

Metastable phases by alloy electrodeposition

P.L. Cavallotti, L.Nobili, A.Vicenzo

Dip. Chimica Materiali e Ing.Chimica G.Natta

Politecnico di Milano

Via Mancinelli, 7 - 20131 Milano, Italy

By electrodeposition it is possible to obtain alloy phases of metastable structure; these phases can be different from those reported for metallurgical equilibrium conditions or can have different compositions for the solubility limits, in some cases with very important enlargements. Typical cases are examined, discussing published results and presenting new findings. To understand the general behavior, free energy versus composition G/x diagrams were calculated and are presented for the alloys examined in equilibrium conditions and after modification to obtain the composition limits for the electrodeposited ECD alloys phases in stable and metastable state.

The first reported case regards Ni-Sn alloys, where the well known metastable phase NiSn is obtained and another one is claimed.

The second case is the electrodeposition of IB-tin alloys from non-cyanide electrolytes, containing thiourea as a strong ligand.

ECD Ag-Sn alloys are obtained with fcc, hcp or β -Sn crystal structure, with exclusion of the ordered intermetallic phase. G/x curves explain the change of composition for the hcp ECD alloy as a consequence of the ordered phase exclusion. Mechanical properties and thermal stability of ECD alloys are also related to the phase structure.

ECD copper-tin alloys from simple acidic solutions with thiourea as ligand are characterized by the following structure sequence: fcc, hcp, cubic, pseudo-hexagonal NiAs type and β -Sn, at increasing Sn content into the deposits. The hcp phase is obtained only depositing Cu-Sn alloys from aqueous or vapor phase; also in this case elimination of ordered intermetallics from the G/x curves permits an interpretation of the behavior.

The sequence of structures for Au-Sn ECD alloys is fcc, a faulted hcp and a NiAs phase at AuSn; the two ordered phases β and ζ' are not observed.

Zn-Ni ECD alloys change their structure depending on the electrolyte. A greatly increased solid solubility of Ni in ECD Zn was claimed. Our interpretation, based on G/x curves, is that the free energy of the gamma phase Ni_3Zn_{21} is increased, because a surface energy contribution from grain boundaries must also be included. The following relation is assumed

$$* g^\gamma = g^\gamma + 3 \frac{V_m}{d} \sigma, \text{ where } g^\gamma \text{ is the bulk free energy,}$$

V_m the molar volume, σ the specific surface free energy of grain boundaries and d the grain size. The importance of the correction depends on the electrolyte and on the deposition conditions.

The very high increase of solid state solubility for Pb, Sb and Bi in ECD binary copper alloys is examined. To interpret this enhancement we must take into account not only the stability of the Cu fcc structure with the dissolved elements, but also nucleation and

dispersion of the new phase.

From the different cases examined, the occurrence of ECD intermediate phases can be interpreted according to a local thermodynamic equilibrium, whilst long range order is difficult to observe in as deposited layers. These phases depend on bath composition and operation conditions (T, stirring, cd, pulse) giving phases of different grain size; a low grain size can increase the free energy G of a phase influencing its stability.