suitability of the Engel-Brewer rules for metal alloying<sup>3</sup> to interpret the observed phases is discussed.

#### Experimental

Plating solutions were prepared from analytically pure chemicals and double distilled water. Silver-tin alloy electrodeposition was carried out by direct or pulse current plating from the following base electrolyte:

Ag	0.05M
Sn	0.017M
Thiourea	2M
Rochelle salt	0.018M
Sulfamic Acid	

Tin was added as sulfate, silver as sulfamate salt. The bath was operated at room T, without stirring.

Copper - tin alloys with either low, less than 9%, or high, above 50%, Sn content, were obtained from an acid methanesulfonate electrolyte with the following composition:

Cu	0.5M
Sn	0.85M
CH <sub>3</sub> SO <sub>3</sub> H	1.5M
Acid	

The bath was operated at room T, with direct current in the range  $10\div20 \text{ mA/cm}^2$  and without stirring.

Brass sheets polished with 0.3  $\mu$ m alumina were used as substrate; before plating, they were slightly etched in dilute sulfamic acid, thoroughly rinsed in distilled water and dried with nitrogen.

Deposits phase structure was determined by X-ray diffractometry (XRD) with CuK $\alpha$  radiation and a powder goniometer. Surface morphology was investigated by Scanning Electron Microscopy (SEM, Cambridge Stereoscan 360). The composition of the deposits was measured by Energy Dispersion Spectroscopy.

#### Results

#### Silver – Tin Electrodeposition

Silver-tin deposits were obtained by electrodeposition from the given acid solution with direct current plating; they consist of only one silvertin intermetallic phase. When the current density was below or above the normal value, at which only the intermetallic phase is obtained, excess of Ag or Sn was obtained, respectively (see Figure 1). The composition of the intermetallic phase is almost stoichiometric with Ag to Sn atomic ratio 3:1.



Figure 1: XRD patterns of Ag<sub>3</sub>Sn samples with Ag and Sn excess (upper and lower pattern, respectively), S brass substrate.



Figure 2: XRD pattern (above) and SEM micrograph (below) of  $Ag_3Sn$  pulse plated from  $Ag\sigma$  0.05M,  $SnSO_4$  0.02M, Thiourea 2M, pH 1, 25 °C; pulse on-time 0.5 s, pulse off-time 1 s and 25 mA/cm<sup>2</sup>.

This result is in agreement with the early findings of Leidheiser and Ghulam<sup>4</sup>, who reported the cathodic formation of such silver-tin mixed phase or, in their opinion,  $Ag_3Sn$  intermetallic compound by pulse

plating from a stannate-cyanide bath. The phase identification as the intermetallic compound  $Ag_3Sn$  was based on the observed quasi-stoichiometric composition.

Stirring of the electrolyte shows a strong influence on the deposit composition: intermetallic phase deposition is shifted towards higher current density or even completely inhibited. The intermetallic composition and structure is more easily obtained with pulsed current; typical conditions are on-time 0.5 s with current density 25 mA/cm<sup>2</sup> and off-time 1 s without current.

Figure 2 shows the x-ray pattern and the surface morphology of a silver–tin deposit of atomic ratio near to the exact value 3:1 and very low tin excess. While the metallurgical intermetallic compound of narrow composition range, also known as  $\varepsilon$  phase, crystallizes with an orthorhombic lattice, in the case of the electrodeposit the crystal structure is clearly hexagonal close packed, similar to the metallurgical  $\zeta$ phase Ag<sub>4</sub>Sn, but with different composition.

The lattice parameters of the ECD sample with hexagonal close packed structure are:

a = 0.2984 nm c = 0.4782 nm

with axial ratio c/a 1.603.

Table 1 lists the lattice spacings of ECD  $Ag_3Sn$ , either as electrodeposited on a brass sheet or as a powder (obtained by deposition onto stainless steel and subsequent detachment), and of the metallurgical hcp  $\zeta$  phase of  $Ag_4Sn$  composition.

Table 1: Lattice spacings d (Å) for ECD Ag<sub>3</sub>Sn (film and powder samples) and the  $\zeta$  phase<sup>5</sup>.

[hkl]	ECD Ag <sub>3</sub> Sn	ECD powder	ζ phase Ag <sub>4</sub> Sn	[hkl]
[100]	2.583	2.585	2.568	[100]
[002]	2.390	2.393	2.391	[002]
[101]	2.272	2.275	2.263	[101]
[102]	1.7543	1.756	1.7501	[102]
[110]	1.4875	1.494	1.4829	[110]
[103]	1.3563	1.357	1.3545	[103]
[200]	1.2914	1.292	1.2842	[200]
[112]	1.2639	1.266	1.2602	[112]
[201]	1.2467	1.247	1.2403	[201]
[004]	1.1947	1.196	1.1956	[004]
[202]	1.1360	1.137	1.1314	[202]
[104]	1.0837	1.085	-	[104]
[203]		1.0043	1.0001	[203]

For the metallurgical  $\zeta$  phase of composition Ag<sub>4</sub>Sn the hcp lattice parameters are, according to King and Massalski<sup>5</sup>:

$$a = 0.2966 \text{ nm}$$
  $c = 0.4782 \text{ nm}$ 

with axial ratio c/a 1.612.

Table 2 lists the relative intensity of the XRD peaks of Table 1 for ECD Ag<sub>3</sub>Sn and hcp  $\zeta$  phase).

The identification of the intermetallic phase as hcp Ag<sub>3</sub>Sn is consistent with the results of lattice spacings change with electron concentration for the Ag-Sn hcp  $\zeta$  phase reported by King and Massalski<sup>5</sup>. In fact, being 1 and 4 the valencies of Ag and Sn, respectively, the electron/atom e/a ratio in Ag<sub>3</sub>Sn alloy is 1.75. The extrapolation of the lattice spacing data, reported by the above authors, to the Ag<sub>3</sub>Sn value e/a = 1.75 gives for c/a a value in the range 1.595  $\div$  1.600, quite in good agreement with the obtained value for the ECD intermetallic.

In order to establish more firmly this findings, ECD Ag<sub>3</sub>Sn samples with hcp structure were heat treated at 250°C for 2 or 4 hours. The X-ray diffraction patterns clearly show the appearance of an hcp intermetallic phase Ag<sub>4</sub>Sn, containing more silver (peaks on the right near to the original ones). The lattice parameters change; for the as-plated material, we have a = 0.2984 nm and c = 0.4782 nm; after heat treatment at 250°C for 4 hours, the following values are obtained, a = 0.2966 nm and

c = 0.4782 nm; correspondingly, the axial ratio of the hcp phase changes from the starting value c/a = 1.603 to 1.612, i.e. the axial ratio of Ag<sub>4</sub>Sn, according to King and Massalski<sup>5</sup>.

[hkl]	ECD Ag <sub>3</sub> Sn	ECD powder	ζ phase Ag <sub>4</sub> Sn	[hkl]
[100]	6	24	25	[100]
[002]	72	38	27	[002]
[101]	100	100	100	[101]
[102]	27	15	13	[102]
[110]	3	10	13	[110]
[103]	36	14	13	[103]
[200]	2	2	2	[200]
[112]	11	11	13	[112]
[201]	2	7	9	[201]
[004]	3	3	2	[004]
[202]		2	2	[202]
[104]	4	2		[104]
[203]			4	[203]

Table 2: XRD relative intensity for ECD Ag<sub>3</sub>Sn with Sn excess (film and powder samples) and the ζ phase.



Figure 3: XRD patterns of as plated hcp  $Ag_3Sn$ sample (A), and after heat treatment at 250°C for 2h (B) and 4 h (C).

Knoop microhardness HK measurements on both Ag<sub>3</sub>Sn and Ag coatings show a noticeable hardness increase for the intermetallic phase. Ag<sub>3</sub>Sn coatings with Sn excess, 15  $\mu$ m thick, obtained by pulse plating with cathodic current (3s at 1 mA/cm<sup>2</sup> and 0.3s at 15mA/cm<sup>2</sup>) and Ag coatings, 30  $\mu$ m thick, electrodeposited from the same bath at 1mA/cm<sup>2</sup>, both on Ag 999 substrate, were tested with a load of 0.5N. Intermetallic phase showed a 150HK value, whilst Ag value was 75HK.

Sulfidation tests on electrodeposited Ag and Ag-Sn coatings on silver were performed according to UNI EN ISO 4538:1998 standard (TAA test). Specimens were exposed to thioacetamide (50 mg/dm<sup>2</sup>) fumes in a glass chamber with relative humidity 75 %, in the presence of a saturated Sodium Acetate solution (CH<sub>3</sub>COONa 3H<sub>2</sub>O / H<sub>2</sub>O ratio equal to 3/1), at 25 °C. Silver coated with 10 µm electrodeposited silver, sample A, and silver coated with 5 µm silver-tin electrodeposit (sample B) show significant differences: sample A is yellowing after two hours exposure time, then it tarnishes and darkens rapidly, while sample B turns to yellow after 8 hours exposure. Tarnish films after seven days exposure to sulfide containing environment, were analyzed by X-ray diffraction, showing that Ag<sub>2</sub>S growth is characteristic of pure silver (sample A), while a very thin  $Ag_2S$  film is formed on sample B<sup>6</sup>.

#### Copper – Tin Electrodeposition

Copper–tin alloys were electrodeposited from an acid methanesulfonate bath. Its behavior during electrodeposition was not completely characterized, especially for what regards the current density–deposit composition relationship. However, two main operating fields were observed: at low current density, below 15 mA/cm<sup>2</sup>, coatings have a low tin content, less than 10%; at high current density, tin content in the deposited layer is greatly increased, in the range of 50%.

This result suggests that the high tin content alloy is actually being deposited in condition near to the limiting current density for copper, as it is the case in many electrodeposited binary alloys, when alloying is made with metals of lower nobility  $^{7}$ .

Figure 4 shows the XRD patterns of three samples obtained at 10 (sample A), 15 (B) and 20 (C) mA/cm<sup>2</sup>. At 10 mA/cm<sup>2</sup>, deposits with a low tin content, <5%, are obtained; SEM investigations show a discontinuous layer with large flat grains (see Figure 5). Crystal size is very low as it is difficult to observe crystalline features even at high magnification. At 15 mA/cm<sup>2</sup>, compact and continuous deposits are obtained, with tin content 8-9%, and similar properties for what regards structure and morphology (see Figure 6).



Figure 4: XRD patterns of copper-tin coatings obtained at 10 (A), 15 (B) and 20 (C) mA/cm<sup>2</sup>.

At low current density an increase of the fcc lattice parameter is observed, as a consequence of Sn dissolution in Cu, giving a supersaturated  $\alpha$  solid solution; lattice parameter was a = 0.363nm and 0.365nm respectively. A peak is observed of high *d*, which cannot be attributed to any copper-tin



Figure 5: SEM micrograph of a CuSn (4%) sample obtained at 10 mA/cm<sup>2</sup>.



Figure 6: SEM micrograph of a CuSn (9%) sample obtained at 15 mA/cm<sup>2</sup>.



Figure 7: SEM micrograph of a CuSn (56%) sample obtained at 20 mA/cm<sup>2</sup>.

equilibrium phase and could correspond to a hcp (10.0) plane; the c/a ratio is near to the theoretical value of 1.633 and the other peaks could be interpreted according to either fcc or hcp planes.

At higher current density, the tin content increases up to about 55% at 20 mA/cm<sup>2</sup>, and a drastic change of structure occurs (see Figure 4, pattern C). Surface morphology changes as well, showing large flattened hemispherical grains (see Figure 7). This structure can be identified as  $\eta$ -phase<sup>8, 9</sup>, that at high temperature in the phase diagram corresponds to the composition Cu<sub>6</sub>Sn<sub>5</sub>. The structure is of the NiAs type, with deposit composition near to Cu<sub>3</sub>Sn<sub>2</sub>. The structure shows the following lattice constants:

a = 0.420 nm c = 0.509 nmand axial ratio c/a = 1.212.

In the case of powdery deposits an increase of lattice parameters was observed to the values:

a = 0.425 nm c = 0.510 nm

with axial ratio c/a = 1.21.

This intermetallic phase corresponds to the high temperature pseudo-hexagonal base of the  $\eta$ -Cu<sub>6</sub>Sn<sub>5</sub> metallurgical phase, but do not show the many small peaks of the monoclinic enlarged structure, which is obtained at low temperature with an order-disorder transformation. At higher thickness, growth structure develops into a very strong [101] preferred orientation (see Figure 8).



Figure 8: XRD pattern of a CuSn (55%) deposit with very strong [101] preferred orientation.

## Gold – Tin Electrodeposition

Gold-tin alloys<sup>10</sup>, electrodeposited from acid gold-tin electrolytes of Au III, show a similar behavior, with formation at increasing current density of supersaturated fcc gold solutions, hcp phase of Au<sub>5</sub>Sn composition, and the Au<sub>3</sub>Sn<sub>2</sub> intermetallic phase of NiAs structure in the sequence. XRD pattern for the last structure is presented in Figure 9. Interplanar spacings of this structure are very near to the metallurgical spectrum presented as ASTM 8-463, only the peak intensities show some variations. In this case the lattice constants are:  $a = 0.432 \text{ nm} \qquad c = 0.552 \text{ nm}$ with axial ratio c/a = 1.278. For ECD Au<sub>3</sub>Sn<sub>2</sub> alloy, the lattice constants are:  $a = 0.430 \text{ nm} \qquad c = 0.548 \text{ nm}$ with axial ratio c/a = 1.277.



Figure 9: XRD pattern of gold-tin deposit with hcp, NiAs-type structure.

## Conclusions

Electrodeposited alloys of group IB metals with tin show peculiar crystal structures, which are a striking evidence of the determining role played by electrochemical super-saturation in giving out-of-equilibrium phases.

Copper-tin and gold-tin alloys deposited from acid baths show a similar trend, with formation of Cu or Au as fcc supersaturated solution with tin. The first intermetallic is Cu<sub>5</sub>Sn or Au<sub>5</sub>Sn of hcp structure with c/a near to the theoretical 1.633 value of exact closely packed structures. The second intermetallic is Cu<sub>3</sub>Sn<sub>2</sub> or Au<sub>3</sub>Sn<sub>2</sub> of NiAs hcp structure with low c/a value.

The silver-tin system behaves quite differently with only one hcp intermetallic Ag<sub>3</sub>Sn.

The s+p electron on atom ratio e/a for these intermetallics can be calculated attributing 1 s+pelectron to Cu, Ag and Au, 4 s+p electrons to Sn. We obtain the following values: e/a is 1.5 for Cu<sub>5</sub>Sn and Au<sub>5</sub>Sn; 2.2 for Cu<sub>3</sub>Sn<sub>2</sub> and Au<sub>3</sub>Sn<sub>2</sub>, 1.75 for Ag<sub>3</sub>Sn. These values are different from those observed for metallurgically stable phases, observed in the phase diagrams even at high temperature.

Hume-Rothery <sup>3</sup> showed that the structure of intermetallic compounds depends on the number of s+p electrons per atom. Engel and Brewer <sup>3</sup> correlated the number of unpaired s+pelectrons with the crystal structures: <1.5 s+pelectrons corresponds to body centered cubic (BCC); 1.6 to 2.1 s+p-electrons to hexagonal closed packed (HCP); >2.5 s+p-electrons to face centered cubic structure (FCC).

Also in the case of electrodeposited alloys the number of s+p unpaired electrons seems to play a special role, determining the intermetallic phase obtained. In the case of electrodeposition, of the two most important factors determining the alloy structure, i.e. relative atomic size and difference of electronegativities, it is the second one to prevail, giving structures not observed in metallurgical diagrams. The NiAs phase observed for Cu-Sn and Au-Sn systems is similar to the phase observed for Ni-Sn and Co-Sn systems; there is however a difference for what regards the composition and this difference can be related to the need of maintaining similar e/a ratio.

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