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Electrodeposition and characterization of Ni–Sn alloy coatings as cathode material for hydrogen evolution reaction in alkaline solutions

Ni–Sn alloy coatings were deposited from the constant composition pyrophosphate–glycine bath at different current densities. Their morphology, composition and phase composition were investigated by SEM, EDS and XRD techniques. It was shown that the morphology of coatings depends on current density, being rougher and more porous with the increase of deposition current density. EDS analysis of the cross sections revealed that the coating composition varies from the substrate surface towards the coating surface, being richer in Ni close to the substrate surface, while the composition on top of the surface was approximately the same for all samples (50 at.% Ni – 50 at.% Sn). XRD analysis showed the presence of only one phase in all deposits, $NiSn_2$. The increase of Ni-Sn coatings catalytic activity for hydrogen evolution with the increase of deposition current density was shown to be the consequence of their porosity, while the sample with the smooth surface showed lower overvoltage for hydrogen evolution than the commercial De Nora's electrode (DN), indicating synergetic effect of Ni-Sn alloys.

Key words: *electrodeposition, plating Ni-Sn alloys, hydrogen, alkaline solutions*

1. INTRODUCTION

The application field for electrodeposited Ni–Sn alloys is wide. Due to their bright appearance and corrosion resistance, they are of great interest for the metal finishing industry [1, 2]. Electronic industry also used electrodeposited Ni–Sn alloys for printed circuit boards as protective and etch-resistant coatings [3]. As highly resistant to tarnish and due to their high value of hardness (6–7 GPa), they have become an alternative for electroplated chromium in hardware, automotive, electrical and electronics accessories [4]. Electrodeposited Ni–Sn alloy films have also found application in fabrication of anode for Li–ion batteries [5–9].

Concerning phase composition of electrodeposited Ni–Sn alloys, in most of the papers it was stated that Ni–Sn alloys exists as single-phase homogeneous intermetallic compound of equiatomic composition NiSn (35 wt.% Ni – 65 wt.% Sn, 50 at.% Ni – 50 at.% Sn) [10, 11].

One of the most interesting properties of electrodeposited Ni–Sn alloys is their catalytic activity for hydrogen evolution in alkaline solutions. In the work of Santos et al. [12] it was shown that electrodeposited Ni–Sn alloy coatings possess low overvoltage for hydrogen evolution in alkaline solution, although the correlation between the characteristics of the alloys and the ability for hydrogen evolution has not been discussed. Detailed investigation of the electrodeposition conditions and their influence on the overvoltage for hydrogen evolution in alkaline solution has been performed in the work of Yamashita et al. [13]. By changing the deposition current density and concentration of $SnCl_2$ in the pyrophosphate–glycin bath, Ni content in the alloy coatings was changed from 20 to 98 wt.%, while the overvoltage for hydrogen evolution was found to be practically independent of the alloy composition in the range 40 – 80 wt.% of Ni. The morphology of the coatings was found to change from relatively smooth, fine grain structure, at low plating current density, to nodular one appearing as large spherical particles with the diameter of about 15 μm at high plating current density [13]. By the XRD analysis it was shown that the deposits prepared from the standard bath were composed of only NiSn phase, irrespective of the plating current density, with the x–ray peaks becoming broader with increasing plating current density. On the basis of these facts the authors concluded that the catalytic ability is closely related to the line broadening of x–ray diffraction peaks and to the surface state [13].

In this work an attempt was made to correlate deposition conditions (deposition current density) with the morphology, composition and phase composition of Ni–Sn alloy coatings electrodeposited from the Ni–Sn pyrophosphate–glycine bath of constant composition and to determine their influence on the catalytic activity for hydrogen evolution in 1 M NaOH at room temperature.

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2. EXPERIMENTAL

2.1. Deposition of Ni–Sn coatings

Deposition was performed in a standard electrochemical cell with two Pt–Ti counter electrodes, placed parallel to the working electrode (Ni mesh of the dimensions 13 x 10 mm – total surface area 2 cm^2) and saturated calomel electrode (SCE) as the reference electrode connected to the working electrode by means of Luggin capillary, using potentiostat Reference 600 and software PHE 200 (Gamry Instruments Inc.). All potentials are given vs. SHE. The plating bath contained 0.126 M $NiCl_2 \cdot 6H_2O$ + 0.075 M $SnCl_2 \cdot 2H_2O$ + 0.6 M $K_4P_2O_7$ + 0.27 M NH_2CH_2COOH (Glycin) at pH 8. All chemicals were p.a. quality.

Mesh substrates (Ni) were only shortly etched in 1:2 mixture of H_2O:HNO_3 and washed with distilled water before the deposition. Four samples were deposited in this bath at different current densities with the deposition time being 3000 s in all cases. After deposition all Ni mesh samples were cut into the dimensions 10 x 6.5 mm so that the total surface area was 1 cm^2 and were investigated in the standard electrochemical cell for polarization measurements. For the SEM and EDS analysis of coating surface samples were cut into suitable parts and placed on the graphite tape. For the SEM and EDS analysis of a cross section, samples were sealed in the epoxy resin and polished on the polishing machine down to the alumina suspension of 0.05 μm.

2.2. Polarization characteristics of Ni-Sn coatings

The polarization characteristics of Ni–Sn samples were tested in 1M NaOH solution in extra pure UV water at room temperature. Experiments were performed in a standard electrochemical cell with Pt counter electrode and saturated calomel electrode (SCE) as the reference electrode. Ni–Sn coatings were first submitted to hydrogen evolution at a constant current density of –0.3 A cm^{-2} for 10 min. and after such pre-electrolysis polarization curves were recorded (using the same potentiostat and software PHE 200 and DC 105) by sweeping potential with 1 mV s^{-1} from the potential of –0.85 V to the value of –1.10 V and recording the current corrected for the IR drop (current interrupt being on).

2.3. SEM and EDS analysis of the coatings surfaces and their cross sections

The appearance and the composition of coated mesh surfaces and the cross sections of the coatings were investigated by SEM, Tescan, VEGA TS 5130 MM equipped with an energy–dispersive X–ray spectroscopy (EDS), INCA PentaFET–x3, Oxford Instruments.

2.4. XRD analysis of the coatings

The XRD analysis was performed on the X'PertPRO, PANalytical.

3. RESULTS AND DISCUSSION

3.1. Deposition of Ni–Sn coatings

Polarization curve for Ni–Sn coating deposition onto Ni mesh recorded at the sweep rate of 1 mV s^{-1} is presented in Fig. 1a. Deposition process is seen to commence at about –0.55 V characterized with the wave of "diffusion controlled deposition" in the potential range between –0.65 V and –0.75 V, followed with the sharp increase of current density at more negative potentials.

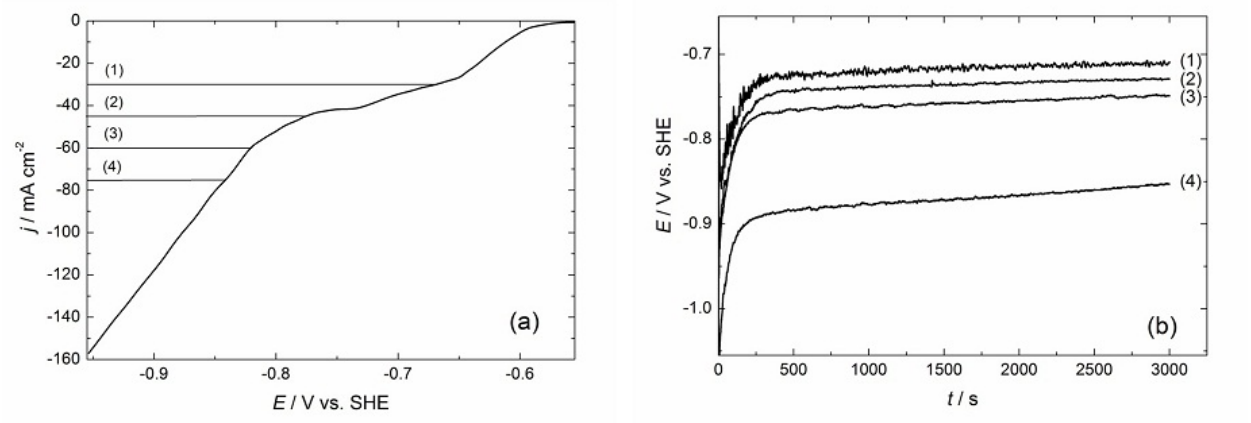


Fig. 1. (a) Polarization curve for Ni–Sn alloy deposition recorded at a sweep rate of 1 mV s^{-1}. (b) E vs. t responses of Ni–Sn alloy deposition for samples deposited at different current densities: (1) – 30 mA cm^{-2}; (2) – 45 mA cm^{-2}; (3) – 60 mA cm^{-2}; (4) – 75 mA cm^{-2}.

From the shape of the polarization curve and the values of the standard potentials of Ni and Sn deposition [14] it could have been assumed that the first wave corresponds to the deposition of Sn, while the Ni–Sn alloy deposition commences at about –0.75 V. According to the alloy composition analysis (see section 3.3), that was not the case. The presence of both metals in the coating deposited at the current density of –30 mA cm^{-2} (1) indicates that both metals deposited already in the region of the "diffusion controlled deposition". Sharp increase of current density at potentials more negative than –0.75 V is a consequence of simultaneous hydrogen evolution, which is visible and more pronounced at more negative potentials. With (1), (2), (3) and (4) are marked current densities for deposition of all Ni–Sn coatings investigated in this work. Corresponding potential vs. time dependences for Ni–Sn coatings deposition are shown in Fig. 1b. As can be seen, all *E* vs. *t* curves are characterized with the initial decrease of negative potential during the first 250 s of deposition, followed with a steady–state potential response. As the current density of deposition increases, the steady–state potential becomes more negative (curves 1–4), as could be expected from the polarization curve presented in Fig. 1a. The initial decrease of negative potential during the first 250 s of deposition indicates the change of the Ni–Sn coating composition at the beginning of the deposition process (see section 3.3).

3.2. Polarization characteristics of Ni–Sn coatings

Polarization characteristics of Ni–Sn coatings for hydrogen evolution in 1M NaOH at room temperature are presented in Fig. 2a for all deposited samples (curves (1) – (4)). All polarization curves possess the same shape, characterized by the presence of two slopes: lower one at lower current densities and higher one at higher current densities. As can be seen, the slopes are identical for all curves, while the overvoltage for hydrogen evolution decreases with increasing the current density of Ni–Sn coatings deposition for samples (1) – (3). Polarization curves for samples (3) and (4) are identical, indicating that the maximum catalytic effect for hydrogen evolution reaction is reached at the deposition current density of –60 mA cm^{-2} (sample (3)).

In Fig. 2b are compared polarization characteristics for the commercial De Nora's cathode (DN) for the zero-gap chlor–alkali cells and the best sample (3). As can be seen, this sample possesses for about 90 mV lower overvoltage for hydrogen evolution at the typical industrial current density of –0.3 A cm^{-2}. Such behavior points out at both synergetic effect and increased surface roughness of the Ni-Sn alloy coatings. According to the literature [15], in a whole potential range for hydrogen evolution reaction (HER) on the Ni electrode only one Tafel slope of about –120 mV dec^{-1} is present. Synergetic effect of Ni and Sn is confirmed by the change of the Tafel slope from –50 mV dec^{-1} at lower current densities (up to about 80 mA cm^{-2}) to –113 mV dec^{-1} at higher current densities (Fig. 2b, (3)), while the decrease of overvoltage for HER with the same slopes for curves (1) – (4) (Fig. 2a) clearly indicates the influence of the surface roughness.

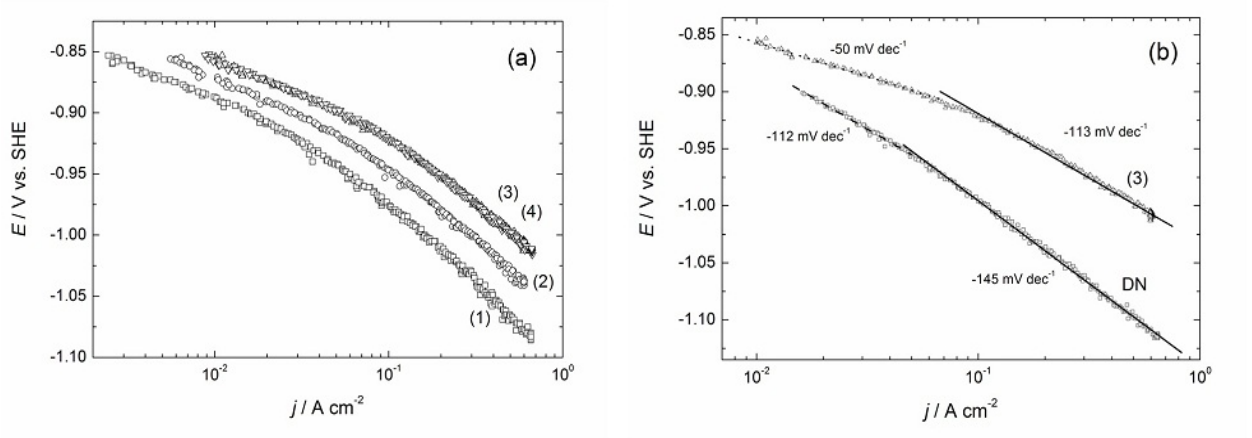
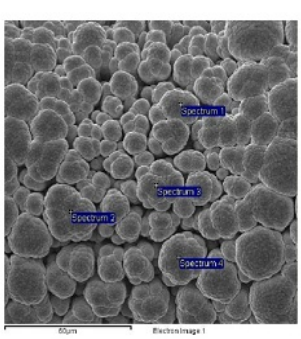


Fig. 2. (a) Polarization curves for HER recorded for all coatings (1) – (4) in 1 M NaOH at room temperature. (b) Polarization curves for HER recorded for coating (3) and commercial DN electrode in 1 M NaOH at room temperature

3.3. SEM and EDS analysis of the Ni–Sn coatings surfaces and their cross sections

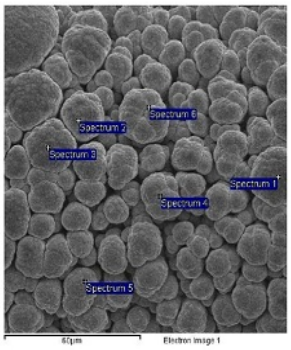
In Fig. 3 are presented top views of all coatings, (1), (2), (3) and (4), together with the results of their EDS analysis. In all cases the surface of samples is characterized with nodules. The dimensions of nodules for samples (1) and (2) are smaller than those for samples (3) and (4). According to the EDS analysis, the composition of the surface for all samples is almost identical, being approximately 50 at.% Ni – 50 at.% Sn.



Spectrum	In stats.	Ni	Sn
Spectrum 1	Yes	50.59	49.41
Spectrum 2	Yes	52.26	47.74
Spectrum 3	Yes	52.21	47.79
Spectrum 4	Yes	50.49	49.51
Mean		51.39	48.61
Std. deviation		0.98	0.98
Max.		52.26	49.51
Min.		50.49	47.74

All results in atomic%

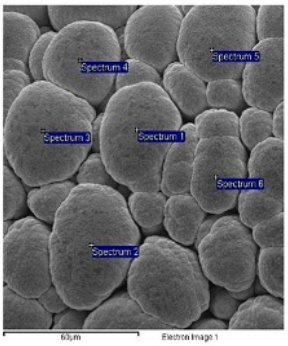
(1)



Spectrum	In stats.	Ni	Sn
Spectrum 1	Yes	51.28	48.72
Spectrum 2	Yes	52.60	47.40
Spectrum 3	Yes	53.03	46.97
Spectrum 4	Yes	52.50	47.50
Spectrum 5	Yes	56.38	43.62
Spectrum 6	Yes	53.01	46.99
Mean		53.13	46.87
Std. deviation		1.71	1.71
Max.		56.38	48.72
Min.		51.28	43.62

All results in atomic%

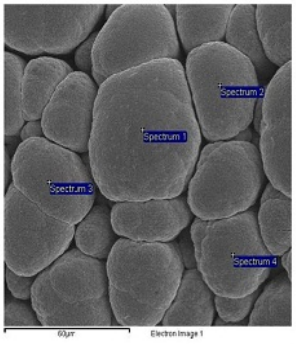
(2)



Spectrum	In stats.	Ni	Sn
Spectrum 1	Yes	48.97	51.03
Spectrum 2	Yes	49.50	50.50
Spectrum 3	Yes	48.39	51.61
Spectrum 4	Yes	48.41	51.59
Spectrum 5	Yes	48.91	51.09
Spectrum 6	Yes	49.52	50.48
Mean		48.95	51.05
Std. deviation		0.50	0.50
Max.		49.52	51.61
Min.		48.39	50.48

All results in atomic%

(3)



Spectrum	In stats.	Ni	Sn
Spectrum 1	Yes	47.88	52.12
Spectrum 2	Yes	49.51	50.49
Spectrum 3	Yes	49.19	50.81
Spectrum 4	Yes	49.24	50.76
Mean		48.96	51.04
Std. deviation		0.73	0.73
Max.		49.51	52.12
Min.		47.88	50.49

All results in atomic%

(4)

Fig. 3. EDS analysis of the surfaces of all coatings (1) – (4).

The cross sections of all samples are shown in Fig. 4. Although, according to the Fig. 3, the surfaces of all samples are practically identical, the cross section analysis presented in Fig. 4 clearly indicates the increase of surface area (porosity of the coatings) with the increase of current density for Ni–Sn coatings deposition. In the case of the lowest deposition current density (1) the surface is practically smooth, following the surface of the substrate, while at higher values of deposition current densities (2), (3) and (4) the coatings are porous with the number and dimensions of pores being more pronounced at higher current densities. It seems that the total thickness of the deposits slightly increases with the increase of current density. Taking into account current efficiencies for samples deposition, which were 80 % for samples (1) and (2), 62 % for sample (3) and 58 % for sample (4), it could be concluded that only for sample (1) (smooth coating surface) thickness is proportional to the applied current density, while for other samples this proportion doesn't exist as a consequence of rough, porous structure of the deposits. The cross section analysis is in accordance with the polarization curves presented in Fig. 2a. The increase of catalytic activity for HER for coatings (2), (3) and (4) is the consequence of the surface area increase, as stated in section 3.2. Taking into account that the morphologies of samples (3) and (4) are practically identical (Fig. 4), as well as their surface composition (see Fig. 3), their polarization curves for hydrogen evolution are also identical (Fig. 2a).

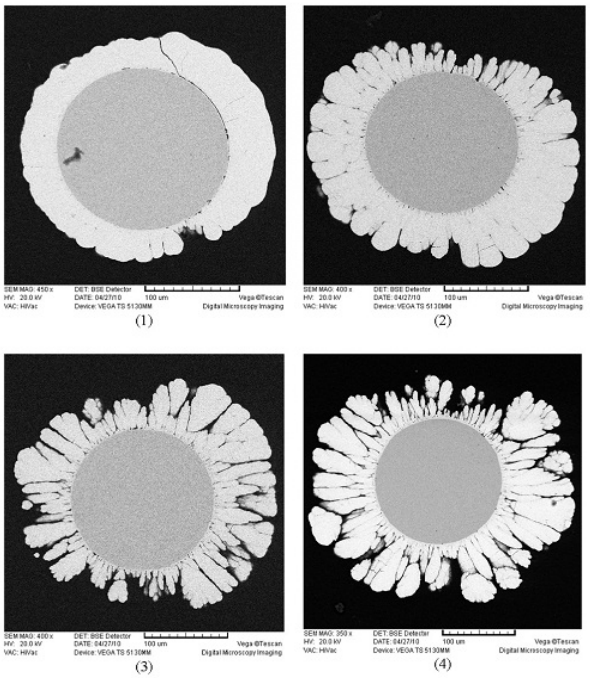
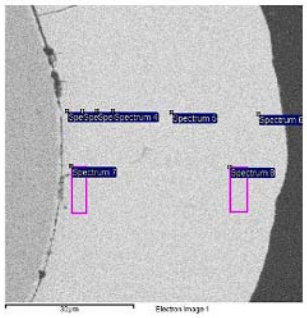


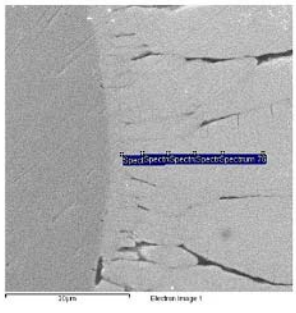
Fig. 4. SEMs of the cross section of coatings (1) – (4).



Spectrum	In stats.	Ni	Sn
Spectrum 1	Yes	57.56	42.44
Spectrum 2	Yes	48.79	51.21
Spectrum 3	Yes	48.18	51.82
Spectrum 4	Yes	44.79	55.21
Spectrum 5	Yes	41.91	58.09
Spectrum 6	Yes	46.22	53.78
Spectrum 7	Yes	52.45	47.55
Spectrum 8	Yes	46.49	53.51
Mean		48.30	51.70
Std. deviation		4.84	4.84
Max.		57.56	58.09
Min.		41.91	42.44

All results in atomic%

(1)



Spectrum	In stats.	Ni	Sn
Spectrum 2	Yes	68.24	31.76
Spectrum 3	Yes	60.17	39.83
Spectrum 4	Yes	51.90	48.10
Spectrum 5	Yes	49.34	50.66
Spectrum 6	Yes	49.59	50.41
Spectrum 7	Yes	49.82	50.18
Mean		54.85	45.15
Std. deviation		7.74	7.74
Max.		68.24	50.66
Min.		49.34	31.76

All results in atomic%

(3)

Fig. 5. Results of the EDS analysis of the cross section of coatings (1) and (3)

According to the shapes of E vs. t responses for samples deposition, one should expect the change of the Ni–Sn composition, particularly in the region close to the substrate. That is exactly the case for all samples. In Fig. 5 are presented results of the EDS analysis of the cross section for samples (1) and (3). As can be seen for both samples, the amount of Ni is higher at the beginning of deposition (closer to the substrate surface), while after reaching approximately the half of the coating thickness the composition of the Ni–Sn alloy is practically constant (50 at.% Ni – 50 at.% Sn). This effect is more pronounced for sample (3) than for sample (1), being in accordance with the change of the shape of E vs. t responses (1) and (3) presented in Fig. 1b.

3.4. XRD analysis of the coatings

The results of the XRD analysis of samples (1) and (3) are presented in Fig. 6. These results clearly indicate that samples (1) and (3) (this applies most probably to all samples) represent Ni–Sn alloys of the same phase composition, since only $NiSn_2$ phase is detected in the deposits. This finding is also in accordance with the polarization characteristics, since all samples possess the same Tafel slope, indicating that the phase composition of the Ni–Sn alloy does not change with the deposition current density. Taking into account that the average composition of all Ni–Sn alloy coatings amounts to approximately 50 at.% Sn – 50 at.% Ni, it seems that crystallites of the $NiSn_2$ phase are big enough to be detected by the x-ray analysis, while the rest of Ni crystallites are practically nano-crystalline and cannot be detected on the diffractograms presented in Fig.6.

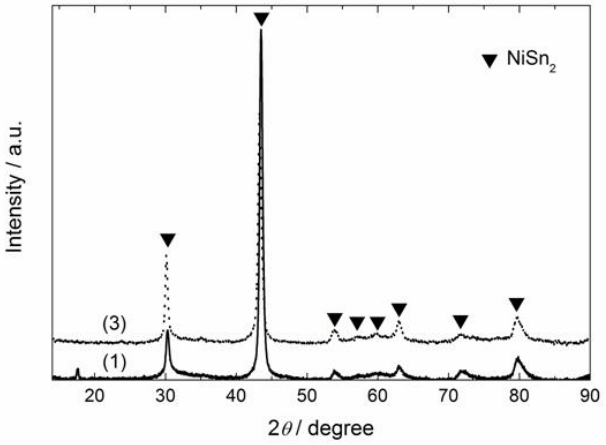


Fig. 6. Results of the XRD analysis of the coatings (1) and (3).

4. CONCLUSIONS

From the results presented in this work it could be concluded that the morphology of Ni–Sn alloy coatings deposited from the bath containing Sn^{2+} and Ni^{2+} ions in the pyrophosphate–glycine solution depend on the deposition current density, being more porous at higher current densities. Their composition and phase composition were found to be independent

of the values of deposition current density. The composition changed from the substrate surface towards the coating surface, being richer in Ni close to the substrate surface, while the composition on top of the surface was approximately the same for all samples (50 at.% Ni – 50 at.% Sn). XRD analysis showed the presence of only one phase in all deposits, $NiSn_2$. The increase of their catalytic activity for hydrogen evolution with the increase of deposition current density was shown to be the consequence of their porosity, while the sample with the smooth surface showed lower overvoltage for hydrogen evolution than the commercial electrode, indicating synergetic effect of the Ni–Sn alloy coatings.

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IZVOD

ELEKTROHEMIJSKO TALOŽENJE I KARAKTERIZACIJA PREVLAKA Ni-Sn LEGURA KAO KATODNOG MATERIJALA ZA REAKCIJU IZDVAJANJA VODONIKA U ALKALNIM RASTVORIMA

Prevlake Ni-Sn legura su elektrohemijski istaložene iz pirofosfatno–glicinskog kupatila konstatnog sastava pri različitim vrednostima gustine struje. Njihova morfologija, hemijski i fazni sastav su ispitivani pomoću SEM, EDS i XRD analize. Pokazano je da morfologija prevlaka zavisi od gustine struje, uz stvaranje hrapavijeg i poroznijeg taloga sa povećanjem gustine struje taloženja. EDS analiza poprečnih preseka otkrila je da se sastav prevlaka menja idući od površine supstrata ka površini prevlake, pri čemu je u blizini površine supstrata talog bogatiji niklom, dok je sastav na površini prevlaka približno isti za sve uzorke (50 at.% Ni – 50 at.% Sn). XRD analizom uočeno je prisustvo samo jedne faze u svim talozima, $NiSn_2$. Pokazano je da je povećanje katalitičke aktivnosti Ni-Sn prevlaka za reakciju izdvajanja vodonika sa povećanjem gustine struje taloženja posledica njihove poroznosti, dok je potencijal izdvajanja vodonika na uzorku sa glatkom površinom pozitivniji u odnosu na komercijalnu De Norinu elektrodu (DN), ukazujući na sinergetski efekat Ni-Sn legura.

Ključne reči: *elektrohemijsko taloženje, prevlake Ni-Sn legura, vodonik, alkalni rastvori*