Cathodic behavior of the dealloyed Ni–Zn coating in sodium hydroxide solution

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Abstract

The goal of the paper is to study the electrochemical behavior of the composite (Ni–Zn)*Ni electrode in 0.1 M sodium hydroxide solution compared with compact nickel. The composite electrode was obtained by alkaline dealloying in 2 M NaOH of Ni–Zn coating preliminarily electrodeposited on Ni substrate from ammonia electrolyte. The morphology of the Ni–Zn coatings before and after modification was studied using scanning electron microscopy. The crystalline structure of the coatings was investigated by transmission electron microscopy, and it was shown that the alloy consists of nanocrystals with size of 40–100 nm. It was shown by voltammetry that the electrochemically active surface area of (Ni–Zn)*Ni material is four times greater than that of the nickel substrate. The chemical composition of the coatings was determined by X-ray analysis. It was found that before the modification the amount of zinc in the coating is four times that of nickel. The rate of cathodic hydrogen evolution reaction on the dealloyed Ni–Zn coating is almost ten times higher compared with nickel substrate. The dealloyed (Ni–Zn)*Ni material is more saturated with hydrogen than compact nickel. The hydrogen dissolution process from the composite electrode is a multi-step process including solid-phase diffusion of hydrogen and its ionization in a non-equilibrium mode.

Keywords: Ni–Zn alloys, electrodeposition, selective dissolution, hydrogen evolution.

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Introduction

Alloys of nickel and zinc are of interest to researchers due to the fact that this material, having a number of useful properties, can be used not only as a catalyst in high-efficiency electrolysis cells for hydrogen production [1, 2], but also as an anticorrosion coating for steel structures in mechanical engineering, aviation, *etc.* [3–7].

Available information on the phase composition of electrolytic Ni–Zn coatings indicates such a feature of Ni–Zn system as abnormal deposition of metals from electrolyte solution [8]. The ratio of metals in the coating differs from the metal ion ratio in the electrolyte solution, and the coating contains not only pure nickel and zinc, but also their intermetallic compounds [9, 10].

The published research results on the influence of the composition of the deposition solution, temperature, deposition conditions (galvanostatic, potentiostatic), *etc.* indicate the

presence of intermetallic compounds NiZn_8 , NiZn_3 , $\text{Ni}_5\text{Zn}_{21}$ (γ -phase) in the coating [11, 12].

It is well known that the γ -phase of binary Ni–Zn systems in electrolyte solutions can be dissolved selectively (dealloyed) with phase transformation [13]. Dealloying of the Ni–Zn phases leads to the formation of nanoporous nickel [14–17], and such a material has improved catalytic and corrosion properties compared with compact nickel [1, 2, 18–20]. The properties of the dealloyed nickel-zinc electrolytic coatings depend on phase composition of the origin alloy. The knowledge of the regularities of the Ni–Zn phases dealloying in aggressive environments will make it possible to predict the protective properties of the electrolytic Ni–Zn coating under the conditions of its operation.

The goal of the paper is to study the electrochemical (cathodic) behavior of the dealloyed Ni–Zn electrode in 0.1 M sodium hydroxide solution compared with compact nickel.

Experimental

This work was divided into two stages. The first part of the work was the study of the composition and morphology of the obtained electrolytic Ni–Zn coating by different physical and chemical methods. In the second part of the work, the electrochemical properties of a composite (Ni–Zn)* / Ni electrode by electrochemical methods (voltammetry, chronoamperometry) in the process of hydrogen evolution were investigated.

The compact nickel and composite (Ni–Zn)* / Ni electrodes were chosen as a subject of this investigation. The composite (Ni–Zn)* / Ni electrode was obtained by modifying the Ni–Zn coating electrodeposited on Ni substrate. Before electrodeposition, the nickel electrode surface (0.5, 1.0, 2.0 cm²) was polished with emery paper (1000 grit size), then washed with distilled water, thoroughly degreased with isopropanol, washed again with distilled water, and dried with a filter paper. The coating was deposited from an electrolyte (g/l): $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ – 57.6; $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ – 56.2; NH_3 – 100 ml; NH_4Cl – 27 (pH 10.1 ± 0.1), at the potential -1.150 V for 600 s. The thickness of the coating formed on the nickel substrate was measured with a microinterferometer MEI-4 (Russia); it was 1.1×10^{-4} cm. The electrolytic Ni–Zn coating was dealloyed by selective dissolution of zinc in 2 M NaOH in galvanostatic mode at a current density of $i = 2.5 \times 10^{-5}$ A/cm². The anodic polarization was stopped when the potential of the modified coating became equal to the potential of nickel in the same electrolyte. A composite (Ni–Zn)* / Ni electrode was obtained as a result.

The morphology and elemental composition of Ni–Zn coatings were studied using the scanning electron microscope (JSM-6380LV JEOL with INCA 250 microanalysis system, Japan) (magnification 3000–100000 and accelerating voltage 30 kV) before and after the modification.

Transmission electron microscopy (LIBRA 120 PLUS, Germany) was used to independently estimate the particle size, crystallographic characteristics, and roughness of the nickel phase in the (Ni–Zn)*Ni electrode. The analysis of the measurement results was carried out using the Gwyddion software [21]. The microscopic results were obtained on the equipment of the Center for Collective Use of Scientific Equipment at Voronezh State University (<http://ckp.vsu.ru>).

The kinetics of cathodic reduction of hydrogen, hydrogenation of nickel electrodes, and dissolution of hydrogen from the hydrogenated electrodes was studied in 0.1 M NaOH by cyclic voltamperometry and chronoamperometry. Electrochemical measurements were performed using an IPC-compact potentiostat (Russia) under computer control. All electrochemical measurements were carried out at room temperature in a three-electrode cell with separated anodic and cathodic spaces exposed to air. A saturated silver chloride reference electrode and a platinum counter electrode were used. All electrode potentials in this paper are given vs. the standard hydrogen electrode. All the solutions were prepared with bi-distilled water.

Results and Discussion

Scanning electron microscopy showed that the Ni–Zn alloy is uniformly deposited over the entire surface of the nickel substrate (Figure 1a).

Figure 1. SEM image of Ni–Zn coating obtained at -1.150 V for 600 s: a) before dealloying; b) after dealloying in 2 M NaOH at 2.5×10^{-5} A/cm².

The energy dispersive X-ray technique showed the presence of Zn and Ni in the electrodeposited coating, and the amount of zinc in the coating is four times that of nickel. These data are in a good accordance with the results of a galvanostatic behavior of the electrolytic coating in 2 M NaOH and with XRD analysis [21], which confirmed the presence of nickel and zinc metals, as well as intermetallic phases of NiZn (β_1 -phase) and Ni₅Zn₂₁ (γ -phase) in the coating electrodeposited from ammonia electrolyte.

Selective dissolution of zinc (dealloying) from the coating in 2 M NaOH leads to the formation of a new phase of nanocrystalline nickel. SEM analysis of the modified Ni–Zn coating showed that after the modification, the coating surface becomes porous and is

covered by microcracks (Figure 1b). It was found that the modified Ni–Zn coating thickness decreases from 1.1×10^{-4} to 0.616×10^{-4} cm.

Figure 2 shows TEM images obtained at two different magnifications. As can be observed, the alloy consists of nanocrystals with the size of 40–100 nm. These results are in very good accordance with the AFM data obtained for the Ni–Zn electrodeposited coatings in [21].

Figure 2. TEM image of the nanocrystalline nickel phase formed after dealloying of the Ni–Zn coating.

It should be expected that the anodic modification of the Ni–Zn alloy, accompanied by dezincification and changes in the surface morphology and phase composition, would lead to a change in its electrochemical properties. A detailed study of the cathodic behavior of the obtained (Ni–Zn)* / Ni electrode, in comparison with the nickel substrate, is presented in the subsequent part of the work.

It is known that nickel and its alloys are capable of forming hydrides, which leads not only to hydrogen embrittlement of the resulting coatings, affecting their anticorrosion properties, but also to a change in their electrochemical activity. The effect of changes in the surface morphology during the dealloying process of the electrodeposited Ni–Zn coatings on its electrochemical properties, such as the rate of cathodic reduction of hydrogen and the degree of hydrogenation, was studied in 0.1 M NaOH.

During the analysis, it was found that the steady-state potential of the (Ni–Zn)* / Ni electrode is 0.100 V more negative than the potential of nickel substrate in the same solution. This fact suggests that the cathodic reduction of hydrogen on the modified coating is facilitated.

Indeed, the rate of cathodic reduction of hydrogen at a potential of -0.800 V on (Ni–Zn)* / Ni is almost ten times higher than on compact nickel, and the polarization of this process is reduced (Figure 3). The area of the electrochemically active surface of the modified Ni–Zn coating increases only four times. So estimating the rate of the processes

occurring on the modified electrode, we can conclude that not only an increase in the area of the working surface, but also a change in its electrochemical activity, due to the size factor and structure imperfection, determine the properties of the modified electrodes.

Figure 3. Cathodic polarization curves in 0.1 M NaOH: 1 – compact Ni (substrate); 2 – (Ni–Zn)*Ni electrode.

A comparative estimation of the hydrogen accumulation degree in the electrodes was carried out by studying the kinetics of the process of hydrogen ionization by the potentiodynamic method. The cyclic voltammetric curves (Figure 4) on a nickel electrode in sodium hydroxide solutions are characterized by a maximum anode current of hydrogen dissolution from a preliminarily cathodically polarized electrode [23]. With increasing the potential scan rate, the peak height (maximum current) increases both for the compact Ni electrode and (Ni–Zn)*Ni electrode. The peak current linearly depends on potential scan rate square root (Figure 4). This confirms that dissolution of hydrogen proceeds with solid-phase diffusion limitations [24, 25]. The potential of the anodic maximum increases with the potential scan rate for both compact nickel and composite (Ni–Zn)*Ni electrodes, so we can conclude that the hydrogen ionization process is non-equilibrium.

Figure 4. The effect of the potential scan rate on the hydrogen ionization rate in 0.1 M NaOH on (Ni–Zn)*Ni at: 1 – 0.010; 2 – 0.015; 3 – 0.20; 4 – 0.25; 5 – 0.30 V/s.

Based on the fact that solid-phase diffusion is a limiting step of the dehydrogenation process, the hydrogen diffusion coefficient in the hydrogen-saturated layer for different electrodes was calculated from the obtained results using the Randles–Ševčík equation [17] (Table 1).

Table 1. Coefficients of solid-phase diffusion of hydrogen in nickel electrodes in 0.1 M NaOH, determined by the voltammetric method

Electrode	$D_H, \times 10^{10} \text{ cm}^2/\text{s}$
Ni	0.96 ± 0.02
(Ni–Zn)* / Ni	2.70 ± 0.07

The data obtained indicate that the rate of hydrogen diffusion from the volume of the hydrogenated layer to the electrode surface depends on the state of the surface of the electrode. The influential factor of this process can be not only the degree of structure imperfection of the layer in which it occurs, but also the different concentration of adsorbed hydrogen on different types of nickel electrodes.

Within the framework of electrochemical studies, the influence of the preliminary cathodic polarization time on the kinetic parameters of hydrogen ionization from hydrogenous electrodes was determined by the chronoamperometric method. Nickel electrodes were polarized cathodically under potentiostatic conditions at potentials in the range from -1.050 to -1.100 V, then polarization was switched to the hydrogen dissolution potentials on the corresponding electrode and maintained at this potential until the current density was completely stabilized (Figure 5).

The kinetics of hydrogen ionization from hydrogenous electrodes was studied at different times of their cathodic polarization (600, 1200, 1800, 3600, 5400 s) (Figure 5).

Figure 5. Chronoamperograms of hydrogen dissolution from different hydrogenated electrodes: a – compact Ni substrate (at -0.350 V); b – (Ni–Zn)* / Ni (at -0.650 V), after hydrogenation in 0.1 M NaOH at -0.950 V for 600 s.

Analysis of the chronoamperometric i, t -curves of hydrogen dissolution from the hydrogen-enriched layer in $i, t^{-1/2}$ criteria coordinates of solid-phase diffusion kinetics (Figure 5) showed that the process of hydrogen ionization is a complex multi-step process. At the beginning of dissolution, the rate of the whole process is significantly affected by the electrochemical step, and at a certain time, which depends on hydrogenation duration and electrode type, the hydrogen dissolution becomes diffusion-controlled (Figure 5).

The thickness of the hydrogen-saturated layer was calculated using the amount of hydrogen dissolving in the solid-phase diffusion mode (Table 2).

Table 2. The solid-phase diffusion coefficient and the thickness of the hydrogenated layer of nickel electrodes in 0.1 M NaOH at different hydrogenation duration (τ) at the potential of -0.950 V.

Electrode	τ, s	$h \times 10^4, cm$	$D \times 10^{10}, cm^2/s$
Ni	600	1.19	1.47
	1200	2.49	1.47
	1800	2.39	1.47
	3600	2.78	0.65
	5400	2.70	0.65
(Ni–Zn) *	600	5.30	0.65
	1200	5.95	0.86
	1800	5.43	1.02
	3600	5.04	1.47
	5400	5.83	1.47

The obtained experimental data showed that with increasing hydrogenation duration, the thickness of the hydrogenated layer becomes constant both for compact nickel and for the modified Ni–Zn coating. This effect indicates possible hydrogen saturation of the electrode surface layer. The layer relaxation time depends on the type of nickel electrode.

It was found that the thickness of the hydrogenated layer (Table 2) exceeds the thickness of the resulting coating (0.616×10^{-4} cm). Upon dissolution of zinc with hydrogen depolarization, hydrogen accumulation will occur not only in the coating volume, but also in the substrate. So when nickel-zinc coatings are used as an anti-corrosive material, its dezincification in an aggressive environment can lead to the destruction of the protective coating and penetration of hydrogen into the protected product. As a sequence, this process can result in hydrogen embrittlement of the protected metal structures and their destruction.

Conclusions

1. The phase of nanocrystalline nickel with crystal size from 40 to 100 nm is formed as a result of selective dissolution of zinc in 2 M NaOH from an electrolytic Ni–Zn coating. The process leads to the change in the coating morphology, as well as to the decrease in the coating thickness.
2. The composite (Ni–Zn)*/Ni electrode is more electrochemically active in the hydrogen evolution reaction, the rate of which in 0.1 M NaOH is ten times higher than in the case of a compact nickel electrode.
3. The amount of hydrogen dissolved and the thickness of the hydrogenated layer in the composite (Ni–Zn)*/Ni electrode is greater than in a compact nickel. For the conditions considered in this work the thickness of the layer of hydrogenated (Ni–Zn)*/Ni electrode exceeds the thickness of the coating, so the dealloying process not only destroys the protective Ni–Zn alloy, but can facilitate destruction of the substrate material due to the hydrogen embrittlement process.

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