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The influence of sulfate ions on the electrodeposition of Ni–Sn alloys from acidic chloride–gluconate baths

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ABSTRACT

Codeposition of nickel and tin from acidic gluconate baths of various compositions was investigated. It was found that cathodic process was seriously affected by sulfate ions resulting in lower nickel percentages in the deposits, changes in the phase composition as well as improved surface morphology of the alloys. Partial cathodic polarization curves have shown that tin ions were reduced under limiting current. Chronoamperometric studies indicated nucleation of the alloys according to the instantaneous mechanism. Anodic stripping analysis confirmed phase composition of the alloys – NiSn and Ni_3Sn_4 were formed in the chloride bath, while NiSn phase was produced in the presence of sulfate anions. It was accordant with thermodynamic predictions. Equilibrium speciation of the baths was also calculated.

1. Introduction

Ni–Sn alloys show excellent anticorrosive properties [1,2] having considerable technological interest. They are used alternatively to decorative chromium coatings [3], as a partial substitute of silver or gold in the printed circuit boards or as oil retaining surfaces in automotive industry [4]. Recently, the alloys have found new prospective application areas, especially as anode material in lithium ion batteries [5–7] or cathode substrate for hydrogen evolution [8].

Electrodeposition of Ni–Sn alloys was firstly described over seventy-five years ago [9] and the process was introduced to the industrial practice relatively fast. Initially, the alloys were obtained from alkaline cyanide–stannate baths, but then acidic fluoride–chloride electrolytes were patented and adopted successfully for the commercial plating [10]. Fluoride–chloride solutions are still predominantly used for electrodeposition of Ni–Sn alloys [4,10], since stable tin(II)-fluoride complexes are formed in such conditions [9]. However, hot fluoride baths are rather hard to operate due to corrosion problems caused by free hydrogen fluoride as well as requirement to use separate nickel and tin anodes working at different current densities [4,9]. Aggressive fluoride–chloride solutions may be replaced by less corrosive baths. Over the years, two types of the baths have been proposed: weak alkaline pyrophosphate solutions with glycine addition [5,9,11] and acidic chloride electrolytes [9,12], but to date no satisfactory substitute plating technology has been developed. Some studies on the Ni–Sn alloy electrodeposition from non-aqueous solutions have been also described [13].

It is interesting that Ni–Sn alloys characterize with multiphase compositions, which are often different from that observed in metallurgical material [9]. The alloys produced from chloride–fluoride solutions are mainly single phase equiatomic electrodeposits, while in other baths and at various nickel contents another intermetallic compounds can be created (e.g.: Ni_3Sn_2, Ni_4Sn, $NiSn_3$, $NiSn_9$) [10,14–16]. It is worth to note that proper identification of metastable NiSn phase in the deposits is difficult due to very similar diffraction patterns of Ni_3Sn_4 and Ni_3Sn_2 equilibrium phases [14,15]. It was found [17] that intermetallic NiSn phase deposited at direct current is stable over the years at ambient temperature, while that obtained under alternate (asymmetric) currents shows a phase transformation $NiSn \rightarrow Ni_3Sn_4 + Ni_3Sn_2$ in few days after deposition.

In recent years new kind of the baths for tin alloys electrodeposition has been proposed. Weak acidic or alkaline solutions contain sodium gluconate as a cheap and nontoxic complexing agent [18,19]. The aim of this work was to study the influence of sulfate anions on the codeposition of nickel with tin from acidic chloride–gluconate solutions at ambient temperature. Previous papers showed that sulfate ions can inhibit kinetics of the cathodic reactions and change the morphology of nickel [20] and tin [21,22] deposits obtained in the similar baths. The present paper describes

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the composition, structure and morphology of the Ni–Sn coatings obtained in the potentiostatic mode. Mechanism of the alloy nucleation and phase formation is also discussed.

2. Experimental

Electrodeposition of the alloys was carried out from acidic baths containing: 0.05 M $SnCl_2$, 0.1 M $NiCl_2$, 0.2 M $C_6O_7H_{11}Na$, 0.5 M H_3BO_3 as well as 0.5 M NH_4Cl or 0.5 M $(NH_4)_2SO_4$ in chloride or chloride–sulfate bath, respectively. pH of the solutions was 3.5. For comparison, additional measurements were performed using electrolytes deprived one of the metal salt. Reagents of analytical purity were used.

Electrochemical measurements were carried out in a three-electrode cell using glassy carbon working electrode (0.2 cm^2), a platinum plate (2 cm^2) as a counter electrode and an Ag/AgCl electrode as a reference electrode (all potentials in the further text are referred to this electrode). Potentiostatic deposition of the alloys was realized on brass substrates (10 wt% Zn; 0.8 cm^2). Before each experiment bright glassy carbon electrode was chemically cleaned in HCl, while brass sheets were chemically polished in a mixture of concentrated acids (HNO_3:H_3PO_4:CH_3COOH with 1:3:1 volume ratio). After deposition brass cathodes were dried at 60 °C to the constant mass. Solution volume of 25 cm^3 was used in each electrochemical test.

Various electrochemical techniques were used. Cyclic voltammograms were registered at potential scan rate of 20 mV/s. First CV sweep was always performed from the initial potential towards more negative values. Anodic stripping analysis (20 mV/s) was carried out immediately after potentiostatic deposition on glassy carbon substrate at fixed potential (10 or 60 s) without removing the working electrode from the solution. Stripping curves were registered from deposition potentials up to 0.5 V in un-agitated and agitated (magnetic stirrer, 500 rpm) baths. Nucleation stage was investigated using chronoamperometry realized at various constant potentials. Potentiostatic deposition was realized at fixed potentials at constant deposition time of 60 min. Autolab potentiostat/galvanostat (PGSTAT302N) controlled by a microcomputer was applied in all measurements. Experiments were performed at room temperature. No bath agitation was used, except as indicated.

Morphology of the layers was examined using scanning electron microscope (Hitachi). Average chemical composition of the deposits was determined by XRF analyzer (Rikagu). Analysis was carried out on the whole surface area of the sample. Additional analyses at various points on the surface as well as on cross-section of the selected deposits were also performed using EDS–SEM method. Structure of the deposits was analyzed by X-ray diffractometry (Rikagu diffractometer, Cu Kα radiation).

Equilibrium speciations of the baths used in this study were calculated using HySS2009 free software for stability complex constants adopted from adequate references.

3. Results and discussion

3.1. Distribution of species in the baths

Divalent tin and nickel cations can be present in aqueous solutions as free ions as well as neutral and/or charged complexes with chloride, sulfate or gluconate ions. Based on the mass balance of the individual ions and equilibrium quotients summarized in the previous papers [20,21] pH-dependent speciation of the baths was calculated and shown in Fig. 1. Equilibrium composition of the electrolytes is multifarious due to formation of a variety of metal species, especially of Sn(II). At pH 3.5 (used in this study) $NiGlu^+$ cations dominate in the chloride–gluconate bath (Cl–Glu), but Ni^{2+} and $SnGlu_2$ species of similar concentrations seems to be also in noteworthy fractions. Comparable concentrations of dominating $Ni(SO_4)_2^{2-}$ and $SnGlu_2$ complexes are expected in the bath with SO_4^{2-} addition (Cl–S–Glu bath). In this case, $NiGlu^+$ complex represents third main species in the electrolyte. In both solutions various chloride and hydroxyl complexes show rather small fractions of total metal amount. No precipitation of sparingly soluble hydroxides is predicted despite of low solubility products.

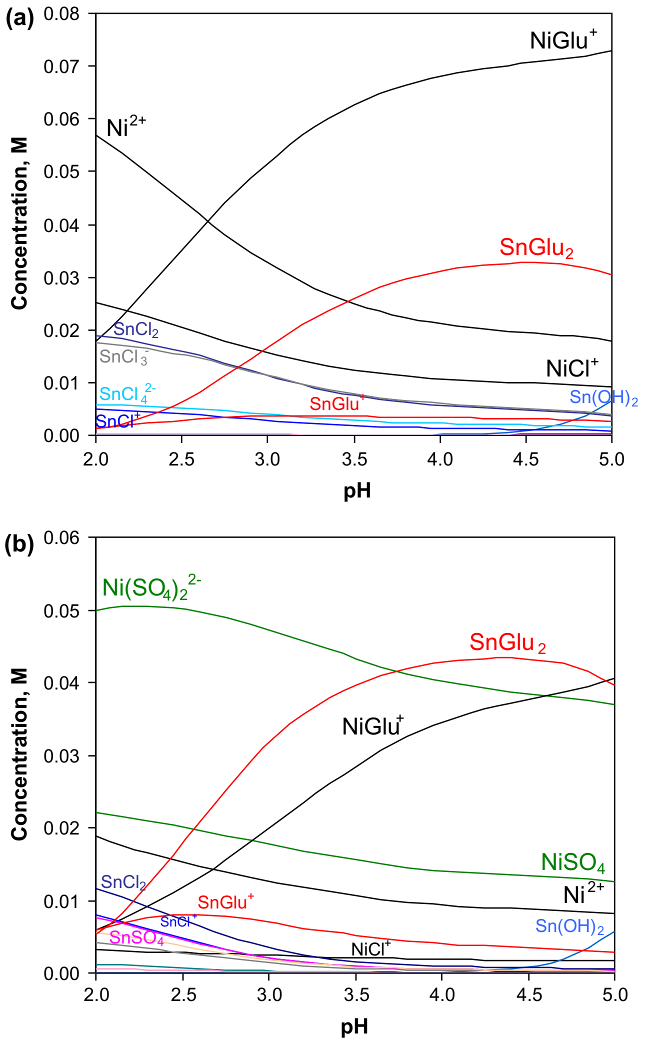

Fig. 1. Equilibrium distribution of Ni(II) and Sn(II) species in: (a) Cl-Glu baths, (b) Cl-S-Glu baths.

3.2. Cyclic voltammetry

Fig. 2 shows CV curves registered in one and two-component systems. It was observed that in both types of the solutions tin and nickel are deposited below −0.7 V and −1.0 V, respectively [20–22]. Dissolution of pure metals is represented by single anodic responses registered in the backward scans, i.e. at −0.45 V for Sn and −0.15 V for Ni. When nickel and tin cations are simultaneously present in the bath, kinetics of the deposition changes and the cathodic currents start to flow in the potential range between the values found for single metals. This leads to the formation of anodic peaks corresponding to the dissolution of tin or tin-rich phase and oxidation of a new phase at potentials different from that observed for pure metals. Anodic currents in the potential range of tin dissolution are seriously lower than these observed