

Electrodeposition of tin alloys. Effect of ligands and surface-active substances

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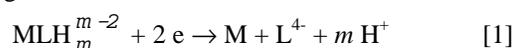
INTRODUCTION

Electrolytic deposition of tin and its alloys has found an extensive application in modern electroplating. Some outstanding properties of tin such as nontoxicity, high corrosion resistance and a good solderability are characteristic of most tin alloys. Optimal conditions for codeposition of two metals may be achieved using ligands or surface-active substances (SAS). Properly chosen ligands make it possible to bring closer the equilibrium potentials of the metals. The rate of codeposition may be also controlled through the certain SAS that exert a selective influence on the partial electrode processes.

CODEPOSITION OF TIN AND COBALT FROM CITRATE SOLUTIONS

As has been shown in (1), the equilibrium potentials of Sn|Sn(II) and Co|Co(II) electrodes come close in citrate solutions in which Sn(II) is properly complexed and the major part of Co(II) exists in the form of aqua-ions. Such solutions should contain no excess of ligand in a slightly acid media.

Two species containing Sn(II), i.e., SnLH⁻ and SnL²⁻ (L⁴⁻ is an anion of citric acid), may be treated as electrically active complexes (EAC) taking part in the charge transfer process. At the same time, CoLH⁻ was found to take part in the partial process of Co(II) reduction. The mentioned above partial processes may be given in general form:



where M²⁺ is Sn²⁺ or Co²⁺, *m* is equal to 0 or 1 for Sn(II) reduction and *m* = 1 for Co(II) reduction. It follows from the well-known kinetic equation at sufficiently high cathodic overvoltages (η) that

$$\log(i/c_s) = \log i_0 - \log c_b + \alpha nF/2.303 RT \eta, \quad [2]$$

Surface concentrations (*c_s*) of EAC given on the left side of Eq. [1] were obtained on the basis of the theoretical model which describes the mass transport of chemically interacting species (2). Linear Tafel plots normalized to the *c_s* were constructed using experimental data and model simulations. Partial voltammograms simulated with established by [2] kinetic parameters (exchange current densities *i₀* and a charge transfer coefficients α) fairly well coincide with respective experimental data.

Sn-Co coatings were deposited at pH 4-5 with amounts of Co ranging from 15 to 86 mass %. Bright deposits were obtained when the content of Co exceeds ca 76 %. According to the XRD data, these coatings may be considered as solid solutions of tin in α -Co and β -Co. The β -Sn phase is predominant in the case of coatings containing less Co.

CODEPOSITION OF TIN AND COPPER FROM SOLUTIONS INVOLVING LAPROL 2402 C

Bronze coatings of high quality may be deposited from solutions involving laprol 2402 C as SAS (3). This compound constitutes a product of copolymerization of ethene and propene oxides with molecular mass ca 3200. According to EIS data, laprol exhibits different adsorption behaviour on Cu, Sn and bronze substrates. Nyquist plots obtained for Cu in 0.6 M H₂SO₄ involve

arcs centered below abscissa axis. An addition of laprol up to 0.1 g dm⁻³ has no significant effect on both impedance and voltammetric characteristics. Similar weak adsorption was found to be typical of bronze substrate.

Quite different effects were established for Sn substrates. Even a 1 mg dm⁻³ of laprol gives rise to the 10-fold decrease in double layer capacity as compared with that in SAS-free solution. At the same time, the shape of Nyquist plot changes from line to semicircle. The rate of Sn(II) reduction also decreases with laprol concentration arriving at the state when the current density becomes independent on forced convection intensity. The most pronounced inhibition effects were found to occur in solutions involving both Cu(II) and Sn(II). A deep voltammetric minimum appears at ca -0.4 V (SHE) where the Sn(II) reduction becomes possible. A negative impedance was obtained in the region of negative slope of voltammogram. Strong inhibition effects seem to be conditioned by formation of adsorption layers involving laprol and intermediate products of Sn(II) reduction.

REFERENCES

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