

ELECTROCHEMICAL PRODUCTION AND CHARACTERIZATION OF Ni-BASED COMPOSITE COATINGS CONTAINING Mo PARTICLES

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Abstract. Composite Ni+Mo coatings were obtained by electrodeposition of Ni with Mo particles on a steel substrate from the nickel bath in which metallic powder was suspended by stirring. The deposition was conducted under galvanostatic conditions. Deposits were characterized by the presence of Mo microsize particles embedded into the nanocrystalline nickel matrix. The influence of the metal powder amount in the bath, as well as the deposition current density on the chemical composition of the coatings was investigated. The content of incorporated Mo increases with the increase in the amount of metal powder in the bath, and diminishes with the increase in the deposition current density. The mechanism of metallic particles embedding is explained on the base of Ni^{2+} ions adsorption process. Incorporation of Mo particles into electrolytic nickel matrix causes an increase in the real surface area of deposits.

Thermal treatment of deposited coatings leads to chemical reactions in the solid state and in a consequence exerts significant influence on their phase composition and surface morphology. As a result of the interaction between the nickel matrix and incorporated Mo particles Ni_3Mo intermetallic phase and Ni-Mo solid solution are arising.

The obtained composite coatings were tested as electrode materials for hydrogen evolution in alkaline environment. Electrochemical characterization of the composites was carried out by steady-state polarization method. It was ascertained, that as-deposited Ni+Mo coatings are characterized by enhanced electrochemical activity for this process, which was confirmed by considerable decrease in the hydrogen evolution overpotential, by a nearly 170-260 mV compared to nickel electrode. Thermal treatment decreases the electrochemical activity of the investigated materials, as the values of hydrogen evolution overpotential on heated coatings are much higher.

1. INTRODUCTION

In order to lower the energy consumption of alkaline water electrolysis many catalytic materials for cathodes have been proposed and examined. The nickel-based materials are commonly known on account of special properties of nickel such as high catalytic activity for hydrogen evolution as well as good corrosive resistance in aggressive environments [1-5]. In order to improve the properties of these materials and to enhance their catalytic ac-

tivity, various modifications could be applied, such as alloying with other elements, incorporation of composite components and other modifications aimed at obtaining the electrodes with very developed, rough or porous electrode surface [6-9]. Many types of particles were used to improve the mechanical, physicochemical or electrocatalytic properties of composite coatings, like carbides, silicides, nitrides and oxides. Recent developments in electrodeposition technology have introduced a technique involving codeposition of metallic par-

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ticles to form electrodeposited metal matrix/metal particle composites [10].

Among these composites the materials of particular importance are those containing metals like Al, Ti, V, Mo, which could not be directly codeposited in cationic form from aqueous solutions. However, it is possible to introduce these metals in a form of powders and galvanic embedding their particles into a metal matrix [11-17]. Incorporating such powdered components to the metal matrix follows to obtain a new kind of composite materials which could be applied as electrode materials. The composite coatings containing Mo particles dispersed in the Ni matrix have not been investigated yet.

According to the literature data the nickel-molybdenum alloys exhibit high electrochemical activity for hydrogen evolution reaction [18-28]. Taking into account the properties of these materials, we have made an assumption, that composite layers containing Mo particles should be very interesting as electrode materials for hydrogen evolution on account of the presence of Mo embedded in Ni matrix and significant development of electrode surface. The purpose of this work was to obtain Ni+Mo composite coatings by an electrolytic method, to investigate the influence of electrolytic conditions of deposition (the concentration of metallic powder suspension and deposition current density) on the amount of incorporated metal particles and to evaluate their suitability as electrode materials for hydrogen evolution reaction in alkaline environment before and after thermal treatment.

2. EXPERIMENTAL

To obtain the composite Ni+Mo coatings a nickel plating bath was prepared of a composition as follows: 0.5M $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5M NH_4Cl , 0.1M $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$. Reagents of analytical purity (POCh Gliwice Poland) and deionized water were used for the solution. To this bath an appropriate amount of metallic powder of Mo (Aldrich, 99+%, 100 mesh) was added. The pH value of the suspension was about 3,5-4,5. Two kinds of bath different in the amount of suspended Mo powder were applied to plating. The Mo powder concentrations were: $6 \text{ g} \cdot \text{dm}^{-3}$ (bath A) and $3 \text{ g} \cdot \text{dm}^{-3}$ (bath B). The deposition was carried out in the vessel ($V = 400 \text{ cm}^3$, $\varnothing = 8 \text{ cm}$) containing 250 cm^3 of the bath with mechanical stirring (150 rpm) to keep the Mo powder in suspension. The temperature of the bath during deposition was 323K.

The coatings were deposited on a steel substrates (St3S), with an area of 4 cm^2 . The steel plates were prepared by mechanical polishing and chemical activation in an alkaline gluconate bath ($170 \text{ g} \cdot \text{dm}^{-3} \text{ NaOH}$, $170 \text{ g} \cdot \text{dm}^{-3} \text{ C}_6\text{H}_{11}\text{O}_7\text{Na}$, $T = 353\text{K}$), which ensures a good adhesion of the plated coatings to the steel substrate. During deposition the steel plates were placed vertically in the vessel.

Electrodeposition was performed under galvanostatic conditions in the current density range of $150\text{-}300 \text{ mA} \cdot \text{cm}^{-2}$. For each type of the coatings a constant value of the electric deposition charge ($Q = 360 \text{ C}$) was applied. After plating the deposits were rinsed with distilled water and dried in air at room temperature. The thickness of the coatings was estimated based on their cross-section images. The influence of the metal powder in the bath and the deposition current density on the chemical composition of the coatings was investigated. For comparison Ni layer was deposited from the same bath without the metallic powder suspension.

The chemical composition of the Ni+Mo composites was determined by the X-ray fluorescence spectroscopy method using a special attachment to the X-ray generator TUR-M62 with flat LiF crystal and self-prepared standards, made with homogenized and compressed powders of Ni (Merck, 99,99%), and Mo (Aldrich, 99+%).

Thermal treatment of the obtained composites was carried out in vacuum by annealing the samples in quartz tubes at $800 \text{ }^\circ\text{C}$ for 3h. According to the Ni-Mo phase diagram in the concentration range of 15-44 at.% of Mo the Ni_4Mo and Ni_3Mo intermetallic phases should be formed during the thermal treatment at this temperature.

Surface morphology as well as cross-section studies of the investigated coatings were carried out by using a scanning microscope (Hitachi S-4200) equipped with a digital system of image recording (Voyager 3500).

Structural investigations were conducted by XRD using a Philips diffractometer (X'Pert model) with $\text{Cu}_{K\alpha}$ radiation ($U = 40 \text{ kV}$, $I = 20 \text{ mA}$). Diffraction patterns were recorded in the 2θ range from 20° to 150° . Phase identification was carried out on the base of ICDD card standards (2000).

The investigated Ni+Mo composites were subjected to electrochemical characterization in an alkaline environment and their activity towards hydrogen evolution reaction (HER) in comparison to nickel electrode was analyzed. The study of HER

Table 1. The atomic concentration of Mo in Ni+Mo composite coatings in dependence on the applied conditions of electrodeposition.

Current density [mA×cm ⁻²]	Ni+Mo	
	Bath A [at.% Mo]	Bath B [at.% Mo]
150	44±3	32±4
225	39±4	26±3
300	21±3	15±4

was done by means of steady-state polarization measurements.

Electrochemical measurements were performed in a Pyrex® (Radiometer No.1734) glass cell. The experiments were carried out in 5M KOH solution at a room temperature with a platinum mesh as a counter electrode and Hg/HgO/6M KOH as the reference electrode. The exposed geometric surface area of the working electrode was 1 cm². Steady-state polarization measurements were conducted using Autolab®/PGSTAT20 (Eco Chemie B.V. the Netherlands), controlled by an IBM compatible PC. Prior to the electrochemical experiments the tested electrodes were activated at a constant cathodic current of 320 mA×cm⁻² for 24h.

Steady-state polarization curves were registered galvanostatically. For this purpose a constant current density ranging between 320 μA×cm⁻² and 0.1 mA×cm⁻² was applied to the electrode and after 45 s the corresponding steady-state overpotential value was registered. Basing on recorded $\eta = f(\log j)$ dependences the kinetic parameters for this process (i.e. Tafel slope b , exchange current density j_0 and overpotential at the current density of 100 mA×cm⁻² - η_{100}) were determined.

3. RESULTS AND DISCUSSION

The results of quantitative analysis of the Ni+Mo coatings done by X-ray fluorescence spectroscopy show that they contain 15–44 at.% Mo (Table 1). The process of electrolytic deposition of composite Ni+Mo coatings depends both on the amount of metallic powder in the bath and the deposition current density. The atomic concentration of Mo increases with the rise of the amount of metallic pow-

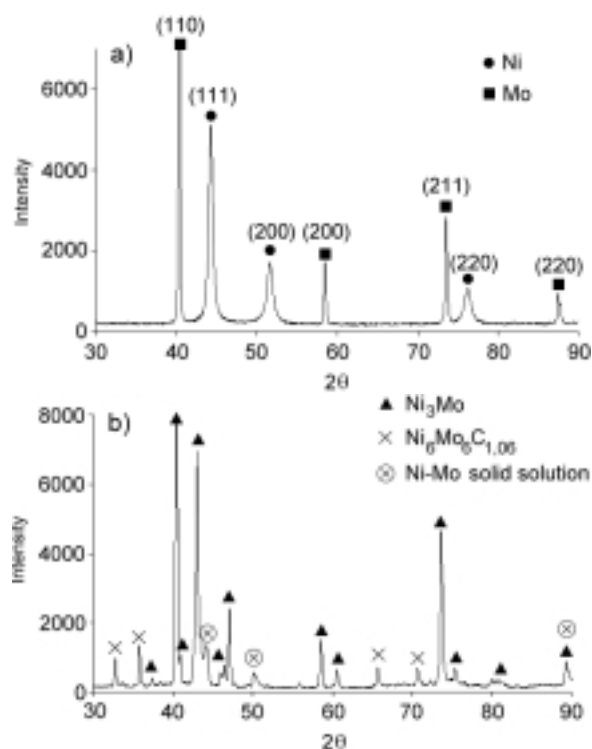


Fig. 1. X-ray diffraction patterns of Ni+Mo composite coatings before (a) and after thermal treatment (b).

der in the bath (Table 1). This fact could be explained by a phenomenon of nickel ions adsorption on the surface of solid particles suspended in the plating bath. When ions originally adsorbed on a particle surface are reduced at the cathode, that particle is captured. Thus, the adsorption of Ni cations facilitates their reduction and, in this way enables the incorporation of solid particles into the electrodeposited matrix.

The other factor influencing the composition of electrodeposited coatings is the current density. For Ni+Mo coatings the content of incorporated Mo powder diminishes with the increase in current density (Table 1). The composites deposited at the highest current density exhibit the lowest contents of embedded Mo. It points at the fact, that the amount of incorporated Mo powder is related to the rate of mass transfer. When the current density is lower a longer time is allowed for the transport of Mo powder, which results in higher amounts of incorporated particles. At high current densities the Ni layer grows more quickly and less time is

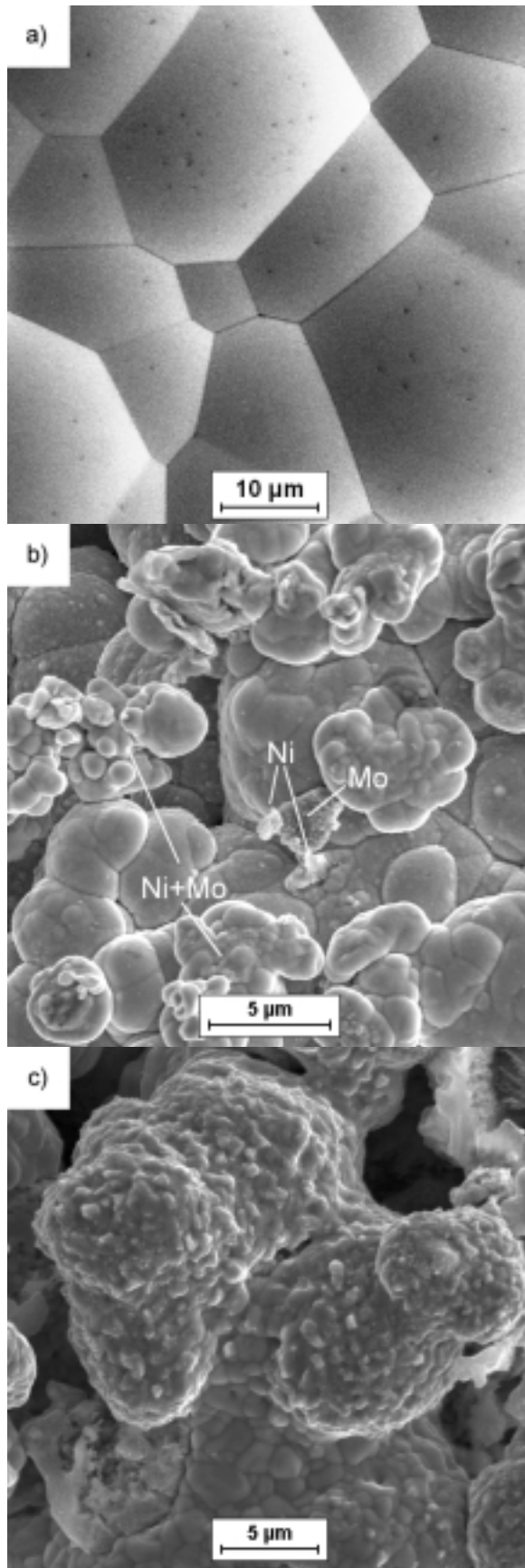


Fig. 2. Surface morphology of a) Ni electrodeposited layer, b) Ni+Mo as-deposited composite, c) Ni+Mo composite after thermal treatment.

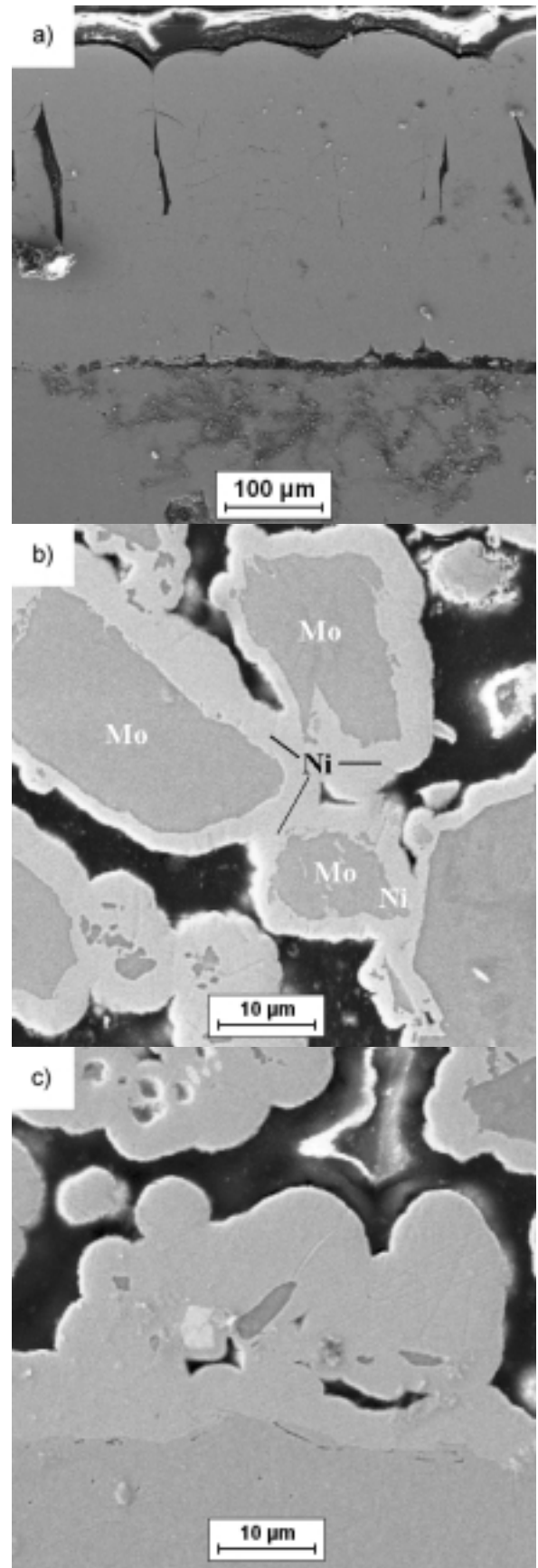


Fig. 3. Cross-section images of: a) Ni electrodeposited layer, b) Ni+Mo as-deposited composite, c) Ni+Mo composite after thermal treatment.

allowed for Mo powder to be transferred from the solution, so a decrease in Mo percentage in deposits is observed. Above relations between the amount of incorporated solid particles and the conditions of electrodeposition are consistent with the adsorption model of electrolytic composite plating, which was proposed by Celis, Roos, and Buelens [29-30] and continued by Valdes [31].

The phase composition of Ni+Mo coatings determined by XRD is independent on the applied deposition conditions. X-ray diffraction patterns of all coatings show the presence of reflexes corresponding to crystalline Ni matrix and embedded Mo crystalline phases (Fig. 1a).

As distinct from a smooth nickel deposit all obtained composite coatings are characterized by a grey, mat surface. From the SEM micrographs it can be seen that Ni layer exhibits a nodular surface structure, whereas the surface of Ni+Mo composites is rough and more developed (Figs. 2a and 2b). On the Ni+Mo surface images it is possible to recognize the metallic powder particles covered with Ni electrodeposit, which confirms the adsorption mechanism of coatings' deposition. Cross-sectional images of the composite coatings also confirm the incorporation of metallic powder particles into the nickel matrix during electrodeposition (Fig. 3b). They also reveal their porous structure which may be a consequence of hydrogen evolution accompanying the process of electrodeposition. The approximate thickness of the composite coatings determined from the cross-sectional SEM micrographs is about 150–300 μm .

Thermal treatment of the deposited Ni+Mo coatings leads to chemical reactions in the solid state and in a consequence exerts significant influence on their phase composition and surface morphology. As a result of interaction between the nickel matrix and incorporated Mo particles new phases like Ni_3Mo and Ni-Mo solid solution are arising (Fig. 1b). The presence of $\text{Ni}_6\text{Mo}_6\text{C}_{1.06}$ phase could be connected with diffusion of carbon from the steel substrate.

It could be also observed that the surface morphology of the composite coatings clearly changes after thermal treatment (Fig. 2c). SEM images of these materials show the effects of integration of initially separated composite components resulting in the formation of intermetallic phases or solid solutions (Figs. 2c and Fig. 3c). A microstructure and phase composition of electrode materials have a significant influence on their electrochemical activity so, details of the microstructure features, the surface roughness, the size and distribution of

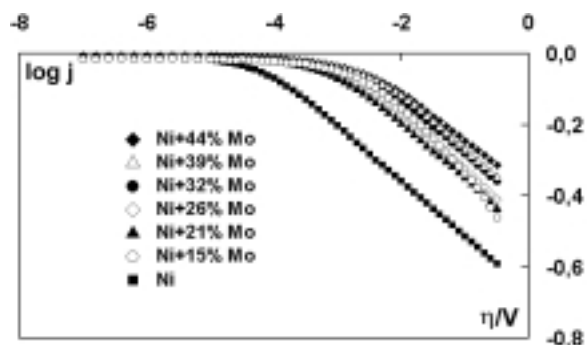


Fig. 4. Tafel polarization curves for the hydrogen evolution process on Ni+Mo composite electrodes in 5M KOH.

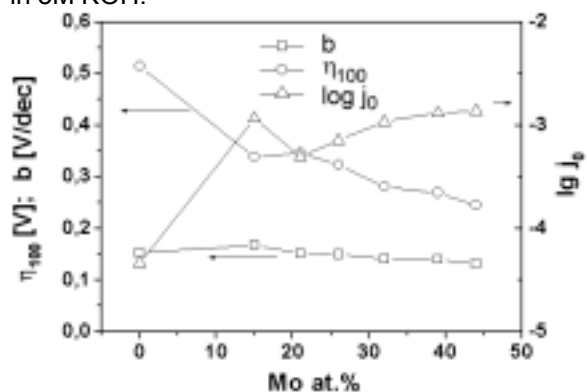


Fig. 5. Tafel slope: b , exchange current density: j_0 and hydrogen evolution overpotential at 100 $\text{mA}\times\text{cm}^{-2}$: η_{100} on electrodeposited Ni+Mo coatings.

pores as well as the phase transformations during thermal treatment have still to be intensively investigated.

The electrochemical activity of the tested electrodes for hydrogen evolution reaction (HER) was studied by analysis of the Tafel plots. The registered $\eta = f(\log j)$ curves in a 5M KOH solution are displayed in Fig. 4. The values of the Tafel slope for the tested electrodes change between -130 and $-170 \text{ mV}\times\text{dec}^{-1}$ and suggest a Volmer-Heyrovsky mechanism for HER (Fig. 5). These slopes are higher than the theoretical value $-120 \text{ mV}\times\text{dec}^{-1}$, probably due to the fact that the electrode surface is covered with a thin film of oxides, which causes an additional potential drop. They are also comparable to the slope obtained for Ni electrode however the values of the exchange current density $-j_0$ for all investigated composite coatings are higher when compared to Ni electrode, suggesting their

higher activity for HER (Fig. 5). This could be related to their large surface area arising from the incorporation of metallic Mo particles into the Ni matrix. These results are in good agreement with the SEM results shown above, where an increase in the composites' surface area is evident, resulting in higher exchange current densities. The highest value of j_0 exhibit Ni+Mo electrodes, containing above 40 at.% Mo.

The practical measure of the electrode activity is overpotential at a given current density, in our studies at $100 \text{ mA/cm}^2 - \eta_{100}$. For all composite electrodes η_{100} values are lower than for Ni electrode (Fig. 5). Considerable decrease in the HER overpotentials, by nearly 230-260 mV compared to a nickel electrode is achieved for the coatings with the molybdenum content of 30 to 40 at.%. The increase in electrochemical activity of the Ni+Mo composite coatings could be attributed not only to their large surface area but it could be also related to the presence of Mo particles in the nickel matrix, as Ni/Mo materials are considered, according to the literature data [18-28], typical electrocatalysts for the HER.

The analysis of obtained results leads to the statement that already small amounts of incorporated Mo particles (15-20 at.%) evoke an increase in the hydrogen evolution rate compared to a nickel electrode.

In order to evaluate the influence of a thermal treatment on the electrochemical properties of Ni+Mo composites, the electrodes containing about 20 at.% of Mo were compared in the process of hydrogen evolution before and after thermal treatment (Fig. 6). On the base of this comparison it could be stated that the activity of Ni+Mo composites decreases after thermal treatment as the values of hydrogen evolution overpotential on heated coatings are much higher. The value of η_{100} for the heated Ni+Mo electrode is about 135 mV higher than for the as-deposited one.

A negative influence of the thermal treatment on the electrochemical performance of similar materials has been reported in literature [24,27]. The lower electrochemical activity is often attributed to losses of effective surface area resulting from the formation of considerably larger crystallites or from the formation of new phases.

4. CONCLUSIONS

Ni-based composite coatings containing embedded particles of Mo metallic particles were produced by using an electrolytic method. The content of in-

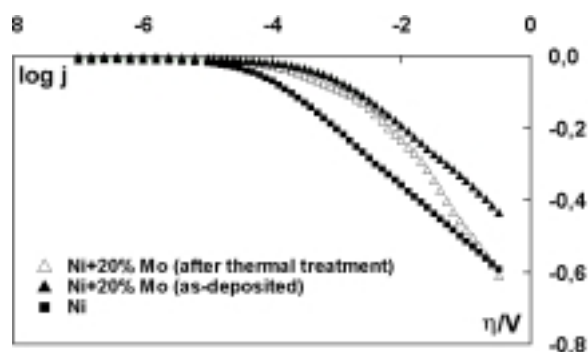


Fig. 6. The effect of thermal treatment on the electrochemical activity of Ni+Mo composites for hydrogen evolution.

corporated Mo particles is about 15-44 at.%. Chemical composition of Ni+Mo coatings is strongly influenced by the conditions of their electrolytic deposition. The content of embedded Mo increases with the increase in the amount of metal powder in the bath, and diminishes with the increase in the deposition current density. Incorporation of metallic particles into the electrolytic nickel matrix causes an increase in the real surface area of the coatings.

The investigated coatings have shown pronounced improvement in the electrochemical performance for hydrogen evolution reaction in alkaline environment compared to nickel electrode. Already small amounts of incorporated metallic particles (15-20 wt.%) are sufficient to evoke an increase in the hydrogen evolution rate. An increase in the electrochemical activity may be attributed to the increase in real surface area of the coatings, although some catalytic effect of Mo cannot be excluded.

Thermal treatment of electrodeposited Ni+Mo coatings leads to chemical reactions in the solid state and exerts significant influence on their phase composition and surface morphology. As a result of the interaction between the nickel matrix and incorporated Mo particles Ni_3Mo intermetallic phase and Ni-Mo solid solution are arising.

Thermal treatment decreases the electrochemical activity of Ni+Mo coatings towards hydrogen evolution in the consequence of the changes of surface morphology leading to the loss of effective surface area.

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