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## The Hydrogen Evolution Reaction on Electrolytic Ni+W+Si and Ni+W+Mo+Si Composite Coatings

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Ni+W+Si and Ni+W+Mo+Si composite coatings were obtained by electrolytic codeposition of crystalline nickel from an electrolyte containing suspension of suitable metallic and non-metallic components (W, Mo and Si). These coatings were obtained under galvanostatic conditions, at the current density of  $j_{dep.} = 0.100 \text{ A} \cdot \text{cm}^{-2}$  and at the temperature of 338 K. Chemical composition of obtained coatings was determined by EDS method. The electrochemical activity of these coatings was studied in the process of hydrogen evolution reaction (HER) from 5 M KOH solution using steady-state polarization and electrochemical impedance spectroscopy (EIS) methods. Basing on the results of EIS measurements the rate constants of the HER were determined. It was found that Ni+W+Mo+Si composite coatings are characterized by enhanced electrochemical activity towards hydrogen evolution as compared with Ni+W+Si coatings. The reason of this is connected with the presence of additional composite component (molybdenum). Thus obtained coatings may be useful in application as electrode materials for the hydrogen evolution reaction.

**Key words:** Nickel, Tungsten, Molybdenum, Silicon, Composite coatings, Hydrogen evolution reaction.

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### Introduction

Many papers have dealt with ways of increasing the effectiveness of cathodes used for the hydrogen evolution reaction in alkaline solutions [1,2]. Many transition metals and metal alloys have been characterized as hydrogen electrodes. Among them, nickel and nickel-based alloys [3,4] have a high catalytic activity. However, their activity and stability are insufficient. They are usually prepared by electrolytic codeposition or dip coating. In order to improve the utilization of these materials and to enhance their electrocatalytic activity, various modifications could be applied, such as the use of alloys or composites instead of pure elements and other modifications to obtain electrodes with very developed, rough or porous electrode surface [1-4].

This study was undertaken in order to obtain the nickel coatings, containing an additional components of metallic (W) and non-metallic (Si) powders (Ni+W+Si coatings) and components of metallic (W, Mo) and non-metallic (Si) powders (Ni+W+Mo+Si coatings). Metallic (W) and non-metallic (Si) components perform a function of surface modifiers. The choice of Mo component was made based on the knowledge of properties of this metal in the hydrogen evolution reaction [3,4], which performs a function of activator in the HER. The purpose of this work was to evaluate effectiveness of these coatings as electrode materials for

hydrogen evolution in an alkaline solution.

### I. Experimental

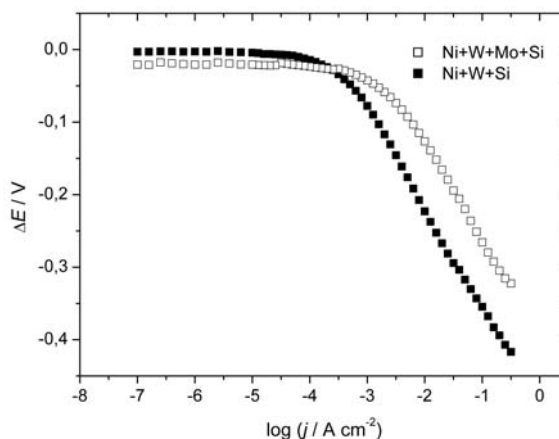
Ni+W+Si coatings were obtained by electrodeposition from the following electrolyte (concentrations in  $\text{g dm}^{-3}$ ):  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  – 84,  $\text{H}_3\text{BO}_3$  – 8,  $\text{CH}_3\text{COONa}$  – 10,  $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$  – 30,  $\text{NH}_4\text{Cl}$  – 10 + 50  $\text{g dm}^{-3}$  of tungsten powder (100 mesh, Aldrich) + 50  $\text{g dm}^{-3}$  of silicon powder (325 mesh, Aldrich). Ni+W+Mo+Si coatings were obtained by electrodeposition from the following electrolyte (concentrations in  $\text{g dm}^{-3}$ ):  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  – 84,  $\text{H}_3\text{BO}_3$  – 8,  $\text{CH}_3\text{COONa}$  – 10,  $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$  – 30,  $\text{NH}_4\text{Cl}$  – 10 + 50  $\text{g dm}^{-3}$  of tungsten powder (100 mesh, Aldrich) + 50  $\text{g dm}^{-3}$  of molybdenum powder (100 mesh, Aldrich) + 50  $\text{g dm}^{-3}$  of silicon powder (325 mesh, Aldrich). Distilled water and 'analytical grade' reagents were used for preparation of the electrolyte. The process was carried out at the temperature of 338 K, with intensive mechanical stirring (200 rpm). Coatings were electrodeposited under galvanostatic conditions, at the current density  $j_{dep.} = 0.100 \text{ A cm}^{-2}$ . A platinum mesh served as an auxiliary electrode. The coatings were deposited on the steel plate (St3S) of the geometric surface area of  $1 \text{ cm}^2$  and were used as working electrodes. Chemical composition of obtained coatings was determined by EDS method.

Investigations of electrolytic hydrogen evolution on the prepared coatings were conducted in a three-electrode cell, using steady-state polarization and electrochemical impedance spectroscopy (EIS) methods. These measurements were carried out in 5 M KOH solution, at the temperature of 293 K, using Autolab<sup>®</sup> electrochemical system. The auxiliary electrode was a platinum mesh and the reference electrode was of the type Hg/HgO/5 M KOH. The EIS measurements were performed approximately after 24 h of the HER at the constant current density,  $j = 0.320 \text{ A cm}^{-2}$ . For each coating, three cycles were recorded. Each cycle consisted of 30 minutes of galvanostatic electrolysis at  $j = 0.320 \text{ A cm}^{-2}$  and 43 minutes of curve recording using galvanostatic polarization (45 s per point) ranging from  $0.320 \text{ A cm}^{-2}$  to  $0.1 \mu\text{A cm}^{-2}$ . At the steady-state, the electrode potentials were corrected for  $iR_s$  drop determined by EIS. In the EIS measurements the amplitude of  $ac$  signal was equal  $0.005 \text{ V}$ . A frequency range from  $10 \text{ kHz}$  to  $0.1 \text{ Hz}$  was covered with 10 points per decade. The real and imaginary components of the complex plane plots were analysed using a modified version of a complex non-linear least-squares fitting program (CNLS) [4] from which the experimental parameters of an electrical equivalent circuit were determined. Kinetics of hydrogen evolution process was determined on basis of the dependences of both the  $1/R_{ct}$  (inverse the charge-transfer resistance) and the total current density  $j$ , on overpotential  $\Delta E$ . The rate constants ( $k_1$ ,  $k_{-1}$ ,  $k_2$ ,  $k_{-2}$ ,  $k_3$ ) were evaluated using the NLS method.

## II. Results and Discussion

The Ni+W+Si composite coatings contain about 39 wt% of nickel, 41 wt% of tungsten and 20 wt% of silicon. The Ni+W+Mo+Si composite coatings contain about 34 wt% of nickel, 30 wt% of tungsten, 22 wt% of molybdenum and 14 wt% of silicon. X-ray diffraction pattern showed that the deposited coatings have a composite character [5-7]. The composite is the mixture of the Ni, W and Si and mixture of the Ni, W, Mo and Si. It means that in the process of nickel electrodeposition, metallic and non-metallic powders grains have been built into a crystalline nickel matrix [5-7]. The process of powders embedding in the Ni matrix is probably based on the ability to adsorb  $\text{Ni}^{2+}$  ions on a surface of powders, which was shown earlier [8]. Such a form of nickel ions, partially devoid of its hydration envelope can be more electrochemically active than hydrated  $\text{Ni}^{2+}$  ions. A suspension of this type moves towards the cathode and by applying considerable current densities, more adsorbed  $\text{Ni}^{2+}$  ions than the ones hydrated in the electrolyte are submitted to the charge-transfer reaction. The composite structure is obtained on this way.

The electrochemical activity of thus obtained coatings was studied in the process of hydrogen evolution from 5 M KOH solution. The steady-state polarization curves obtained on different electrodes are presented in Figure 1 and the kinetic parameters are presented in Table 1. On the bases of steady-state of the hydrogen evolution, the rate of this process was



**Fig. 1.** The steady-state polarization curves obtained for HER in 5 M KOH on obtained coatings.

**Table 1**

Kinetic parameters of the HER in dependence from the type of coating.

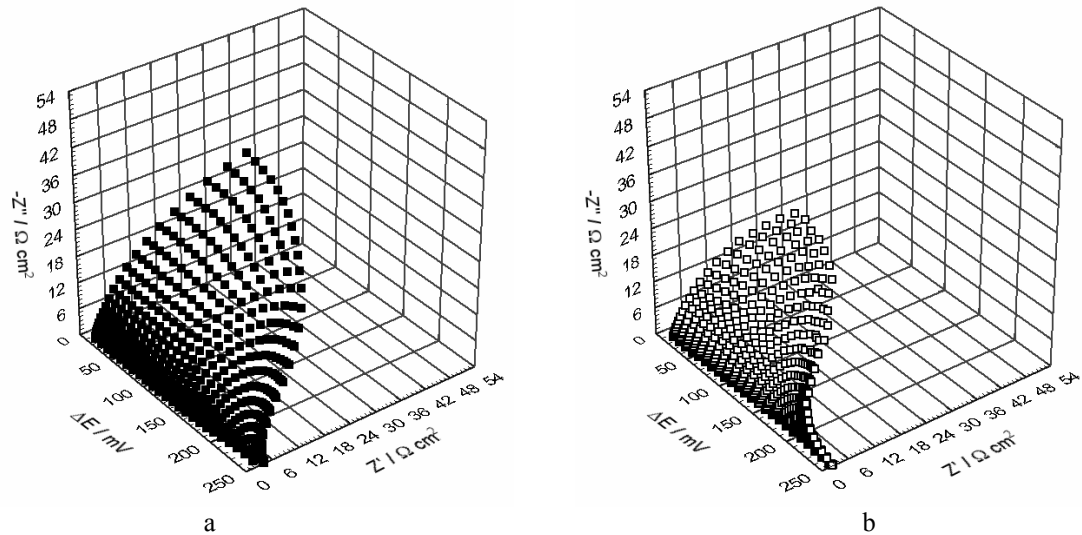
Type of coating	$\Delta E_{100}$ [V]	$j_0$ [A cm <sup>-2</sup> ]
Ni+W+Si	-0.357	$2.58 \cdot 10^{-4}$
Ni+W+Mo+Si	-0.266	$1.03 \cdot 10^{-3}$

estimated depending on the type of coatings. The value of hydrogen evolution overpotential at the current density of  $100 \text{ mA cm}^{-2} - \Delta E_{100}$  is lower for the Ni+W+Mo+Si coatings than for the Ni+W+Si coatings. Value of exchange current density  $-j_0$  for the Ni+W+Mo+Si coatings is higher than for the Ni+W+Si coatings. It suggests an influence of presence additional composite component (Mo) on the rate of hydrogen evolution. It was found that in the Ni+W+Mo+Si coatings the increase in the rate of hydrogen evolution was observed.

The complex impedance was analysed using a modified version CNLS fitting program [4]. Character of dependence of imaginary impedance component on electrode overpotential and real impedance component is show in the three-dimensional diagrams (3D):  $-Z'' = f(Z', \Delta E)$  (Figure 2). These diagrams show influence of real impedance component and electrode overpotential on values of imaginary impedance component. The values of real and impedance components are lower for the Ni+W+Mo+Si coatings than for the Ni+W+Si coatings. This means that Ni+W+Mo+Si coatings are characterized by enhanced electrochemical activity for HER compared to Ni+W+Si coatings.

It has been found that the  $ac$  impedance behaviour of obtained coatings may be well described by the one-CPE electrode model. This is typical model for the HER on solid, rough or porous electrodes. Such equivalent circuit is characteristic of electrode materials composed of cylindrical pores of radius  $r$  and length  $l$ . As was shown for short and wide pores  $l^2/r$  is very small and only one semicircle on the complex plane plot was observed (model CPE1) [9].

One-CPE model consists of the solution resistance  $R_s$  in series with the parallel connection of the CPE element



**Fig. 2.** Dependences of  $-Z'' = f(Z', \Delta E)$  for the Ni+W+Si coatings (a) and Ni+W+Mo+Si coatings (b).

and charge-transfer resistance  $R_{ct}$  (Figure 3) [4].

The impedance of CPE element is given as:

$$Z_{CPE} = 1 / (Tj\omega)^\phi$$

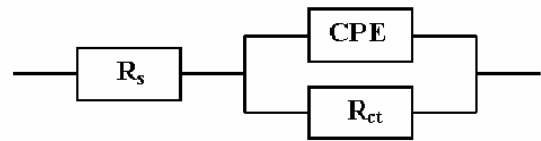
where  $T$  is the capacitive parameter,  $\omega$  is the angular frequency of  $ac$  voltage and  $\phi$  is the coefficient of dispersion. As a result of approximation of experimental data in the case of CPE1 model the following parameters could be obtained:  $R_{ct}$ ,  $T$ ,  $\phi$ ,  $R_s$ .

The charge transfer resistance values,  $R_{ct}$ , are higher for the Ni+W+Si coatings than for the Ni+W+Mo+Si coatings (Figure 4). An approximation of the values of  $1/R_{ct}$  in function of  $\Delta E$  (in the range from  $-0.25$  V to  $-0.12$  V) and  $j$  in function of  $\Delta E$ , was carried out by adjusting the rate constants  $k_1$ ,  $k_{-1}$ ,  $k_2$ ,  $k_{-2}$ ,  $k_3$  [4,10,11] and are presented in Table 2. For all obtained coatings, value of  $k_3$  rate constant is at least of two orders smaller than values of  $k_1$  and  $k_2$  rate constants. Is suggesting that the main pathway for the HER at above mentioned electrode materials is Volmer – Heyrovsky, and Tafel reaction has a small contribution to this process. Values of  $k_1$ ,  $k_{-1}$ ,  $k_2$ ,  $k_{-2}$  and  $k_3$  for the Ni+W+Mo+Si coatings are higher than for the Ni+W+Si coatings. This confirms that Ni+W+Mo+Si coatings characterized enhanced electrochemical activity for HER compared to Ni+W+Si coatings.

Increase in the activity of HER of Ni+W+Mo+Si coatings (higher values of  $j_0$ ,  $k_1$ ,  $k_{-1}$ ,  $k_2$ ,  $k_{-2}$ ,  $k_3$  and lower values of  $\Delta E_{100}$ ,  $R_{ct}$ ) in comparison with Ni+W+Si coatings is connected with presence of additional composite component (Mo).

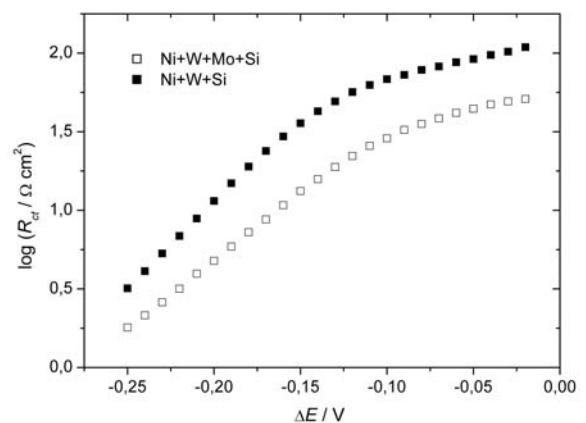
## Conclusions

Ni+W+Si and Ni+W+Mo+Si composite coatings



**Fig. 3.** Equivalent circuit scheme for the one-CPE electrode model,  $R_s$  [ $\Omega \text{ cm}^2$ ] – solution resistance, CPE – constant phase element,  $R_{ct}$  [ $\Omega \text{ cm}^2$ ] – charge-transfer resistance.

could be obtained by electrolytic codeposition of crystalline nickel with suitable metallic and non-metallic components (tungsten, molybdenum and silicon). It was found that Ni+W+Mo+Si composite coatings are characterized by enhanced electrochemical activity towards hydrogen evolution as compared with Ni+W+Si. The reason of this is connected with the presence of additional composite component (molybdenum), which performs a function of activator in the HER. Thus obtained coatings may be useful in application as



**Fig. 4.** Dependences of  $\log R_{ct} = f(\Delta E)$  for the obtained coatings.

**Table 2**

The rate constants of the HER in dependence from the type of coating.

Type of coating	$k_1$ [mol cm <sup>-2</sup> s <sup>-1</sup> ]	$k_{-1}$ [mol cm <sup>-2</sup> s <sup>-1</sup> ]	$k_2$ [mol cm <sup>-2</sup> s <sup>-1</sup> ]	$k_{-2}$ [mol cm <sup>-2</sup> s <sup>-1</sup> ]	$k_3$ [mol cm <sup>-2</sup> s <sup>-1</sup> ]
Ni+W+Si	$1.68 \cdot 10^{-9}$	$1.87 \cdot 10^{-8}$	$3.96 \cdot 10^{-11}$	$3.56 \cdot 10^{-12}$	$2.47 \cdot 10^{-13}$
Ni+W+Mo+Si	$3.04 \cdot 10^{-9}$	$5.65 \cdot 10^{-8}$	$1.35 \cdot 10^{-10}$	$7.27 \cdot 10^{-12}$	$9.11 \cdot 10^{-13}$

electrode materials for the hydrogen evolution reaction in comparison with Ni+W+Si coatings. *T08C 009 28*

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## Реакція водневої еволюції в електролітичних композитних сумішах Ni+W+Si та Ni+W+Mo+Si

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Композитні суміші Ni+W+Si і Ni+W+Mo+Si були одержані електролітичним осадженням кристалічного нікелю з електроліту, що містить домішки відповідних металевих і нерудних компонентів (W, Mo і Si). Ці суміші були одержані в гальваностатичним осадженням, при густині струму  $j_{\text{dep.}} = 0,100 \text{ cm}^{-2}$  і при температурі 338 K. Хімічний склад одержаних сумішей був визначений методом EDS. Електрохімічна діяльність цих сумішей вивчалася в процесі реакції водневої еволюції. Знайшли, що суміш Ni+W+Mo+Si характеризуються збільшеною електрохімічною діяльністю у напрямку до водневої еволюції порівнянно з сумішшю Ni+W+Si. Причина цього пов'язана з присутністю додаткового складового компоненту (молібден).

**Ключові слова:** нікель, вольфрам, молібден, кремній, композитні суміші, реакція водневої еволюції.