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THE INFLUENCE OF POTENTIAL-CURRENT CONDITIONS ON THE ELECTRODEPOSITION OF Ni-Sn ALLOYS FROM ACIDIC CHLORIDE-SULPHATE SOLUTION

WPLYW WARUNKÓW POTENCJAŁOWO-PRĄDOWYCH NA WSPÓŁSADZANIE STOPÓW Ni-Sn Z KWAŚNEGO ROZTWORU CHLORKOWO-SIARCZANOWEGO

Ni-Sn alloys were electrodeposited from acidic chloride-sulphate solution in potentiostatic and galvanostatic conditions. Cyclic voltammetry and Hull cell were used for the selection of the appropriate deposition potentials and cathodic current densities, respectively. In the potentiostatic conditions (-1.0 – -1.2 V vs. Ag/AgCl) porous deposits (~7-10 wt% Ni) were obtained, while dense coatings (~15-34 wt% Ni) were produced in the galvanostatic conditions (0.5-1.5 A/dm²). In both cases, deposits consisted of β -Sn and Ni₃Sn₄ phases. Speciation of the bath was also calculated.

Keywords: electrodeposition, nickel, tin, alloy, speciation

Stopy *Ni-Sn* osadzano katodowo z kwaśnego roztworu chlorkowo-siarczanowego w warunkach potencjostatycznych i galwanostatycznych. Warunki elektrolizy wytypowano na podstawie pomiarów chronowoltamperometrycznych i testów w komórce Hulla. W warunkach potencjostatycznych (-1.0 – -1.2 V wzgl. Ag/AgCl) otrzymano warstwy porowate (7-10% mas Ni), natomiast w warunkach galwanostatycznych (0.5-1.5 A/dm²) tworzyły się warstewki zwarte (15-34% mas Ni). We wszystkich przypadkach uzyskano dwufazowe osady katodowe zawierające β -Sn i Ni₃Sn₄. Obliczono także rozkład form jonowych w stosowanej kąpieli.

1. Introduction

Electrodeposited Ni-Sn alloys show properties (e.g. hardness, chemical and tarnish resistance) that seriously excel features of pure nickel and tin, but simultaneously they are not the average of the properties of the individual components [1]. Ni-Sn alloys are used usually as corrosion protective [2, 3] and alternative to decorative chromium coatings [4, 5], a partial substitute of gold in the printed circuit board manufacturing industry or as oil retaining surfaces in automotive industry [5]. Recently, the alloys have found new application areas, especially as anode material in lithium ion batteries [6-8] or cathode substrate for hydrogen evolution [9].

Electrolytic deposition of Ni-Sn alloys (from alkaline cyanide-stannate bath) was firstly described in late 1930s [1]. Twenty years later, the basis for the present commercial plating was developed [10] and acidic fluoride-chloride baths operating at increased temperature (65-75°C) were introduced successfully to the industrial practice [1, 5]. Fluoride-chloride based solutions are still commonly used for Ni-Sn alloys electrodeposition [3-5, 8, 11, 12] due to formation of stable tin(II)-fluoride complexes. Such alloys contain approx. 65 wt%

of tin corresponding to NiSn intermetallic phase stable up to 320°C [5, 13]. They characterize with attractive rose-pinkish colour, high hardness and good corrosion and wear resistances. However, the fluoride baths are hard to operate due to corrosion problems caused by free hydrogen fluoride and necessity to use separate nickel and tin anodes working at various current densities.

Plating technology based on the aggressive hot fluoride-chloride electrolytes may be replaced by more friendly solutions, but to date no successful results have been obtained. Two kinds of the baths have been proposed: weak alkaline chloride-pyrophosphate solutions with glycine addition used at ambient temperatures [5-7, 9, 11, 13] or acidic chloride electrolytes [1, 14]. The aim of this work was to study the influence of potential-current conditions on the codeposition of nickel with tin from acidic chloride solutions containing sulphate anions. Previous works showed that sulphate ions can inhibit kinetics of the cathodic reactions and change the morphology of nickel [15] and tin [16] deposits produced from chloride-type baths. The present paper describes the composition, structure and morphology of the Ni-Sn coatings obtained in potentiostatic and galvanostatic modes.

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2. Experimental

Electrodeposition of alloys was carried out from the chloride-sulphate bath containing: 0.1 M NiSO₄, 0.05 M SnSO₄, 0.5 M NH₄Cl and 0.5 M H₃BO₃. pH was 1. 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 a brass (10wt% Zn) working electrode (0.2 cm²), a platinum plate (2 cm²) as a counter electrode and an Ag/AgCl electrode as a reference electrode (all potentials in the further text are referred to this electrode). Before each experiment brass sheets were chemically polished in a mixture of concentrated acids (HNO₃:H₃PO₄:CH₃COOH with 1:3:1 volume ratio). After deposition, cathodes were dried at 60°C to the constant mass. Solution volume of 25 cm³ was used in each electrochemical test.

Various electrochemical techniques were used. Autolab potentiostat/galvanostat (PGSTAT302N) controlled by a microcomputer was applied in all measurements. Cyclic voltammograms were registered at potential scan rate of 10 mV·s⁻¹. First CV sweep was performed from the initial potential below 0 V (vs. Ag/AgCl) towards more negative values to avoid substrate dissolution. Potentiostatic deposition was realized at various potentials at constant deposition time of 10 min. Galvanostatic method was also used for the study of the electrodeposition process. Hull cell was used to determine the range of the cathodic current densities for galvanostatic deposition (10 min). Measurements were performed at current intensity of 0.5 A for 10 min. using 0.2 dm³ of the bath. All experiments were performed at room temperature. No bath agitation was used.

Morphology of the layers was examined using both optical (Nikon) and scanning electron (Hitachi) microscopes. Chemical composition of the deposits was determined by XRF analyzer (Rikagu). Structure of the deposits was analyzed by X-ray diffractometry (Rikagu diffractometer, CuK_α radiation).

3. Results and discussion

3.1. Distribution of Ni(II) and Sn(II) species

In aqueous solutions of simple salts (chloride, sulphate), nickel(II) and tin(II) appear mainly as free ions or soluble complexes (hydroxide, chloride or sulphate type) with formulas dependent on the solution pH [17, 18]. Precipitation of sparingly soluble hydroxides is also observed. Fig. 1 shows pH-dependent speciation of the bath calculated for the ions concentrations used in this study. Equilibrium quotients assigned to the reactions considered in the calculations are compiled elsewhere [15, 16]. It was found that specific composition of the solutions in the pH range of 0-5 is rather complicated. In chloride-sulphate solution free Ni²⁺ ions dominate, while tin(II) is present mainly as SnCl₂ neutral complex up to pH 4. Various soluble hydroxy-complexes show negligible percentages of total metal concentration and no precipitation of metal hydroxides in the acid solution can occur in spite of low solubility products. Data presented for simple salt solution

do not show the possibility of tin(II) hydroxide precipitation. In fact, tin salts hydrolyze easily and in aerated solutions SnO₂ as a solid phase is expected by E-pH diagrams at pH above 2 [19].

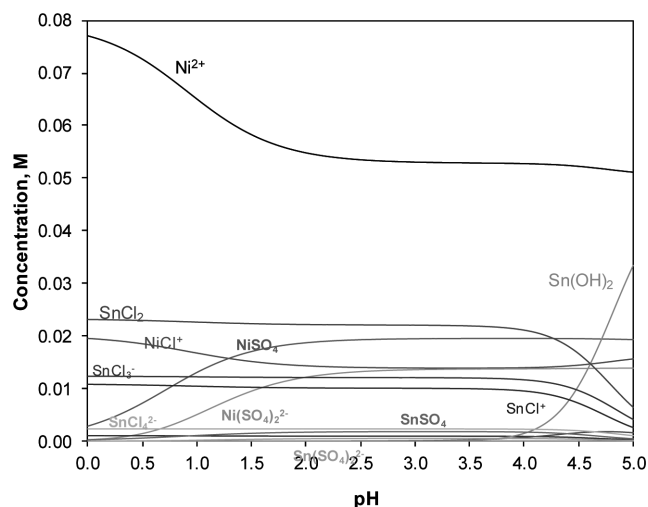


Fig. 1. Speciation of nickel-tin(II)-chloride-sulphate baths calculated for: 0.1 M Ni(II), 0.05 M Sn(II), 0.5 M Cl⁻, 0.15 M SO₄²⁻

3.2. Potentiostatic deposition

At the beginning of the studies, the cathodic potentials for Ni-Sn alloys deposition were selected according to the data obtained in the cyclic voltammetric measurements. Fig. 2 shows the CV curves registered in nickel, tin and nickel-tin solutions registered on the brass substrate. Deposition of pure tin was observed below -0.45 V vs. Ag/AgCl, while reduction of nickel ions starts below -0.90 V. The course of the CV curves in the nickel-tin system reflects the cathodic behavior of the individual metals and separated cathodic nickel and tin reduction peaks can be distinguished. However, the material of the cathode substrate could not allow to study anodic responses owing to anodic dissolution of the brass at potentials above -0.2 V.

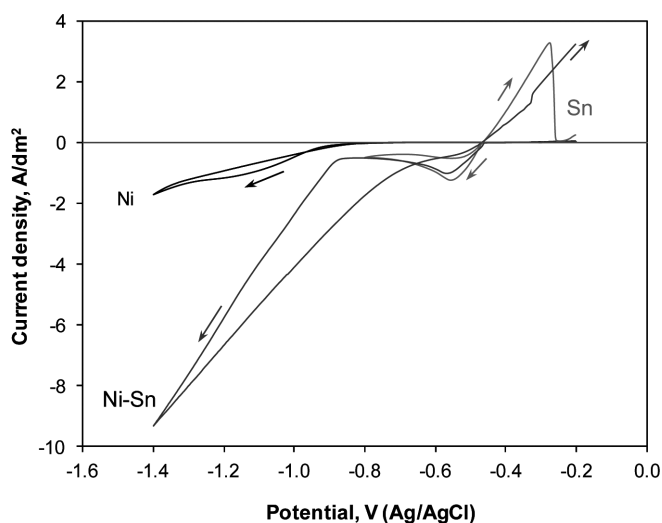


Fig. 2. CV curves registered in the nickel, tin and nickel-tin baths

Deposition Ni-Sn alloys was realized at potentials below -1.0 V due to nickel electrochemical characteristics. It was

found that more negative potentials enhanced nickel deposition, but the metal content was relatively low. For the potentials of -1.0V, -1.1V and -1.2V the alloys with 9.8 wt%, 8.9 wt% and 7.3 wt% of nickel were obtained, respectively. The results were consistent with the CV curves, since tin as more noble metal was deposited preferentially. Despite that nickel can produce alloys according to the anomalous type (i.e. weight percentage of the less noble metal in the deposit is higher than in the bath) [1], this is not the case, since at comparable weight percentages of nickel and tin ions in the bath (50 wt%) no favorable nickel deposition was observed.

Morphology of the alloys was observed using SEM microscope. Fig. 3 presents exemplary images of the deposits. It was found that in acid solution very porous, but stable and not loose, layers, were obtained. They consisted of long, dendritic grains. Such deposits are useless as protective layers, but can be favored as large-surface electrodes for lithium-ions batteries [8, 20].

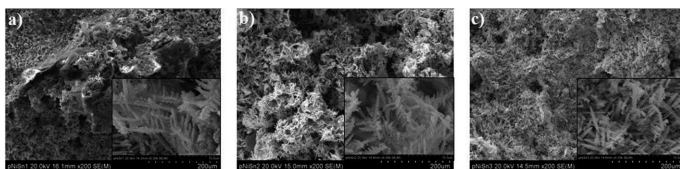


Fig. 3. Morphology of Ni-Sn alloys deposited from chloride-sulphate at various potentials: a) -1.0 V, b) -1.1 V, c) -1.2 V

X-ray diffraction analysis (data not shown) confirmed that the Ni-Sn alloys produced potentiostatically from the chloride-sulphate solution consisted mainly of Sn and Ni_3Sn_4 phases. No peaks for pure nickel were found. Comparison of the deposit total composition and the diffraction data allowed estimating that the deposits were the mixture of approx. 70% tin and 30% Ni_3Sn_4 phase. The results are only partly similar to that obtained in other porous Ni-Sn alloys (from alkaline chloride-pyrophosphate bath), where two phases NiSn and Ni_3Sn_4 were detected [20].

3.3. Galvanostatic deposition

Selection of the current densities for the galvanostatic deposition of Ni-Sn alloys were preceded by the tests carried out in the Hull cell. Results in Fig. 4 show that dense tin deposits can be produced only at very low current densities (up to approx. 0.5 A/dm^2), while at higher currents deposits with separated dendritic grains are formed. Nickel can deposit mainly as matt or semibright coating at current densities up to approx. 1.8 A/dm^2 . The appearance of the deposit obtained from the nickel-tin bath suggests that only at low current densities (below 1 A/dm^2) non-porous layers can be plated. Therefore, detailed studies on the galvanostatic alloys deposition were carried out at three current densities from the range of $0.5\text{-}1.5 \text{ A/dm}^2$.

It was observed that increase in the cathodic current affected the composition of the Ni-Sn alloys and for 0.5 A/dm^2 , 1.0 A/dm^2 and 1.5 A/dm^2 deposits contained 19.0 wt%, 34.4 wt% and 15.3 wt% of nickel, respectively. It was accompanied by the decrease of the current efficiency from approx. 57% for 0.5 A/dm^2 to 8% for 1.5 A/dm^2 . It seems to be consistent with the predictions from the Hull cell measurements,

since the increase in the current density was accompanied by the worsening the quality of the deposit suggesting diffusion limitation of the cathodic reactions.

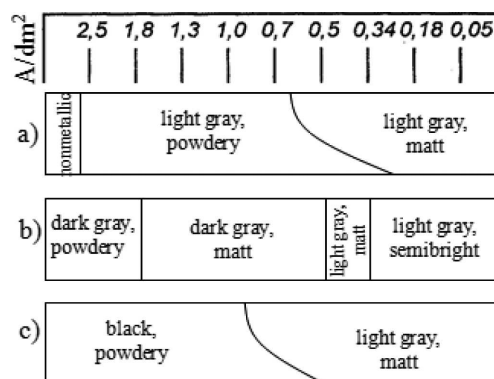


Fig. 4. Results of tests in the Hull cell: a) Sn, b) Ni, c) Ni-Sn

Fig. 5 shows morphology of the alloys. Relatively even coatings were obtained, no dendrites formation was found as it was observed previously for potentiostatic deposited alloys. However, the tendency for the increase of the surface roughness existed with increased current density. The layer consisted of cauliflower-like structures characteristic for nickel electrodeposits [15], while pure tin forms separate grains [16].

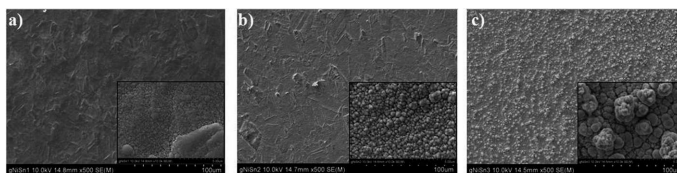


Fig. 5. Morphology of Ni-Sn alloys deposited at various current densities: a) 0.5 A/dm^2 , b) 1.0 A/dm^2 , c) 1.5 A/dm^2

Diffraction analysis (Fig. 6) confirmed that Ni-Sn alloys produced consisted of two phases $\beta\text{-Sn}$ and Ni_3Sn_4 , similarly to the earlier results.

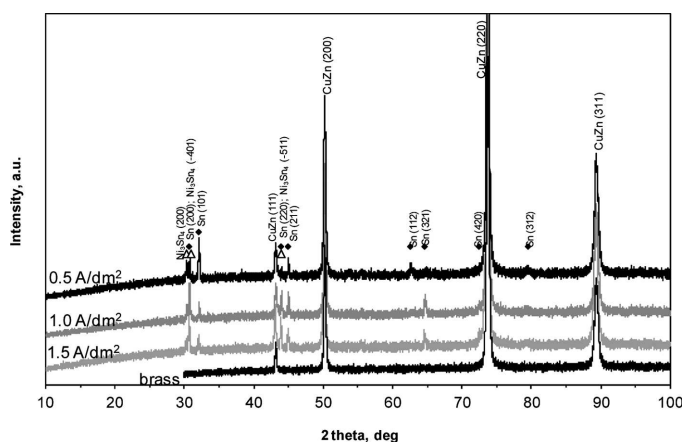


Fig. 6. X-ray diffraction patterns of Ni-Sn alloys deposited at various current densities

Comparison of the total deposit composition and the diffraction data allowed estimating that the deposits were the mixtures of 9-55% tin and 91-45% Ni_3Sn_4 phase.

3.4. Discussion of the results

Comparison of the data on the codeposition of nickel and tin from the acidic chloride-sulphate solution shows that the type of deposition mode seriously influences the composition and morphology of the produced layers, but not the phase composition.

It is known that simultaneous electrodeposition of two elements is determined not only by the equilibrium electrode potentials, but also by the cathode overvoltages. Despite that Sn(II) ions could exist in the form of various soluble chloride complexes, while free nickel ions dominated in the bath (Fig.1), tin deposition potential did not shift seriously towards more negative value of nickel electrode and two separated Sn(II) and Ni(II) reduction peaks were recorded in the CV curves (Fig.2). Codeposition potentials below -0.9 V (Ag/AgCl) enabled indeed simultaneous reduction of both metal ions, but the latter occurred under Sn(II) diffusion control. It resulted in low nickel incorporation and fabrication of tin based alloys of similar composition (approx. 9 wt% Ni). Total cathodic charge recorded during the potentiostatic plating corresponded to the current densities of 6-10 A/dm² calculated to the substrate area, but actual current densities were lower due to large development of the cathode area. In the consequence, porous deposits were obtained. This could be useful for electrochemical synthesis of metallic foams, which is a new field of electrodeposition application and represents a novel way of creating porous structures that allow fast transport of gas and liquid as well as rapid electrochemical reactions due to high surface area [20, 21].

Galvanostatic alloy deposition improved both nickel incorporation and quality of the coating. The process was carried out at low current densities, hence no serious diffusion limitations occurred during the plating. This shows that dense, tin-rich, Ni-Sn alloys can be plated from the organic additive-free simple salt solution.

Phase composition of the alloys was different from that obtained in typical chloride-fluoride solutions, where single phase electrodeposits (i.e. non-equilibrium NiSn) are detected [1, 13]. However, alloys of a range nickel contents deposited also from non-fluoride baths can consist of one or more phases, for example: NiSn, Ni₄Sn, NiSn₃ [10-13]. Deposits produced from the chloride-sulphate electrolyte represented a mixture of tetragonal tin and monoclinic Ni₃Sn₄ phases.

4. Conclusions

Electrodeposition of nickel-tin alloys from acidic chloride-sulphate bath was investigated. Type of the deposition mode (potentiostatic or galvanostatic) affected the metal percentages in the deposits and morphology of the layers, but not the phase composition. In the potentiostatic conditions

porous deposits with approx. 7-10 wt% Ni were produced, while dense coatings with 15-34 wt% Ni were obtained under constant current. In all deposits β -Sn and Ni₃Sn₄ phases were detected.

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