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ELECTROCATALYTICALLY ACTIVE Ni-Re BINARY ALLOYS ELECTRODEPOSITED WITH SUPERIMPOSED MAGNETIC FIELD

KATALITYCZNIE AKTYWNE STOPY Ni-Re OSADZANE W ZEWNĘTRZNYM POLU MAGNETYCZNYM

The aim of this work was to obtain Ni-Re binary alloy by a simple method of electrodeposition. Nickel – rhenium alloys have been deposited from nickel sulfamate and ammonium perrhenate electrolyte with citrate-anion additives. The effect of magnetic field superimposed during electrodeposition was studied. The impacts of that parameter on hydrogen evolution process for obtained Ni-Re alloys were examined. The deposited layers were determined by optical and scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray fluorescence (XRF).

Keywords: Electrodeposition, Ni-Re alloys, magnetic field, hydrogen evolution

Celem pracy było uzyskanie stopów Ni-Re metodą osadzania elektrolitycznego. Stop niklowo renowy osadzano z elektrolitu zawierającego sulfaminian niku oraz nadrenian amonu. Stosowano bufor cytrynianowy. Badano wpływ przyłożonego zewnętrznego pola magnetycznego podczas osadzania stopu na wydzielanie wodoru na tak uzyskanym stopie. Badano osadzone warstewki stopowe za pomocą mikroskopu optycznego oraz mikroskopu skaningowego i metodami XRD oraz XRF.

1. Introduction

Until recently, chromium coatings were considered as irreplaceable coverage for elements of metals surfaces working in different, usually difficult, conditions. Unfortunately, manufacture and application of conventional chromium coatings are a serious threat to the environment because of toxic and carcinogenic character of chromates compounds used to produce the layers. Hence, it is necessary to replace the production methods of chromium coatings by technologies which are more friendly to the environment and offer more possibilities for developing and incorporating processes of alternative techniques [1-4]. This problem can be solved by using coatings from alloys such as Ni-W, Ni-Re, Co-W and ternary alloys with addition of other elements. Ni-Re alloys seem to be very promising due to their high hardness, low grindability, satisfactory anticorrosive properties and also high bath stabilization for electrochemical deposition [5-10, 15-17].

Coatings based on nickel and cobalt with addition of rhenium as well as nickel and cobalt modified by rhenium powder are more and more frequently used as cathode materials characterized by lower overpotential for hydrogen evolution in electrocatalytic processes [18]. Materials presenting high electrocatalytic properties are usually expensive and often demonstrate low mechanical strength. Therefore, electrodeposited Ni-Re alloys can be used as active electrodes obtained by applying the active coating on a surface that is available, durable and easy to machining. The cathode materials characterized by low hydrogen evolution overpotential and high catalytic activity include electrodes made from precious metals, mainly platinum or nickel and cobalt-based coatings produced by electrochemical methods [11-14]. For the modification of electrocatalytical activity by change the composition or morphology of deposit magnetic field superimposed during electrodeposition have been applied [19-22].

It seems that it is advisable to obtain Ni-Re alloys by electrolytic deposition from aqueous solutions. These coatings are characterized by a high electrocatalytic activity, low overpotential for hydrogen evolution, large extension of the surface and good corrosion resistance. Thus, obtained alloys can be used, inter alias, in solar-powered water electrolysis systems and the hydrogen obtained though decomposition of water could be

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used for the production of methane by hydrogenation of carbon dioxide.

2. Experimental procedure

According to Naor [17], Ni-Re alloys were deposited from aqueous solution containing 0.1 M NH_4ReO_4, 93 mM $Ni(NH_2SO_3)_2 4H_2O$ and 34 mM $C_6H_8O_7$ as a complexing agent and the pH value was 5, bath temperature – 70°C; current density – 25 mA/cm^2; time of the deposition – 120 minutes.

All of the experiments were carried out in a 150 ml cell. The cathode was a copper disc of an area of 3.14 cm^2 and a platinum was used as a counter electrode.

The cells used for electrodeposition were 40 mm wide, 100 mm long and 45 mm high. Platinum metal anodes were placed vertically at both ends of the cell, facing each other at a distance of 90 mm. A copper metal cathode was placed vertically in the centre of the cell. Electrodeposition of Ni-Re alloys in a magnetic field was performed in the same conditions as the above listed ones. The magnetic field was generated by the LakeShore laboratory electromagnet. The process was carried out with differently oriented lines of magnetic field towards the cathode surface: parallel and perpendicular.

Before the deposition, substrates were chemically etched in a 1:1 mixture of concentrated H_2SO_4 and HNO_3 for 30 s. According to preliminary experiments, agitation of the electrolyte did not affect significantly the composition and hydrogen evolution performance of the deposits because of violent hydrogen evolution during electrodeposition, and for this reason the electrodeposition was carried out in a stagnant condition.

The composition of metallic elements in the electrodes prepared in this way was analyzed with the use of XRF Philips MiniPal. The current efficiency for electrodeposition was estimated based on the mass and composition of the deposit. The structure of the electrodes was identified by X-ray diffraction using Cu Kα radiation. The grain size of the deposits was estimated from the full width at half maximum of the most intense diffraction line by Scherrer's equation [23].

The hydrogen evolution activity of the electrodes was examined in 8 M NaOH solution at 90°C by galvanostatic polarization. A cell of acrylic resin with the specimen electrode, a platinum counter electrode and an external saturated calomel reference electrode of a reversible potential of 0.810V for the hydrogen reaction were applied. The potential was calculated from Nernst equation. The ohmic drop was corrected using the current interruption method.

3. Results and discussion

Based on the previous research [24] the condition of Ni-Re alloys deposition are bath temperature – 70°C; current density – 25 mA/cm^2; time of the deposition – 120 minutes. Ni-Re alloys were deposited from aqueous solution containing 0.1 M NH_4ReO_4, 93 mM $Ni(NH_2SO_3)_2 4H_2O$ and 34 mM $C_6H_8O_7$ as a complexing agent and the pH value was 5.

In the electrodeposition process in magnetic field Ni-Re alloys of the following composition were obtained: 70-91% at. of Ni and 29-8% at. of Re when the cathode was oriented parallel to the magnetic field (Fig. 1.). A change of the cathode orientation to perpendicular altered the content of alloys elements to: 66-97% at. of Ni and 33-2% at. of Re.
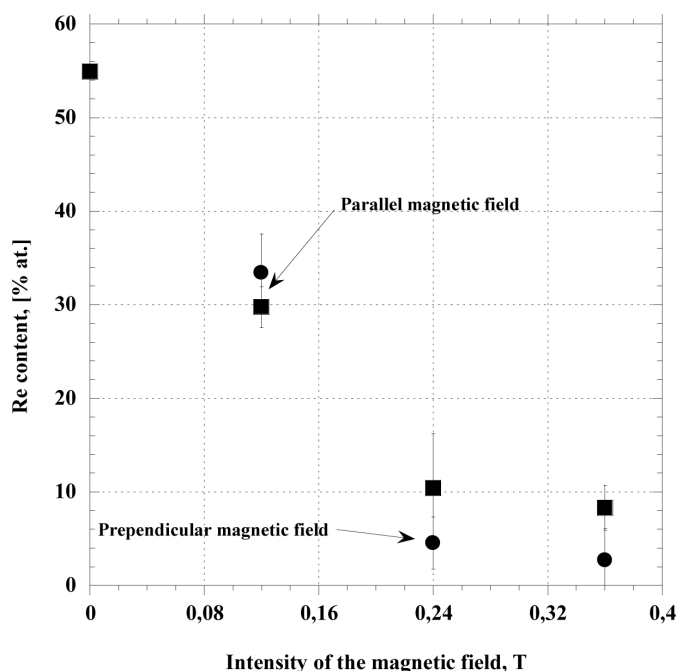

Fig. 1. Effect of the magnetic field orientation and intensity on the composition of Ni-Re coatings

The increase of the magnetic field intensity caused an increase of ferromagnetic metal content, namely nickel. It resulted in a decrease of rhenium content, which reduced mechanical and physicochemical properties of the alloy. In case of the cathode situated in different position towards the magnetic field, it was observed that coatings from parallel orientation were more homogeneous and their quality was better than the coatings obtained from perpendicular orientation. As for the composition of the deposit, the higher content of Ni metal was observed for perpendicular orientation. It could be explained by the fact that in perpendicular orientation the ferromagnetic Ni ions travelled faster along the magnetic field lines. This led to additional Ni ions flux toward the cathode and as a result the deposit got enriched with nickel.

The electrodepositon in a magnetic field is not an efficient process. Without a magnetic field the process efficiency was about 57%. When the field was applied, the efficiency decreased to 5.79% at perpendicular orientation and intensity equal to 0.36 T (Fig. 2.).
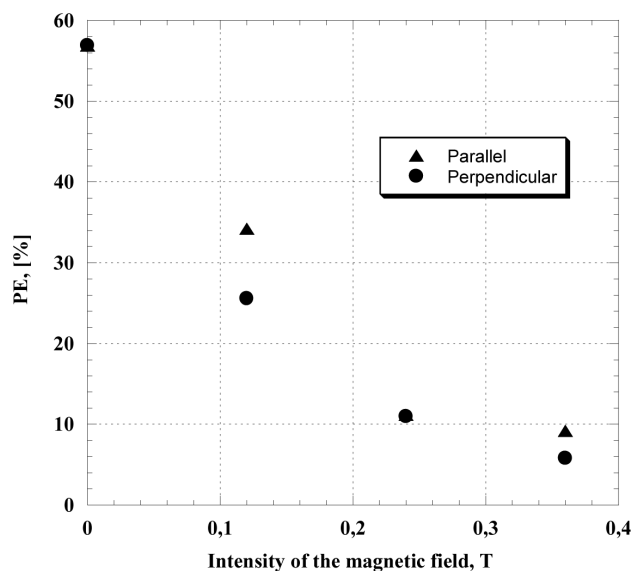

Fig. 2. Effect of the magnetic field orientation and intensity on the process efficiency

It was observed that the orientation of the cathode to the direction of magnetic field lines and also their intensity had a significant effect on the morphology of the alloys. Considering the position of the cathode in relation to direction of the magnetic field lines, it appeared that, in terms of quality, better coatings were obtained from parallel orientation. The structure was compact and homogeneous and the quality was similar to the alloys obtained by electrodeposition without a magnetic field (Fig. 3.). The increase of intensity of the magnetic field caused a reduction of rhenium content in the alloy and decreased the process efficiency. The obtained coatings were dull, cracked and with the tendency to peel off.

The alloy deposited without a magnetic field and at the lowest field intensity of 0.12 T had an amorphous structure. Additionally, at parallel orientation of the cathode the peaks from nickel and copper were observed which means that the coatings obtained from this orientation were thinner than those from perpendicular orientation. Increasing the magnetic field intensity to 0.24 and 0.36 T decreased the process efficiency and rhenium content in the alloy. Sharp reflection on the diffraction patterns for perpendicular orientation and smaller peaks for the parallel one indicating the presence of crystalline hcp rhenium and fcc nickel could be observed. There was a change in the structure from amorphous to the crystalline one. In both cases, sharp peaks attributed to fcc copper were observed. It was also found that an in-

crease of the magnetic field intensity increased the grains size (Fig.4-5.). However, in case of parallel orientation of magnetic field, the grain size increase is smaller.

Electrocatalytical properties of alloys or metals are related to morphology of alloys and/or intrinsic activity of alloys components. By changing the deposition conditions we could tune up the electrocatalytic activity of the deposit due to different morphology or composition.
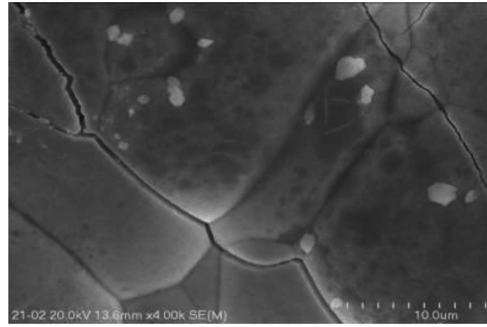
The best electrocatalytic properties were found in alloys with the highest rate of rhenium content. The highest activity for hydrogen evolution was demonstrated by alloys deposited at 70°C [24].

The number of depositions was carried out in a superimposed magnetic field in parallel and perpendicular orientation of magnetic field lines toward the cathode. The presence of the magnetic field caused the change in rhenium content in the alloy. It means that catalytic properties of these alloys should also change.
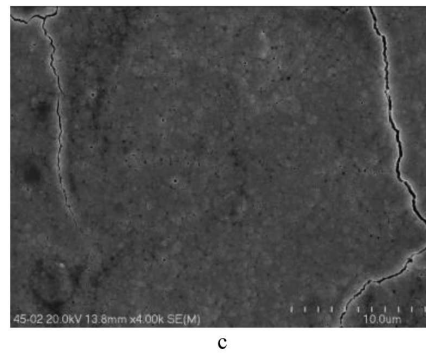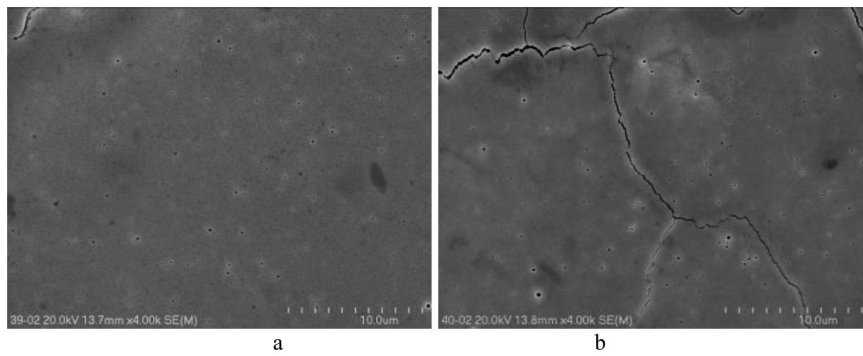
The superimposing of the magnetic field during electrodeposition led to a radical decrease of rhenium content in alloy from 54.9 to 8.3% at. and 2.7% at. for parallel and perpendicular orientations of magnetic field, respectively. That content of rhenium in the deposit should not improve catalytical properties of the alloy, as from the previous parts of the research it was found that the minimum content should be over 23% at. Such alloy composition showed improvement of catalytical activity due to intrinsic properties of the alloy components. However, when the external magnetic field was applied during electrodeposition, the alloys showed excellent catalytical activity at the magnetic field intensity of 0.36 T. Those alloys had low Re content. In those cases the electrocatalytical activity seemed to be related to the morphology of alloys. Alloys morphology presented in Fig. 6 showed that increasing magnetic field intensity made the deposited alloys less rough. The cracks caused by internal stresses or hydrogen evolution during electrodeposition disappeared. The grains boundaries were less and less visible, and the size of grains decreased. The alloys became smoother and smoother and in this way the number of active sites for hydrogen evolution was likely to increase.

The magnetic forces generated by the passage of the current and the superimposed magnetic field created additional convection which affected the morphology of the deposits. In theory, the size of grain of the deposits is a function of nucleation rate and growth of the nucleus; the more numerous the nuclei are, the lower size of grain is. A magnetic field applied parallel to the surface of the electrode generates convection (magneto hydrodynamic effect MHD) of the electrolyte; it results in a laminar flow on the surface of the electrode which reduces the diffusion layer and increases the concentrations gradi-
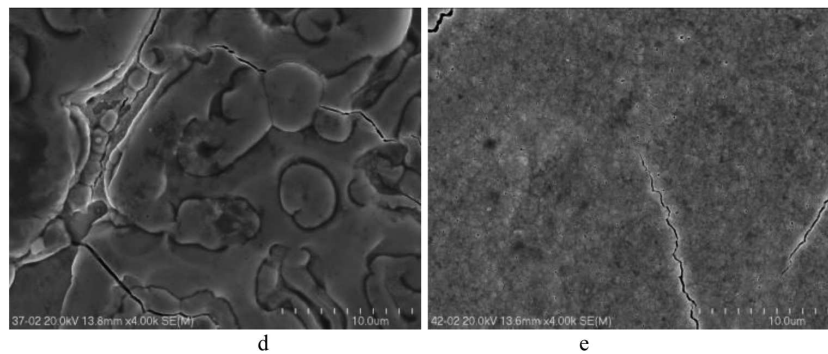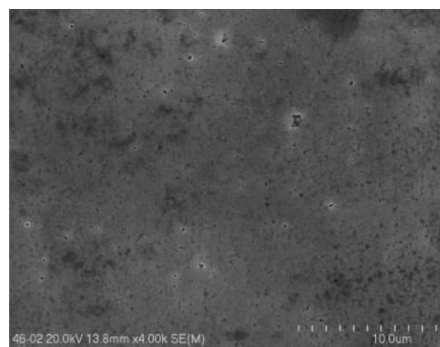
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Basic sample – WITHOUT MAGNETIC FIELD

PARALLEL CATHODE ORIENTATION

a

b

c

PERPENDICULAR CATHODE ORIENTATION

d

e

f

Fig. 3. Microphotography obtained Ni-Re alloys from electrodeposition under magnetic field: o – 0 T; a,d – 0.12 T; b,e – 0.24 T; c,f – 0.36 T
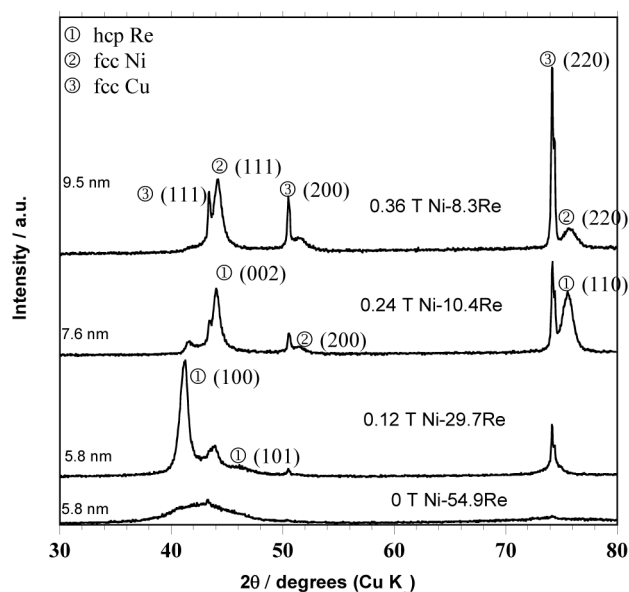

Fig. 4. XRD pattern of Ni-Re layers obtained from the electrodeposition under magnetic field – parallel cathode orientation. The estimated grain sizes were written in the figure
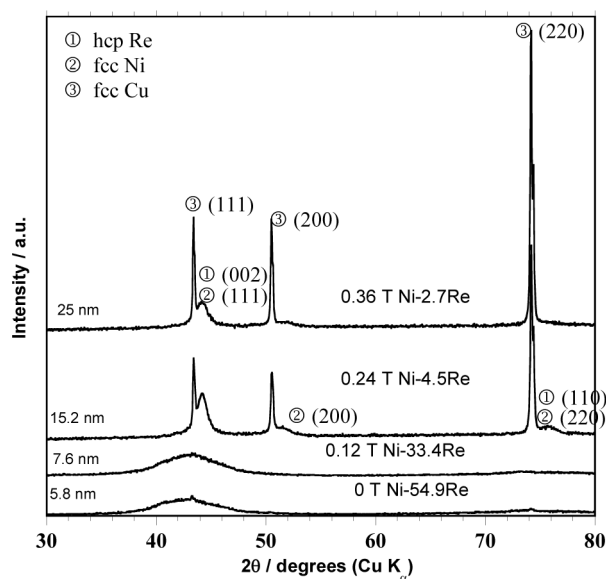

Fig. 5. XRD pattern of Ni-Re layers obtained from the electrodeposition under magnetic field – perpendicular cathode orientation. The estimated grain sizes were written in the figure

ents. This results in a change of the size of the grains and thus can also influence formation of various phases of the deposits. These various effects can be caused at the same time by the above mentioned convection but also by the magnetic properties. When the field is superimposed, the growth in the direction of easier magnetization appears.

The superposition of the magnetic field parallel to the substrate surface led to generation of magneto hydrodynamic effect (MHD). MHD effect reduced the thickness of the diffusion layer and led to an increasing concentration gradient, which should have an effect on the grain size. An increase of number of grains led to deposition of alloys with larger number of active centres on the surface of the electrode. And hence, a desired decrease in overpotential was achieved by increasing the active centres of the electrode. The increase of number of active centres allowed keeping high activity for hy-

drogen evolution even when the rhenium content in alloy was low.

While comparing Fig. 6. and Fig. 7. it was concluded that the highest catalytic activity was found in alloys deposited at the highest intensity of the magnetic field. Electrocatalytical properties also depended on the cathode orientation. Better properties were observed for the alloys deposited in parallel orientation, where rhenium content was higher than in perpendicular configuration. The Tafel slope for a perpendicular orientation was 110 mV/dec, in comparison to 40 mV/dec for parallel orientation.

The polarization curves are composed of two regions with different Tafel slopes. The Tafel slope at lower current densities was about 110 mV/decade for alloys deposited at perpendicular magnetic field orientation but decreased to about 40 mV/decade for the alloys deposited in parallel magnetic field configuration. These Tafel
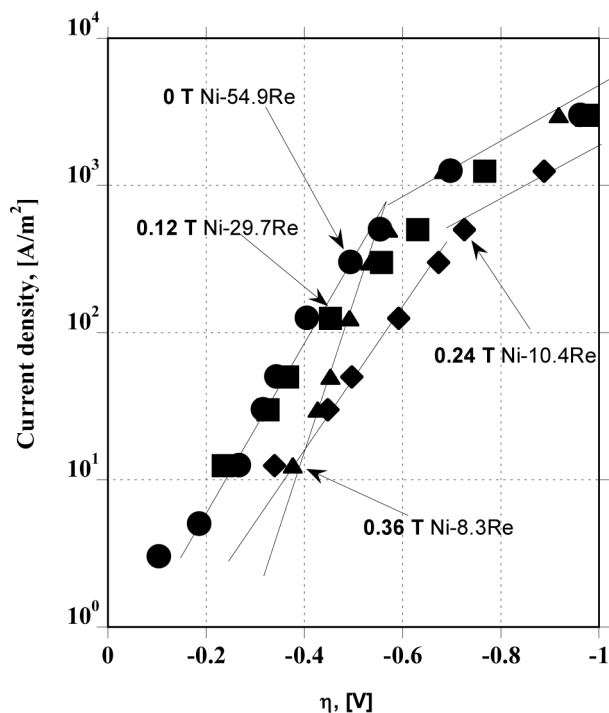
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Fig. 6. Galvanostatic polarization curves for Ni-Re alloys electrodeposited under magnetic field – parallel cathode orientation
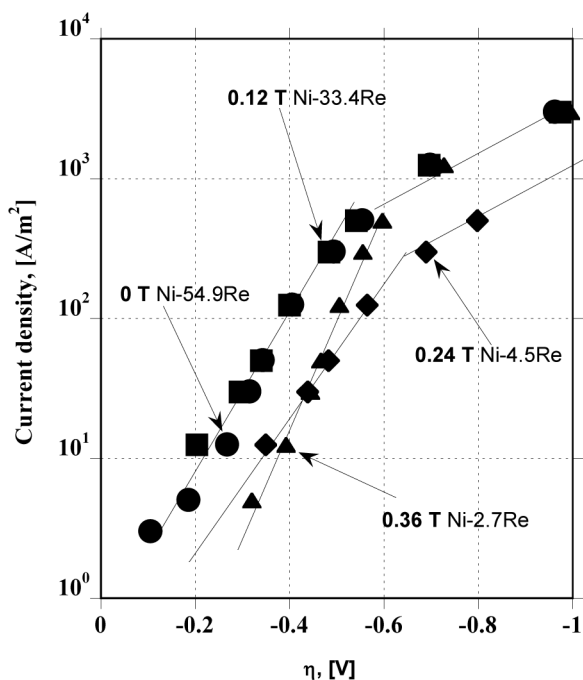

Fig. 7. Galvanostatic polarization curves for Ni-Re alloys electrodeposited under magnetic field – perpendicular cathode orientation

posited in parallel magnetic field orientation. However, when the rate of hydrogen evolution for the alloys deposited in parallel configuration becomes high at higher current density, the Tafel slope again increases to about 110 mV/decade, that is 2RT/F. When the proton discharge becomes significantly fast, the hydrogen coverage on the electrode surface will reach to unity and electrochemical desorption of an adsorbed hydrogen combined with a proton in the solution will be faster than the recombination of two adsorbed hydrogen atoms. When the rate determining step is electrochemical desorption of hydrogen at $\theta \approx 1$, the Tafel slope is 2RT/F. Consequently, deposition of Ni-Re alloys in high magnetic field superimposed parallel to the cathode significantly accelerates proton discharge, and hence enhances hydrogen evolution.

4. Conclusion

The studies carried out over the electrolytic deposition of Ni-Re alloys resulted in the following conclusions. Electrodeposition with the presence of the magnetic field had an influence on the morphology of the obtained coatings. The cathode orientation to the direction of the magnetic field lines and their intensity had an impact on the structure of the cathode deposit. An increase of the rhenium content in the alloy improved the catalytic properties of Ni-Re alloys. The superimposing external magnetic field increased ferromagnetic metal content in the alloy. Electrodeposition in the magnetic field improved catalytic properties of Ni-Re alloys in spite of low rhenium content in the deposit.

slopes correspond to 2RT/F and RT/2F, respectively. Under the assumption that the hydrogen coverage θ is nearly 0 and that the transfer coefficient is 1/2, the change in the Tafel slope indicates the change in the rate-determining step of hydrogen evolution from the proton discharge for alloys deposited in perpendicular configuration to recombination of adsorbed hydrogen for the alloys de-

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