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Ni nanostructures in porous anodic alumina matrices: structure and cathodic properties in hydrogen release reactions

R.G. Valeev^{*,a}, V.V. Stashkova^b, A.I. Chukavin^a, V.A. Volkov^a, A.S. Alalykin^b,
A.V. Syugaev^a, A.N. Beltiukov^a, F.Z. Gil'mutdinov^a, V.V. Kriventsov^{a,c}, N.A.
Mezentsev^d

^aPhysical-Technical Institute of the Ural Branch of RAS, Kirova str. 132, Izhevsk, 426000 Russia

^bInstitute of Mathematics, Information Technology and Physics of Udmurt State University, Universitetskaya str. 1, Izhevsk, 426034 Russia

^cBorisev Institute of Catalysis of the Siberian Branch of RAS, Lavrentieva str. 5, Novosibirsk, 630090 Russia

^dBudker Institute of the Siberian Branch of RAS, Lavrentieva str. 5, Novosibirsk, 630090 Russia

Abstract

A synthesis has been performed of Ni nanostructures by magnetron deposition on the matrices of porous alumina obtained by the two-stage anodic oxidation. The scanning electron microscopy method is used to investigate alumina films before and after nickel deposition. Investigations by X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy and EXAFS show that the nickel deposited on porous alumina is in an oxidized state, in contrast to nickel deposited on a substrate with a smooth surface. No influence of the porous structure of matrices on the structure of nickel and the composition of near-surface layers has been detected. The catalytic properties of the nanostructures in hydrogen release reactions in a 5 M NaOH solution are analyzed. It is shown that the nickel films deposited on porous alumina exhibit a greater catalytic activity in hydrogen release reactions than the nickel film deposited on a smooth aluminum substrate.

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* Corresponding author. Tel.: +7 3412 430163; fax: +7 3412 722529.
E-mail address: rishatvaleev@mail.ru

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1. Introduction

Interest in hydrogen as an alternative source of energy is currently motivated by two factors [1-3]: first, by environmental pollution due to the use of fossil fuels, which are the main sources of energy at present [2], second, by the fact that fossil fuel reserves are finite [3]. Hydrogen as an alternative to fossile fuels is a solution to the above-mentioned challenges [2].

At present there exist many methods for obtaining hydrogen [4,5]. One of them is the electrolytic reaction of hydrogen release from aqueous solutions of acids and alkalis [5]. In this reaction, a lot of attention is paid to cathodes, which were formerly manufactured mainly of platinum metals. Recently they have been succeeded by cathodes containing various metals, among which nickel is the most widely used [6]. It should be noted that the hydrogen release reaction proceeds the more effectively the larger the area of the cathode surface [7]. In this paper, nickel deposited on the highly developed surface of porous anodic alumina matrices by magnetron deposition is proposed to be used as cathode material for hydrogen release reactions.

Thus, the goal of this work is to perform a synthesis of nickel nanostructures into porous alumina matrices and to investigate their catalytic activity in hydrogen release reactions in an alkaline medium.

2. Materials and methods

The synthesis of porous alumina films was performed in a two-electrode electrochemical cell. A stainless steel electrode was used as cathode material. The current was supplied from a power unit, which allowed us to set anode voltage and current within the range of 0 to 299 V and 0 to 299 mA, respectively. The average pore diameter was estimated by statistical methods using the image processing software ImageJ [8].

The crystal structure and the phase composition of the samples were analyzed by X-ray diffraction (XRD) using the diffractometer RugakuMiniflex 600 with $\text{Co} - K_{\alpha}$ excitation (Physical-Technical Institute of UB RAS) and by Raman light scattering by means of the Raman spectrometer/microscope RenishawInVia (Department of Material Sciences, Lomonosov Moscow State University) using an Ar^+ laser as an excitation source with a wave length of 514 nm.

The chemical composition and the electronic structure were analyzed by X-ray photoelectron spectroscopy (XPS) using the X-ray electron spectrometer SPECS (Physical-Technical Institute of UB RAS). The photoelectron spectrum was excited using AlK_{α} radiation. The depth analysis of the chemical composition of the samples was carried out by ionic etching with an ion gun voltage of 1 keV within 4 cycles, each cycle lasting 1 minute.

Analysis of the microstructure of the samples was performed using the scanning electron microscope FEI Inspect S50 (Udmurt State University). The voltage on the accelerating electrode was 20 kV; magnification were from 100x to 150000x.

The EXAFS spectra (Ni-K edges) of the studied samples were obtained at the “EXAFS spectroscopy” station, Beamline No.8 of VEPP-3 storage ring at the Siberian Synchrotron and Terahertz Radiation Center (SSTRC), Novosibirsk, Russia. using Si (111) crystal monochromator.

The hydrogen release reaction was performed in a three-electrode electrochemical cell in a 5 M NaOH solution. An alumina film with deposited nickel with a visible surface of 0.28 cm^2 was used as the main electrode, and a platinum electrode submerged into a 5 M aqueous NaOH solution was used as an auxiliary electrode. A silver-silver chloride electrode submerged into a 3.5 M KCl solution served as a reference electrode.

3. Experimental

3.1. Preparation of porous anodic alumina films

To obtain porous Al_2O_3 films, 0.2 mm aluminum foil was used. Before anodization, the samples were

electrochemically polished in a solution of chrome oxide and phosphoric acid (CrO_3 – 185 g/l, H_3PO_4 – 1480 g/l) at 80 °C to reduce the surface roughness. This is followed by two-stage anodic oxidation in a 0.3M oxalic acid solution ($\text{C}_2\text{H}_2\text{O}_4$ – 27 g/l) at 5 °C [9]. The duration of the first stage of anodic oxidation was 24 hours; after that, the oxide film was removed in a chromic mixture (CrO_3 – 20 g/l, H_3PO_4 – 35 ml/l) at 60 °C for 20 minutes. The duration of the second stage was 48 hours. To increase the pore diameter, the samples were etched in a 0.5M H_3PO_4 solution. 2 types of samples were obtained at anode voltages of 40 and 80 V, respectively. Then three samples of the first type were etched for 45, 60 and 75 minutes, and three samples of the second type were etched for 60, 75 and 90 minutes. One sample of each type remained unetched. Samples were named as AAO_XXV_YYmin, where XX indicate the anodizing voltage, and the YY stand for the duration of etching in a 0.5M solution of phosphoric acid. SEM images are shown in Fig.1.

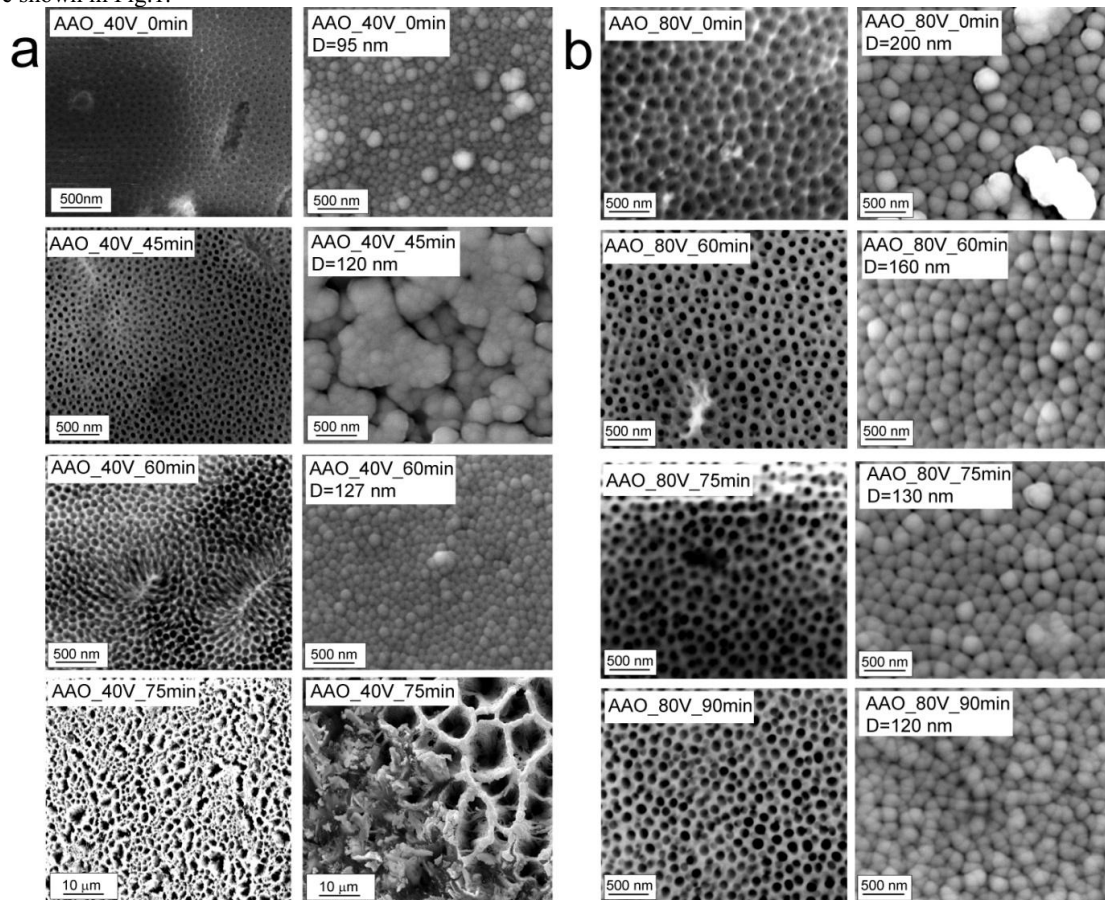


Fig.1. SEM images of the surface of the samples of AAO films synthesized at anodic voltages of 40 V (a) and 80 V (b) before (left pictures) and after (right pictures) deposition of Ni.

3.2. Synthesis of Ni nanostructures in porous alumina matrices

The deposition of nickel into porous alumina matrices by magnetron deposition was performed on a vacuum universal station (VUP – 5) [10]. This facility was additionally equipped with a DC magnetron deposition system MAG-2000 (manufactured by PROTON-MIET).

The magnetron deposition was carried out using a nickel plate with a

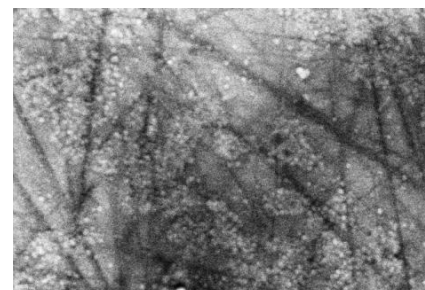


Fig.2. SEM image of the surface of a nickel film sputtered on an aluminum substrate.

purity of 99.99 %. The following deposition regime was used: the magnetron current was 150 mA, sputtering was performed in 20 cycles 75 sec. each, with the magnetron being cooled between the cycles for 5 minutes. Nickel was deposited on porous alumina films and on an aluminum substrate. The thickness of the nickel film deposited on the aluminum substrate was measured by the interferometric method using a MII–4 unit and was 200 nm. All samples have good electroconductivity, which was tested by a multimeter.

As is seen from the micrograph in Fig.2., the nickel film on the surface of the aluminum substrate has many discontinuities due to mechanical stresses at the film/substrate interface and does not form a continuous layer. A periodic structure with hexagonal arrangement of nickel nanostructures has built up on the surface of most porous alumina films (see Fig.1a and 1b, right pictures), which confirms the assumption of the possibility of obtaining nanostructured nickel films with a highly developed surface. It is also seen that the size of the nanostructures is determined by the pore diameter of the matrix: the larger the pore diameter, the larger the size of the nanostructures.

3.3. Analysis of the structural-phase state and the chemical composition of samples

Analysis of the structural-phase state of nickel by XRD has revealed peaks belonging to nickel (JCPDS No 4-850) and aluminum (JCPDS No 4-787) in the substrate (Fig.3). The peaks of nickel are appreciably broadened, which is indicative of a small size of the coherent scattering units and also suggests that the globular structures of Ni, in their turn, consist of nanoscale particles.

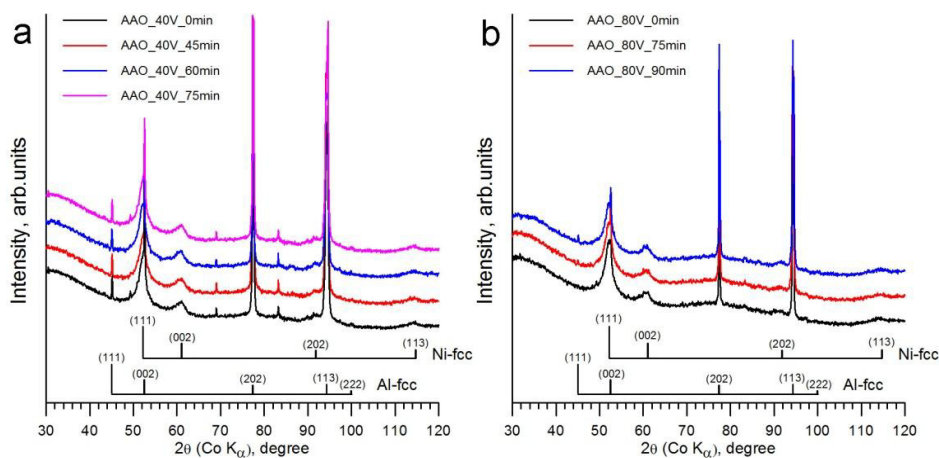


Fig.3. X-ray diffraction patterns of the samples of nickel coatings obtained by deposition on AAO matrices synthesized at 40 V (left) and 80 V (right).

Analysis of the structural-phase state of nickel by Raman spectroscopy has shown that the nickel surface on AAO is in an oxidized state, in contrast to nickel on the aluminum substrate (Fig.4.). It is well known that pure nickel has no vibrational modes in the optical range, and so the appearance of a maximum of 550 cm^{-1} on the spectra can be linked to the presence of a thin NiO film on the surface, which is confirmed by literature data [11]. In addition, the peaks are appreciably broadened, which is indicative of an amorphous state of the oxide.

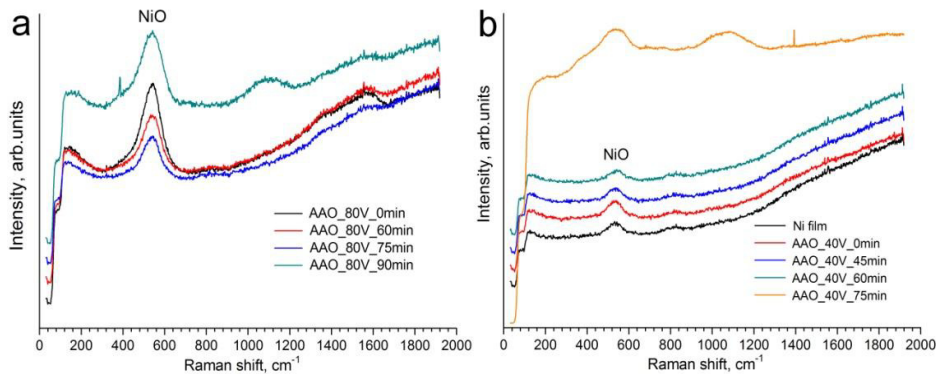


Fig.4. Raman scattering spectra of samples of nickel coatings obtained by deposition on AAO matrices synthesized at 40 V (left) and 80 V (right).

Figure 5 shows XPS of O1s, Ni2p_{3/2} and C1s of an AAO_40V_0min sample in the initial state and after a 2 min and a 4 min etching with argon ions. The O1s spectra (Fig.5a) are multicomponent spectra. Peak **a** with $E_b = 529.7$ eV corresponds to oxygen in the O-Ni bond in NiO monoxide, peak **b** to oxygen in OH groups interacting with metal (or oxygen in Ni(OH)₂), and peaks **c** and **d** to adsorbed oxygen and oxygen bound to carbon and hydrocarbons. In the case of ionic etching, peaks **c** and **d** naturally recede first. The peak of OH (**b**) during etching decreases in intensity and is ahead in time of the peak with 529.7 eV (NiO). Thus, the Ni-OH bonds are mainly concentrated nearer to the free surface. In general, in the case of ionic etching the relative oxygen concentration decreases (Table 1). Already after 1 min etching (~1 nm) the ratio C(O)/C(Ni) is below the homogeneity limit of NiO monoxide or Ni(OH)₂ hydroxide, but a considerable amount of oxygen mainly bound to nickel (O-Ni) is observed even after a 4 min etching. Probably this is oxygen introduced at the inner interfaces or oxygen that cannot be etched because of the developed film surface.

Figure 5b presents an example of decomposition using spectra of reference samples of Ni, NiO and using data from well-known publications. In general, an unambiguous “exact” decomposition of nickel oxide spectra is problematic due to their complex multiplet and satellite structure [12,13]. There is no sense in decomposing the spectra after ionic etching, since the nickel oxides are unstable with respect to external influences under high vacuum conditions. This is why in this paper we use ionic etching only to estimate the distribution of components at the depth of the surface layers without taking into account the analysis of their chemical state.

The Ni2p_{3/2} spectrum of the initial surface before etching is typical of the nickel surface after its short low-temperature oxidation in the air. The sample has a superthin oxide film with a thickness smaller than the depth of X-ray photoelectron spectroscopy analysis (one can observe both the oxide component (855-857 eV) and the pure metal spectrum). The main peak **a** with $E_b = 852.8$ eV is metallic nickel with satellite peaks **a'** and **a''**. The split doublet **b1-b2** and its intensive shake-up satellite **b'** are typical of Ni²⁺ cations in NiO monoxide. Peak **c** with satellite **c'** can be related to Ni(OH)₂ hydroxide. The presence of a shake-up satellite in the region 861-862 eV is a salient feature of the chemical state of divalent nickel (Ni²⁺). After a 4 min etching, the characteristics of the Ni2p_{3/2} spectrum are similar to those of the spectrum of pure nickel.

The multicomponent spectrum of C1s (Fig.5c) of the nickel film surface differs from the “usual” spectrum of hydrocarbon pollutions arising on metallic surfaces in the air. The component with $E_b = 283.5$ eV (carbide-like bonds C-Ni) is released already before etching and, along with the peak with $E_b = 285$ eV (C-H), there are intensive components with $E_b = 286.3$ eV (C-OH) and 289 eV (O-C=O), which decrease during ionic etching. This is due to the fact that the evaporation of the nickel film has been carried out under dynamical vacuum in a medium containing hydrocarbons, which determines the probability of their chemical interaction with the sputtered substance.

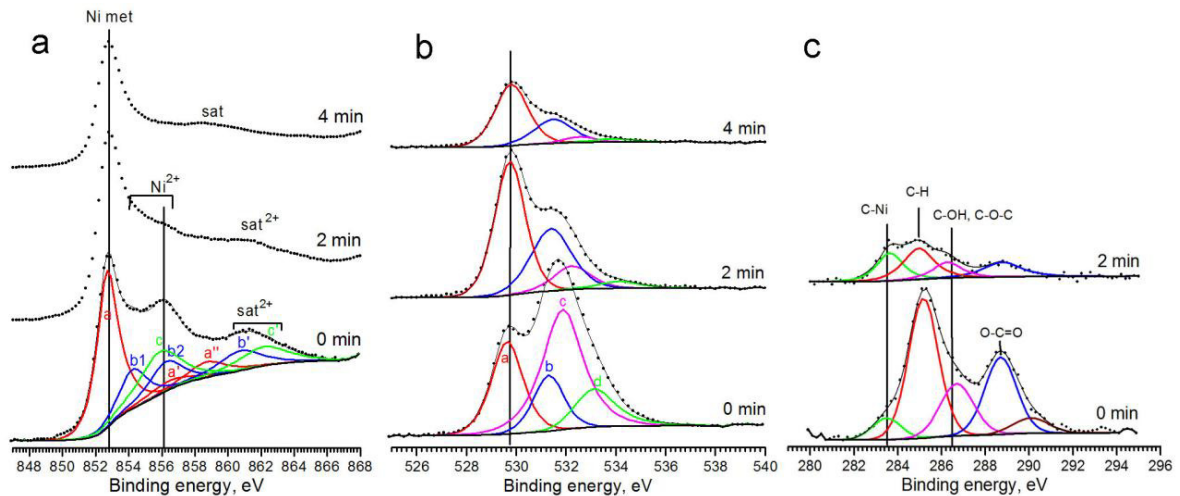


Fig.5. X-ray photoelectron spectra of O1s, Ni2p_{3/2} and C1s of an AAO_40V_0min sample.

Table 1. Concentration of elements at various depths of analysis.

Etching time, min	c_{Ni}	c_{O}	c_{C}
0	37.3	40.3	22.4
1	51.4	34.4	14.2
2	66.3	27.6	6.1
3	71.5	23.8	4.7
4	78.2	17.0	4.8

Analysis of the structural-phase state of the studied nickel samples by EXAFS method (Fig.6) has revealed peaks similar to nickel fcc Ni structure (reference nickel foil - ICSD Database Code 41508, 43395, 64989). However, amplitudes of the peaks of nickel samples are greatly decreased (in comparing with reference Ni foil), that is pointed to a small particles size and also proposes that the globular structures of nickel, consist of nanosize particles and/or some structural distortion of nickel fcc structure.

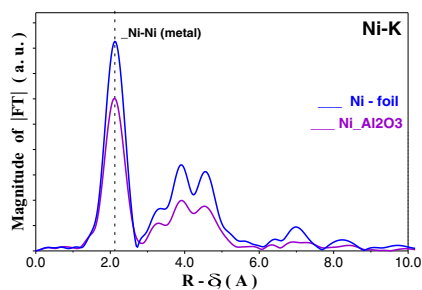


Fig.6. Curves of radial distribution function of atoms (RDFs) describing of Ni local arrangement for samples studied.

3.4. Results of the hydrogen release reaction

In the process of the hydrogen release reaction the nickel films of all samples under study decayed. This can be explained by the presence of microcracks on the nickel film surface and by an active release of hydrogen from the nickel film surfaces, which leads to mechanical ruptures of the films.

The overvoltage of hydrogen release on the nickel film deposited on the aluminum substrate arises at a higher cathode current than that on the samples AAO_40 V_60 min and AAO_80 V_90 min (Fig.6). The overvoltage of hydrogen release on the samples AAO_40 V_60 min and AAO_80 V_90 min arises earlier as a result of their greater catalytic activity, which is due to the developed surface.

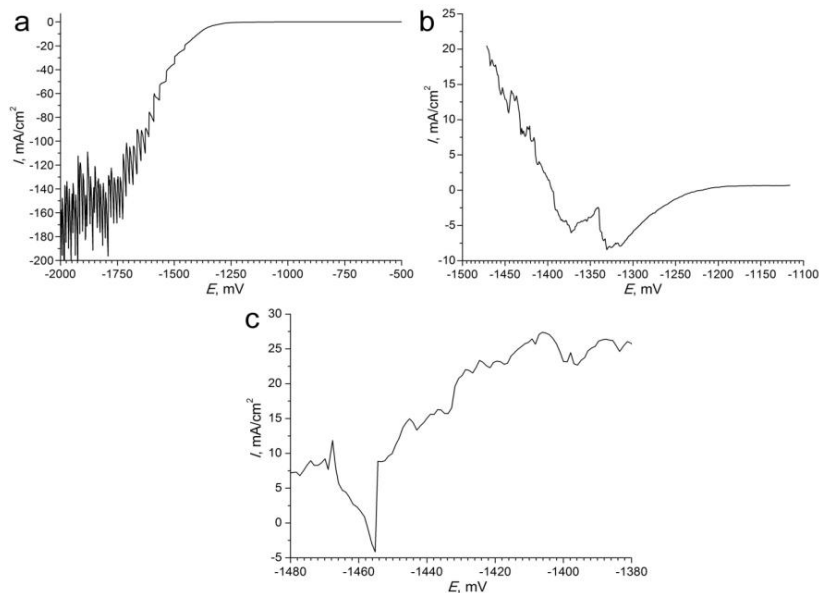


Fig.7. Dependence of cathode current on the overvoltage of hydrogen release on the nickel film deposited on the aluminum substrate (a), on the sample AAO_80V_90min (b) and the sample AAO_40V_60min (c).

4. Conclusion

A synthesis of nickel nanostructures by magnetron deposition into the matrices of porous alumina obtained by two-stage anodic oxidation has been carried out.

Analysis by X-ray diffractometry, Raman spectroscopy, X-ray photoelectron spectroscopy and EXAFS method has shown that the nickel on the surface of the samples is in an oxidized state, in contrast to the metallic nickel on the aluminum substrate. It has been shown that the nickel films deposited on anodic alumina exhibit a greater activity in the hydrogen release reaction than the nickel film deposited on the aluminum substrate, which occurs as a consequence of its worse conductivity due to discontinuity of the film.

As a result of the hydrogen release reaction, we have obtained dependences of cathode current on the overvoltage of hydrogen release, which were recorded in a 5 M aqueous NaOH solution on the samples AAO_40V_60min, AAO_80V_90min and on the nickel film sputtered on the aluminum substrate. In the course of the hydrogen release reaction the nickel of all samples under study decayed. Therefore, thicker films should be used as cathodes in the hydrogen release reaction.

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