

Investigation of electrochemical behaviour of Co sulphide in nickel plating electrolyte

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The electrochemical behaviour of Co_2S_3 formed on glassy carbon in a colloidal solution of $\text{Co}(\text{OH})_3$ and/or $\text{CoO}(\text{OH})$ has been investigated in Watts nickel plating and Ni^{2+} -free background electrolytes by cyclic voltammetry and XPS methods. Analysis of experimental data has indicated that the electroreduction of Co_2S_3 in the Ni^{2+} -free background solution occurs to CoS , but not to metallic Co . After reduction the coating consists of Co_2S_3 and CoS . During the cathodic reduction of Co_2S_3 coating in Watts nickel plating electrolyte in the potential range -0.1 to -0.35 V, owing to an electrochemical reaction, conversion of Co_2S_3 to NiS takes place. When the potential is swept in the cathodic direction < -0.45 V the NiS is reduced to Ni on which nickel electrodeposition occurs. NiS is not completely reduced even at $E < -1.0$ V.

Key words: Co_2S_3 coating, Ni plating, cyclic voltammetry, XPS analysis

INTRODUCTION

Metal sulphides are applied as electroconductive layers for a direct metallization of insulating substrates. The non-stoichiometric copper sulphide Cu_{2-x}S was widely used for this purpose. Investigations of its electrochemical behaviour in electrolytes of nickel or copper plating as well as in supporting solutions have shown that metals can be directly deposited on sulphides only after a reduction of metal sulphide to the metal has occurred [1, 2].

Thin layers of cobalt sulphide have an advantage over a Cu_{2-x}S layer, because one cycle of deposition is necessary *versus* 3 to 4 cycles for a copper sulphide layer [3]. Co_2S_3 can be also electroplated by nickel, although the square resistance of Co_2S_3 is about 10^5 ohm/ \square lower than that of Cu_{2-x}S . In contrast to copper sulphide, nickel does not deposit on Co_2S_3 if it has been first electroreduced in a Ni^{2+} -free background electrolyte and then transferred to a nickel plating electrolyte. Electrodeposition of Ni on an ABS polymer activated by cobalt sulphide takes place by the propagation of primary and secondary Ni layers formed by different mechanisms [4]. Formation of the primary layer is attributed to Ni deposition reaction on cobalt sulphide clusters. The secondary layer is formed on the primary one by metal deposition on a metal substrate. A conclusion has been made that the reduction of cobalt sulphide to metallic Co is a ne-

cessary stage to induce the process of Ni electrodeposition [5]. However, the role of Ni^{2+} ions in the electroreduction of Co_2S_3 as well as the its electrochemical behaviour are not yet clear.

The purpose of this study was to investigate the processes occurring during the electroreduction of Co_2S_3 deposited on glassy carbon from a colloidal solution of $\text{Co}(\text{OH})_3$ and/or $\text{CoO}(\text{OH})$ in Watts nickel plating and the Ni^{2+} -free background electrolytes.

EXPERIMENTAL

Co_2S_3 coatings were deposited on a CY-1200 glassy carbon (GC) plate ($50 \times 15 \times 2$) polished with $1 \mu\text{m}$ diamond paste. Prior to formation of a Co_2S_3 layer the GC plate was covered with polyvinyl chloride lacquer (PVC-10) leaving a 1 cm^2 square unacquered, and the coating was deposited on the whole plate. Then the sulphidized lacquer was removed mechanically, and the same area was insulated again with the same lacquer. Only 1 cm^2 of the coating area remained electrochemically active.

The Co_2S_3 coatings on the GC were formed using the successive ionic layer adsorption and reaction (SILAR) method. First, the plates were immersed at ambient temperature for 3 min in a colloidal solution of $\text{Co}(\text{OH})_3$ and/or $\text{CoO}(\text{OH})$ allowing the colloidal particles to be adsorbed at a plated surface (ionic layer adsorption stage). Then, after rinsing the treated surface with distilled water, the plates were

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dipped for 1 min into a solution of ambient temperature containing 0.1 M Na_2S and 0.2 M NaOH (reaction stage) and again rinsed with distilled water. The whole cycle was carried out repeatedly for a required number of times for the Co_2S_3 layers to become thicker.

The colloidal solution of $\text{Co}(\text{OH})_3$ and/or $\text{CoO}(\text{OH})$ is an improved version of the so-called PLATO processes activation solution [3, 4]. Such solutions contain cobalt(II) sulphate, specific ligand for $\text{Co}(\text{II})$, ammonia and oxidizer.

The electrochemical measurements were performed in a standard cell in Watts electrolyte containing (M): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ – 1.2, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ – 0.2, H_3BO_3 – 0.5, or a Ni^{2+} -free background electrolyte at 20 ± 1 °C, using a PI-50-1 potentiostat, a PR-8 programmer and an XY RECORDER A3 potentiometer (Russia). The auxiliary electrode (platinum net) was separated from the working electrode by a glass filter. The electrode potential was measured with respect to an $\text{Ag} | \text{AgCl} | \text{KCl}_{\text{sat}}$ reference electrode. The values of electrode potential are quoted with respect to SHE.

The sulphide coatings were analysed by X-ray photoelectron spectroscopy. The XPS and Auger spectra were recorded by an ESCALAB MK II (VG Scientific, Great Britain) spectrometer using Mg K_α radiation (1253.6 eV, pass energy of 20 eV). Samples were sputtered in the preparation chamber by ionised argon at a vacuum of $6 \cdot 10^{-3}$ Pa and a current of $\sim 20 \mu\text{A} \cdot \text{cm}^{-2}$, which corresponded to an etching rate of $2 \text{ nm} \cdot \text{min}^{-1}$. The XPS and Auger spectra were recorded for Co, Ni and S. The binding energies were calibrated to the C 1s level of graphite at 284.6 eV. The empirical sensitivity factors of these elements were taken from [6]. The spectra obtained were compared with the standard ones [7].

RESULTS AND DISCUSSION

In Fig. 1, voltammograms recorded in Watts nickel plating electrolyte at pH 4.0 using a glassy carbon

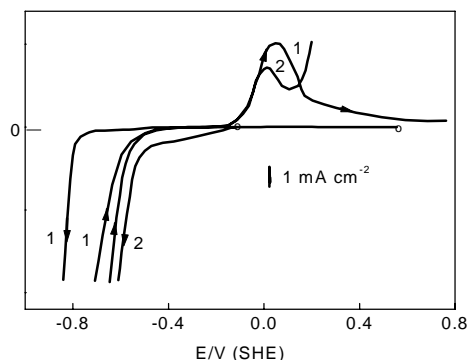


Fig. 1. Cyclic voltammograms (CVs) recorded in Watts Ni electroplating electrolyte at 20 °C for electrode: 1, glassy carbon (GC); 2, GC electroplated with 10 mm nickel. Sweep rate $5 \cdot 10^{-2} \text{ V cm}^{-1}$

(GC) electrode are presented. The potential was swept in the cathodic direction from its stationary value $E_s = 0.54 \text{ V}$ to -0.9 V and back in the anodic direction to 0.75 V (curve 1). For a GC electrode plated with a $10 \mu\text{m}$ Ni layer the potential was swept in the cathodic direction from $E_s = -0.11 \text{ V}$ to -0.9 V and back in the anodic direction to 0.2 V (curve 2). As is seen from the curves (Fig. 1), no current peaks are observed in the range of the cathodic potentials. The increase in the rate for a glassy carbon electrode at $E < -0.7 \text{ V}$, and for a GC electrode electroplated by Ni at $E < -0.45 \text{ V}$ can be attributed to nickel electrodeposition from the solution and H_2 evolution. In the anodic range, in both cases an anodic current peak emerges at $E > 0.05 \text{ V}$. The oxidation process of nickel deposited on the electrode during the cathodic sweep determines it [8].

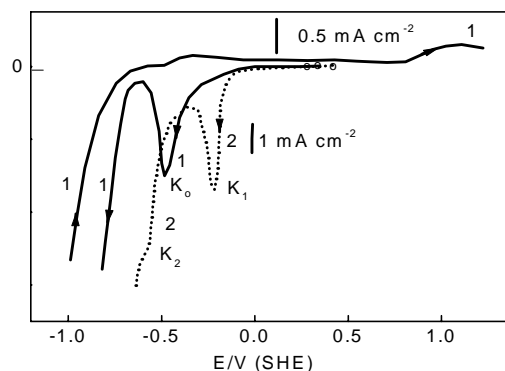


Fig. 2. CVs of Co_2S_3 formed by two deposition cycles on glassy carbon electrode and recorded in: 1, Ni^{2+} -free background electrolyte; 2, Watts Ni electroplating electrolyte. Sweep rate $5 \cdot 10^{-2} \text{ V cm}^{-1}$

In the case when the GC electrode is plated with a Co sulphide coating deposited in a Co (III) colloidal solution [3, 9], a cathodic peak K_0 emerges in the potential range -0.2 to -0.6 V in the CV recorded in the Ni^{2+} -free background electrolyte at pH 4.0. Its maximum potential depends on solution pH and with its increase shifts in the direction of more negative potential values (Fig. 2, curve 1). After cathodic sweep, when the potential is swept in the anodic direction to 1.3 V , no anodic peaks are observed; at $E > 0.85 \text{ V}$ a slight current increase, which may be related to the oxidation of non-reduced Co compounds, is observed [10, 11]. In the anodic region an oxidation current peak of metallic Co, which should be formed after reduction of Co sulphide compounds in the background electrolyte, does not emerge. This anodic current peak was observed in the CV in the potential range -0.4 to -0.6 V for Co sulphide coatings deposited in solutions of different composition [10, 11].

The analogous voltammograms are also recorded in other background solutions, for instance in 0.4 M NaCl or $1.2 \text{ M Na}_2\text{SO}_4$ solutions at pH 4.0.

The appearance of voltammograms changes in the case when Co sulphide formed on GC electrode is reduced in Watts nickel plating electrolyte at pH 4.0. In the CV cathodic current peak K_1 in the potential range -0.1 to -0.35 V and current shoulder K_2 , rather than a distinct peak, are observed at $E < -0.45$ V (Fig. 2, curve 2). The experimental data showed the size of the peaks to depend on the number of deposition cycles of Co sulphide coatings. The increase in Watts electrolyte temperature up to 50 °C does not induce any significant changes in the appearance of CV as well as in the areas of cathodic peaks K_1 and K_2 , however, the peaks mentioned are shifted by about 100 mV in the direction of more negative potentials.

The nature of the peaks emerged is not clear. It was presumed that the cathodic peak K_1 in the voltammograms could be determined by chemical interaction of cobalt sulphide coating with the components of Watts electrolyte. With this in mind, a Co sulphide coating was exposed to Watts electrolyte at 50 °C for 10 min, and after that it was reduced in the Ni^{2+} -free background electrolyte. The CV recorded was identical to that presented in Fig. 2, curve 1. The appearance of the curve did not change after exposure to Watts electrolyte, and cathodic peak K_1 did not emerge in the potential range -0.1 to -0.35 V.

The composition of Co sulphide coatings was studied by using the X-ray photoelectron spectroscopy method (XPS). Approximately 2 at. % Co, 18 at. % O, 15 at. % S were detected on the surface of non-reduced coating. A high quantity of C (59 at. %) was detected, presumably due to the fact that the surface of glassy carbon was not completely plated with Co sulphide coating. After the coating was etched with Ar^+ ions for 30 s, only up to 2 at. % O was detected in the layer at a depth of ~ 1 nm, however, higher quantities of Co and S were detected (about 20 and 34 at. %, respectively).

As the recorded Co $2p_{3/2}$ spectra in Fig. 3a illustrate, Co in the layer of a coating etched for 30 s is bound into two sulphides: Co_2S_3 and CoS, whose binding energies (BE) are 778.2 eV and 779.0 eV [12], the presence of $CoO(OH)$ with BE 781.1 eV [13] was also detected. Along with these compounds, elemental sulphur (BE = 163.9 eV) is present in the coating, as shown by S 2p spectrum in Fig. 3b. The ratio S/Co is equal to 1.7 in the layer etched with Ar^+ for 30 s. The fact that this ratio in Co_2S_3 is 1.5 shows that a small amount of elemental sulphur ($\sim 4\%$) may be present in the coating deposited in the colloidal solution of $Co(OH)_3$ and / or $CoO(OH)$. After etching into depth the ratio S/Co decreases to 1.2, which is indicative of CoS presence in the coating. Only about 2 at. % O present in the etched layer shows that adsorbed $CoO(OH)$ or other oxygen compounds are only formed on the surface of the coating.

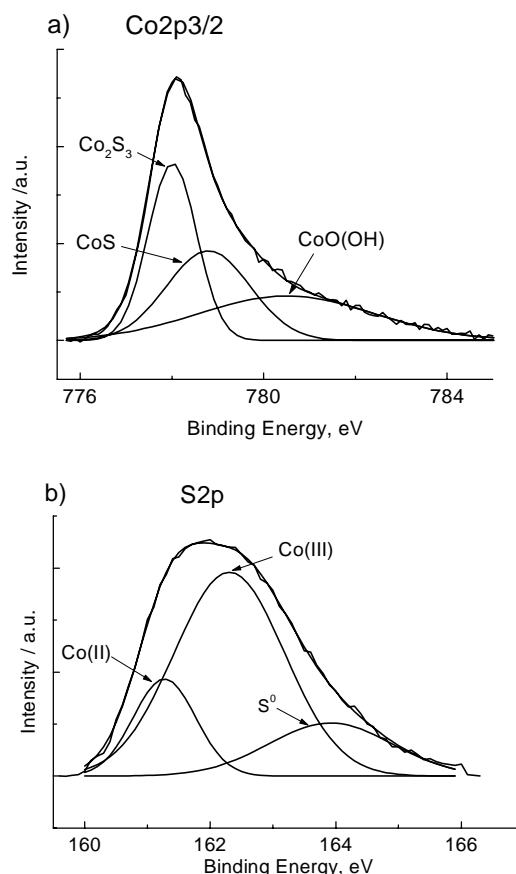
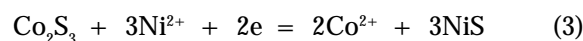


Fig. 3. X-ray photoelectron spectra of Co $2p_{3/2}$ (a) and of S 2p (b) for Co_2S_3 coating etched for 30 s

Studies of electrochemical behaviour of copper sulphide in Watts nickel plating electrolyte have shown that the cathodic peak emerging in the potential range -0.2 to -0.4 V is determined by reduction of elemental sulphur, and reduction of $Cu_{2-x}S$ occurs at the potential more positive than the potential of $Ni(II)$ ion reduction. Inasmuch as elemental sulphur in sulphide coating deposited in the colloidal solution of $Co(OH)_3$ and/or $CoO(OH)$ was also detected by the XPS method, it can be suggested that in the potential range -0.1 to -0.35 V of the cathodic current peak K_1 , S reduction can occur with formation of NiS :



Co_2S_3 is believed to be reduced in the potential range of the cathodic current peak K_1 along with elemental sulphur while reducing in the nickel plating electrolyte to -0.35 V:

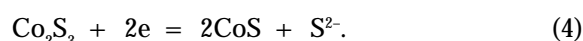


Therefore, during the cathodic potential scan to -0.35 V, reduction of Co_2S_3 and S occurs along with

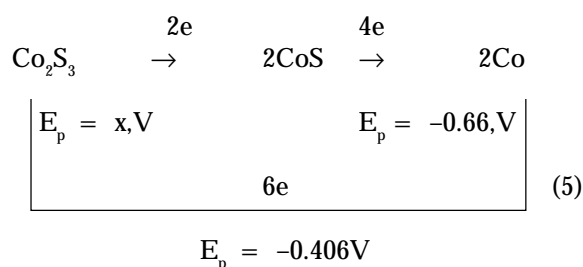
the formation of NiS (in the Ni $2p_{3/2}$ spectrum BE of 853.2 eV). The possibility of the reaction (3) is also supported by XPS analysis data. After the reduction, the quantity of cobalt in the coating decreased from ~20 at. % to ~5 at. % and nickel appeared (~19 at. %) while the quantity of S remained unchanged.

At $E < -0.45$ V, *i.e.* at the potential of the shoulder K_2 , supposedly reduction of the substances formed in the potential range of K_1 and Ni^{2+} ions from solution occurs.

A completely different situation occurs in the case when a Co sulphide coating is reduced in the Ni^{2+} -free background electrolyte. Then the reduction of Co_2S_3 proceeds according to reaction (4):



In the CV, the cathodic current peak K_0 (Fig. 2, curve 1) is supposedly determined by this process. The thermodynamical possibility of reaction (4) is supported by calculations of the equilibrium potential E_p according to scheme (5) [14]:



The value of the calculated $E_p = 0.104V$.

These propositions are partly supported by the XPS analysis of the Co_2S_3 coatings reduced in the Ni^{2+} -free background electrolyte sweeping the potential from the stationary value to -0.6 V (E range of peak K_0). The analysis data have shown that the coating consists of a mixture of CoS and Co_2S_3 . The ratio S / Co was ~2 on the surface of the coating, and it decreased when the coating was etched with Ar^+ ions: at etching time 10, 20 and 60 s the ratio S / Co is equal to 1.4, 1.02 and 0.9, respectively. A decrease in the ratio shows that after coating reduction in the Ni^{2+} -free background electrolyte to -0.6 V, CoS dominates in its deeper layers owing to reaction (4).

In Fig. 4, the CV recorded in the Ni^{2+} -free background electrolyte when a Co sulphide coating was cyclically reduced with E swept in the cathodic direction from E_{st} to -0.6 V and then back in the anodic direction to 0.3 V (curve 1). The cycles were repeated as long as K_0 practically disappeared. After that the electrode was transferred to the nickel plating electrolyte and the CV was recorded when E was swept from its stationary value to -1.0 V (Fig. 4, curve 2). As may

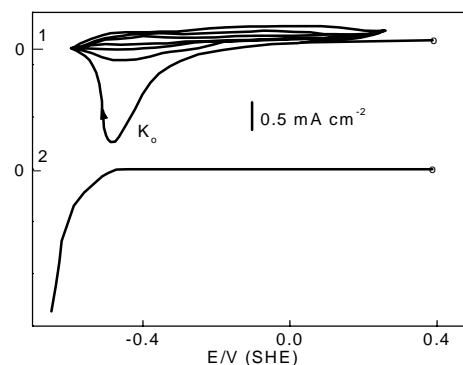


Fig. 4. CVs of Co_2S_3 formed by two deposition cycles on glassy carbon electrode and recorded in Ni^{2+} -free background (1) and Watts Ni electroplating (2) electrolytes. 1 – cyclical reduction of Co_2S_3 by sweeping E from its stationary value to -0.6 V and back to 0.3 V; 2 – CV of Co_2S_3 reduced cyclically under conditions of curve 1. Sweep rate $5 \cdot 10^{-2} V cm^{-1}$

be seen in the recorded CV, the cathodic peak K_1 does not emerge in the potential range -0.1 to -0.35 V. Therefore, it can be asserted that it is a compound that reduces in the potential range of the peak K_0 which affects formation of K_1 . It could be Co_2S_3 .

In order to confirm this presumption, a CV of coating reduction in nickel plating electrolyte was recorded when the potential was swept from E_{st} to -0.4 V (the potential range of K_1) (Fig. 5, curve 2). After such a partial reduction, the electrode was rinsed and transferred to the Ni^{2+} -free background electrolyte, and the CV was recorded sweeping the potential in the cathodic direction to -1.0 V. In the recorded CV, the cathodic current peak K_0 did not emerge in the range -0.2 to -0.6 V (Fig. 5, curve 3), though it was clearly seen when a Co_2S_3 coating was reduced in the Ni^{2+} -free background electroly-

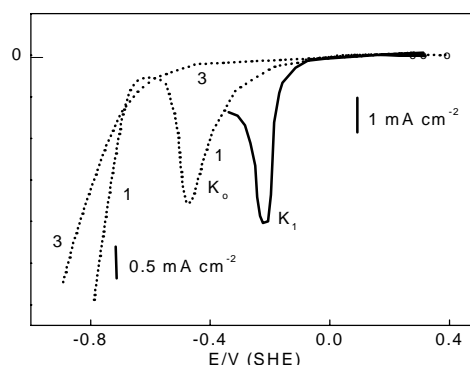


Fig. 5. CVs recorded in the Ni^{2+} -free background (1, 3) and Watts Ni electroplating (2) electrolytes for: 1, 2 – Co_2S_3 formed by two deposition cycles on glassy carbon electrode, 3 – Co_2S_3 reduced under conditions of curve 2 by sweeping E from its stationary value to -0.4 V. Sweep rate $5 \cdot 10^{-2} V cm^{-1}$

te (Fig. 2, curve 1). This means an interrelation between K_0 and K_1 . When Co_2S_3 is absent there is no K_0 , either.

To be certain that Co_2S_3 coating is completely reduced in Watts nickel plating electrolyte, a Co sulphide layer formed by 5 cycles was deposited on an ABS specimen and after that a 30 μm Ni coating was plated overhead. XPS analysis from the substrate side was performed after the deposited coating had been torn off the specimen. Ni compounds were determined to dominate in the coating, since ~ 0.2 at. % Co at the surface and after coating etching for 30 s at a depth of ~ 1 μm up to 2 at. % Co was detected. No metallic Co was detected. At the surface Co was present in the form of oxygen compounds, while in deeper layers CoS (BE of 778.2 eV) was detected. In Fig. 6, Ni $2p_{3/2}$ spectra are presented after the torn off coating was etched with Ar^+ ions for 30 s and 390 s. The determined BE values of 852.3 ± 0.1 and 853.1 ± 0.1 eV are characteristic of metallic Ni and NiS [15]. The quantity of the latter was determined to be ~ 10 at. % (Fig. 6a), while after etching for 390 s the quantity was less

by half, ~ 8 at. % (Fig. 6b). The data show that the NiS formed is not completely reduced during nickel electroplating and that nickel deposits on a partially reduced sulphide layer.

As mentioned above, on the CVs recorded while reducing Co_2S_3 coating in the Ni^{2+} -free background electrolyte, there are no anodic current peaks to testify that oxidation of the metallic Co formed takes place after a cathodic reduction of sulphide. It is anticipated that after Co_2S_3 reduction (the potential range of K_0) in the Ni^{2+} -free background electrolyte the CoS formed is not further reduced due to dominating H_2 evolution. The coatings treated in such a manner cannot be electroplated by nickel in Watts electrolyte.

CONCLUSIONS

The electrochemical behaviour of Co_2S_3 coating deposited in a colloidal solution of $\text{Co}(\text{OH})_3$ and / or $\text{CoO}(\text{OH})$ differs in the Watts nickel plating electrolyte and in the Ni^{2+} -free background electrolyte.

When the coating is reduced in the Watts nickel plating electrolyte, conversion of Co_2S_3 into NiS occurs according to the reaction $\text{Co}_2\text{S}_3 + 3\text{Ni}^{2+} + 2e = 2\text{Co}^{2+} + 3\text{NiS}$ in the potential range -0.1 to -0.35 V. At $E < -0.45$ V, the NiS is reduced to Ni on which nickel electrodeposition from solution occurs. The NiS is not completely reduced even at $E < -1.0$ V.

In the Ni^{2+} -free background electrolyte, Co_2S_3 cannot be reduced to metallic Co. After reduction the coating consists of a mixture of CoS and Co_2S_3 .

ACKNOWLEDGEMENTS

We acknowledge Dr. Leonas Naruškevičius from Institute of Chemistry (Vilnius) for providing the colloidal solution of $\text{Co}(\text{OH})_3$ and / or $\text{CoO}(\text{OH})$.

Received 28 April 2005

Accepted 23 May 2005

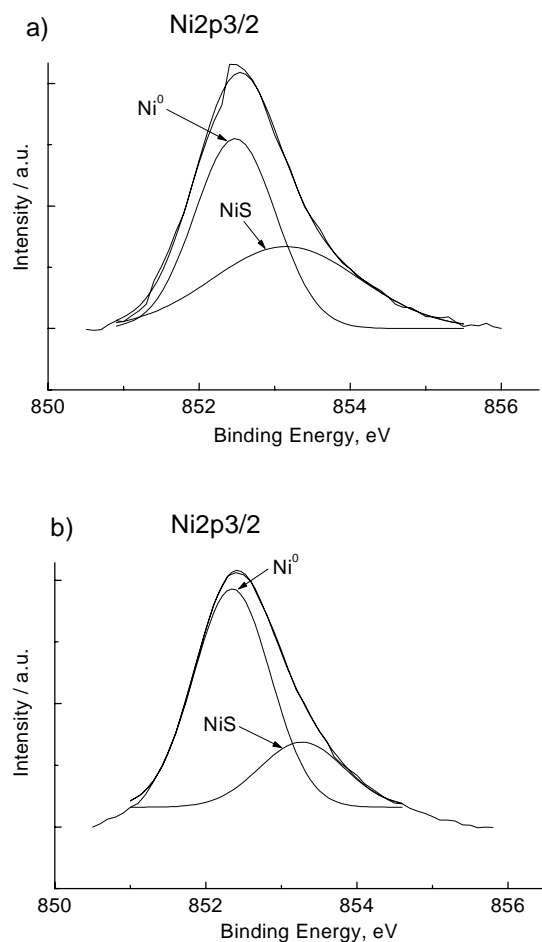


Fig. 6. XPS spectra of Ni $2p_{3/2}$ for Co_2S_3 coating electroplated by ~ 30 nm Ni in Watts electrolyte. The etching time: a – 30 s, b – 390 s

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KOBALTO SULFIDO DANGŲ ELEKTROCHEMINĖS ELGSENOS TYRIMAS NIKELIAVIMO ELEKTROLITE

Santrauka

Co₂S₃ dangų, nusodintų ant stiklo anglies elektrodo Co(OH)₃ arba/ir CoO(OH) koloidiniame tirpale, elektrocheminė elgsena buvo tirta Voltso nikeliavimo ir foniniame be Ni²⁺ tirpaluose ciklinės voltamperometrijos ir RFES metodais. Eksperimentinių duomenų analizė parodė, kad foniniame be Ni²⁺ tirpale Co₂S₃ redukuojasi ne iki metalinio Co, bet iki CoS. Po redukcijos dangą sudaro Co₂S₃ ir CoS mišinys.

Redukuojant Co₂S₃ dangą Voltso nikeliavimo elektrolite potencialo intervale nuo -0,1 iki -0,35 V vyksta elektrocheminė reakcija, kurios metu Co sulfidas pakeičiamas NiS. Kai E < -0,45 V, NiS redukuojasi iki Ni, ant kurio elektrolitiškai nusodinamas nikelis. RFES metodu nustatyta, kad NiS visiškai nesuredukuojamas net esant E < -1,0 V.