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Thermal Stability of Nano-Crystalline Nickel Electrodeposited into Porous Alumina

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Abstract. Through-pores alumina membranes of 50 μm thickness and 70 × 70 mm size have been fabricated to deposit Ni nanowires by electrochemical processing. Due to highly ordered microstructure of the membranes, the pores were filled by nanowires almost to 100%. The membrane nanowires composite morphology, structure and thermodynamic characteristics have been studied by scanning electron microscopy, atomic-force microscopy, X-ray diffraction and differential thermal analysis. The thermal stability of Ni nanowires into porous alumina template and whole composite was determined.

Introduction

One of the problems of fundamental character is the problem of nanocrystals thermal stability as the extended surface of grain boundaries does nanocrystal structure extremely unstable.

The review of publications on a research of phase transitions in low-dimensional particles showed, that the mechanical tension which arises in composite materials when heating because of distinction of thermal coefficient of linear widening (TCLW) of composite elements, can give the significant contribution to the general energy of a system. It is considered that deterioration in thermal stability (heat stability) in nanocrystal materials is a consequence of very high free energy accumulated on grain boundaries which leads to the big driving force promoting growth of grain [1].

In a number of researches it was established that at high-temperature annealing of composite, consist of nanocrystalline nickel nanowires (NC NWs) electrodeposited into porous anodic alumina oxide (PAA), the radial pressure which oxide render on NWs, because of distinction of matrix and NC nickel TCLW, can be softened with their axial expansion, if NWs are single-crystal [2].

In view of the aforesaid the purpose of this work is: a complex research of structure, composition and thermodynamic characteristics of composite material consisting of Ni NWs, which are electrodeposited into pores anodic alumina membrane (Ni NWs/PAA).

Experimental

In this study we used domestic made PAA membranes with highly ordered through-hole nanopores. The membranes were synthesized by two-step anodizing in oxalic acid at 50 V and 15 °C with auxiliary technological frame around the perimeter to be mechanically stable enough to handle under the following processing steps. In detail the membrane technique and its property are described in works [3, 4].

Ni nanowire arrays were fabricated by simple DC galvanostatic electrodeposition into the pores of as-prepared through-hole PAA templates. The thickness uniformity length ~ 25 μm (a.r. = 500) for NWs' arrays may be achieved over the 20 × 24 mm area. In detail the Ni NWs technique into PAA membrane was described earlier [5].

To deposit Ni NWs into PAA was used usual electrolyte, composed from $NiSO_4 \times 7H_2O$, $NiCl_2 \times 6H_2O$ and H_3BO_3 (pH=3). Fabrication of NWs was performed in two-electrode cell with graphite auxiliary electrode by galvanostatic DC-deposition at room temperature under constant

current density 3 mA/cm^2. The control of electrochemical anodizing and deposition parameters was performed with P-5827 potentiogalvanostat.

Surface topography of the samples was investigated by scanning electron microscopy (Philips XL 30S FEG) and atomic-force microscopy (AFM – Solver P47H, NT-MDT Co Russia and Nanotop NT-206, "Microtestmachines", Belarus). Electronic data were processed with the surface explorer document (SED) software kit. Phase composition investigation was performed by XRD analysis with X-ray diffractometer DRON-2 (CuK$_\alpha$ with $\lambda = 0.154056$ nm).

The DTA and thermo-gravimetric analysis (TGA) of the samples were performed on a NETZSCH STA 409 PC/PG Luxx synchronous thermal analyzer with vertical sample loading (Germany). A sample weight of 30-50 mg was placed in an open-type alundum crucible. The measurements were performed in a dynamic air atmosphere (at an air flow rate of 50 ml/min; the protective gas was argon). The temperature ranged from room temperature to 900°C and the heating rate ranged within 10–20 deg/min.

Results and Discussion

In Figure 1 the surface and cross-section SEM images of a membrane before (A) and after (B) NWs deposition are shown.

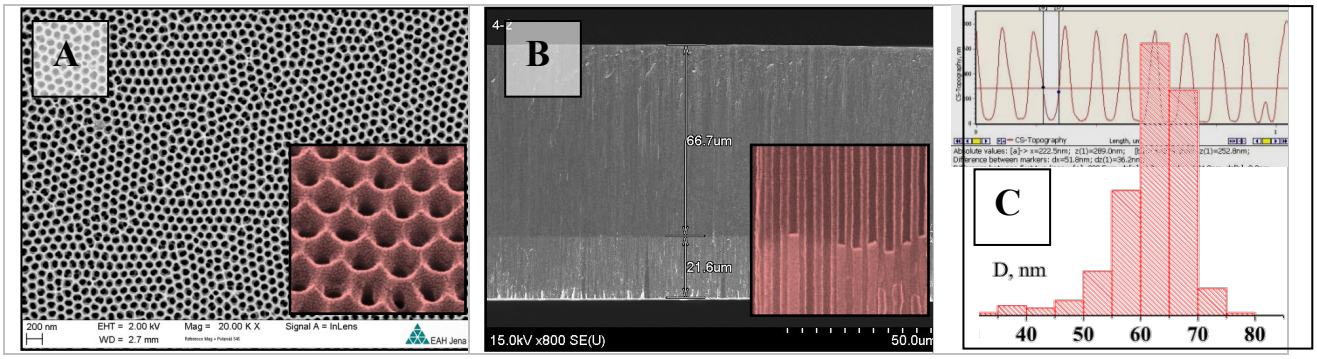

Fig. 1. A – Surface SEM image of domestic made PAA membrane before NWs deposition; B – cross-section SEM image after NWs deposition, C – AFM profile for A and histogram for B images.

From this data it is visible, as the membrane, and NWs have the uniform geometrical sizes. Diameter of NWs is equal to diameter of a membrane pore (65±5) nm; length of NWs depends on time of deposition and membrane thickness.

Figure 2 presents the results of TGA data for Ni NWs/PAA in air. At the beginning of heating process, up to 150ºC, there is (1) a loss of weight (4.47% of a reference value) connected with removal of the remaining water, used for washing of samples and (2) a loss of carbon dioxide from a surface and the blank part of PAA.

When temperature increase to 300^{0}C considerable reduction of sample mass (almost for 10%) because of rapid growth of grains (primary recrystallization) is observed. This temperature is close to values for the electrodeposited Ni and Ni-Fe films (270-300^{0}C) reported in other publications [6, 7]. According to literary data activation of recrystallization processes within Ni NWs in limited space environment (in a narrow pore of oxide), leading to growth of the grain sizes, begins at a temperature of 271^{0}C [6]. It is possible to assume that at this temperature the grains with size of several tens of nanometers begin to be formed on the NWs surface, as in case of continuous-solid Ni films condensed on flat substrates.

Increase in temperature to 496 °C leads to increase in the lateral sizes of grains located along a vertical axis of NWs. PAA in this range at first loses the adsorbed water (in the range of temperatures of 25-100 °C), and then the bound water in the temperature range of 350-550 °C [8]. This transition is followed by reduction of PAA volume with simultaneous insignificant increase in diameter of a

pore. Thermal compression of PAA continues up to 900 °C. This phenomenon is reversible up to 700 °C, after 900 °C irreversible transformation of γ-Al_2O_3 in corundum begins [8].

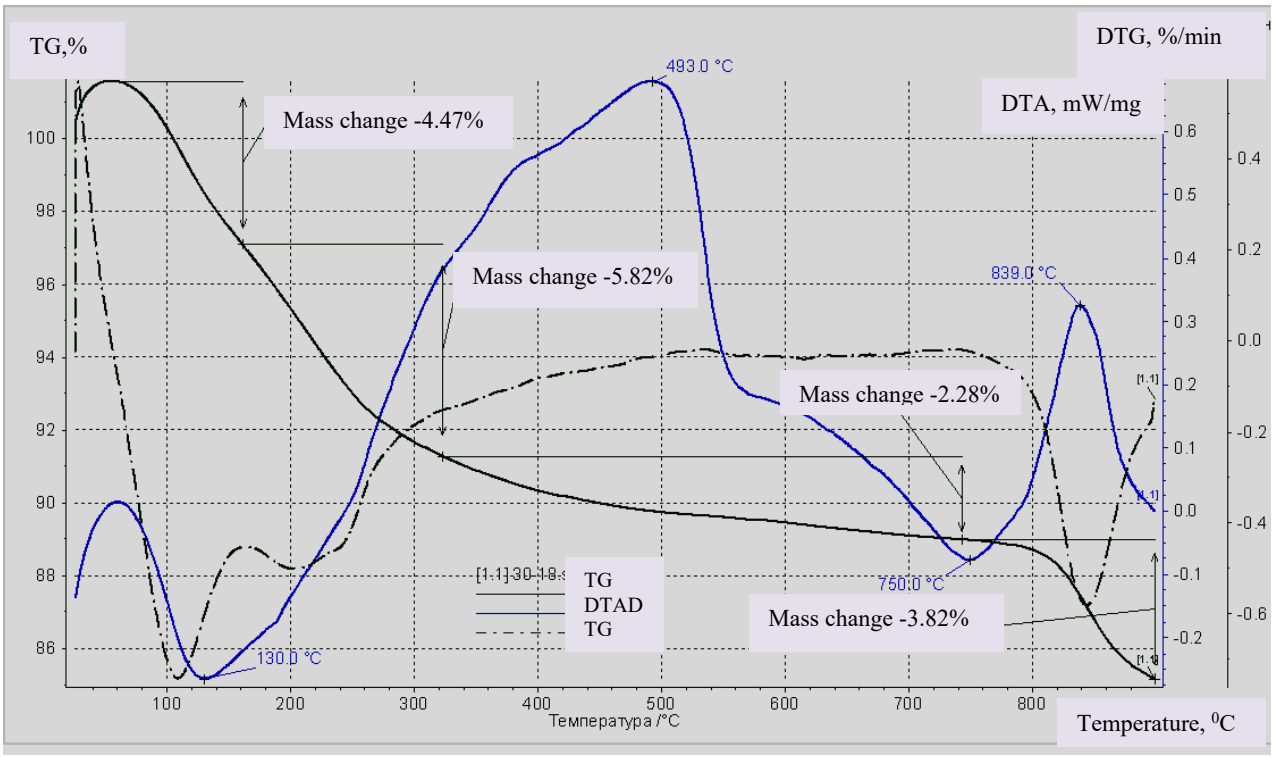

Fig. 2. TGA data for PAA membrane in air.

Thermal transformations in PAA, squeezing a crystal lattice at rather big value, when maintaining initial pattern of structure, lead to strong local thermal stress.

However, apparently from Figure 2, annealing at a temperature of 493^{0}C and above (to 700^{0}C) does not lead to phase transition (to nickel melting, as it was observed for Ni NWs with 5 nm diameter [9]). The area of endothermic peak is equal to 62.34 J/g (or 3.7 kJ/mol), that is nearly 5 times less than the specific heat of melting (J_0) of bulk nickel and in 4.5 times less J_0 of NC Ni.

Two obviously expressed exothermic effects at temperatures of 493 and 840 °C are connected with the processes taking place in the elements of composite: (1) recrystallization and oxidation of grains in Ni NWs (493 °C); (2) with the beginning of crystallization of alumina after removal of impurity, which penetrated into walls of PAA pore in the course of anodizing (840^{0}C). Up to this temperature only the inside layer of oxide of aluminum which is not containing electrolyte impurity crystallizes.

From Figure 2 it is obvious that DTA signal in the temperature interval defining range of thermal stability consists of two parts. The low-temperature area (200 – 500 °C) with sharply expressed central thermal peak of 493 °C corresponds to the abnormal growth of Ni grains. And high-temperature area (550 – 900 °C), in which there is a thermo-destruction of composite base (PAA). The difficult nature of the first area is caused by appearing of the additional thermal effects, reflecting behavior in Ni NWs of structural processes other than growth of grains (oxidation).

The poli-extreme nature of DTA and DTG dependences shows also that simultaneously with processes of recrystallization there can be NWs oxidation process.

Thus, T_1 temperature (320 °C) corresponds to the beginning of intensive growth of grains and thermal-oxidative process of NWs in a composite (curve DTA rises up). Then process of thermo-destruction of a composite basis (PAA) begins at T_2 temperature (600 °C) — the curve is down). The temperature range T_1 — T_2 defines thermal stability of Ni NWs. The temperature range T_2 — T_3 (up to 850 °C) defines thermal stability of a whole composite — ability to keep the chemical composition and ordered structure at influence of the increased temperature.

For specification of a possibility of NWs oxidation in a composite, samples were previously annealed at a temperature of 350 °C, which is slightly exceeding temperature of the beginning of thermal-oxidative process, within 3 hours and then investigated by XRD method.

In Figure 3 results of the X-ray diffraction analysis of the composite material Ni NWs/PAA before and after annealing are shown. Shaped lines designated positions of diffraction lines of reference powder Ni of the database of the International Center for diffraction data (JCPDS).

Comparison of diffraction lines intensity (I) with a card for powdery Ni (shaped lines) allowed estimating crystal structure of a sample.

The sizes of coherent areas (d) to which there correspond received peaks, Table 1, were calculated by a Sherera formula. Values from the JCPDS are given in brackets of column 2θ.

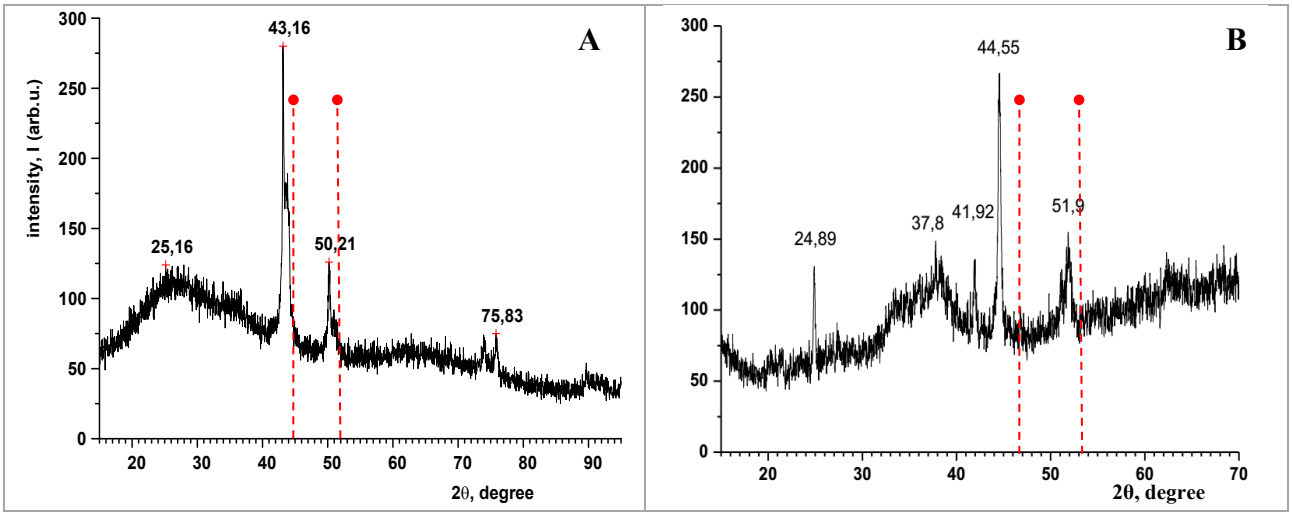

Fig. 3. XRD patterns of Ni NWs/PAA composite before (A) and after (B) annealing.

Table 1. Results of the X-ray diffraction analysis of Ni NWs/PAA composite.

Crystallographic direction	2θ, deg.	d, nm	I, %
Ni(111)	43.16 (44.51)/44.55*	23.5	100
Ni(200)	50.21 (51,85)/51.9*	18.4	45
Ni(220)	75.83 (76.37)	18.1	27

* after annealing

The Ni NWs crystallite size (~20 nm) calculated from the (111) fcc Ni peak is smaller than the mean Ni NWs diameter (~ 60 nm). This indicates that Ni NWs are poly-nanocrystalline material.

Comparison of XRD patterns of the initial and annealed samples shows, that the peak characteristics of NiO (37.8 and 42.92) appeared in a spectrum. It shows that throughout of isothermal annealing at a temperature of 350 °C within 3 hours the sample begins to be oxidized and confirms the assumption that in the temperature range of 300 – 600 °C along with process of recrystallization there can be NWs oxidation process.

It should be noted that annealing at this temperature improves degree of crystallinity of phases with orientation (111) and (200). The shift of a diffraction maximum of standard crystal phases with texture (111) and (200) appears significantly less for the annealed sample, than for not annealed. It demonstrates that after annealing in the grains of NWs Ni with these crystal phases, internal deformations decrease due to reduction of interplanar spacing and growth of the grains size.

Alumina (PAA) at this temperature remains X-ray amorphous (peak 25.16 before annealing), but emergence of diffraction line 24.89 can testify to a possibility of formation of crystallites with structure of $NiAl_2O_4$ spinel type [10,11].

Conclusions

By DTG researches on air have been determined the range of thermal stability of Ni NWs and whole composite. Temperature of 320 °C corresponds to the beginning of intensive growth of grains and thermal-oxidative process of NWs in a composite. At a temperature of 600 °C process of thermo-destruction of composite base begins. The temperature range of 300 - 500 ° C defines thermal stability of Ni NWs in oxide. The temperature range of 550 - 850 °C defines thermal stability of a composite. The poliextreme nature of DTA and DTG dependences with two obviously expressed exothermic effects (493 and 839 °C) shows that simultaneously with process of grains recrystallization there is an oxidation process of Ni NWs.

Structure researches of composite material before and after annealing confirmed a possibility of Ni NWs oxidation in the course of high-temperature annealing. NWs consist of the Ni crystallites having face-centered cubic structure with the main crystallographic direction [111] before and after annealing. Despite of essential differences of thermo-elastic characteristics of the materials forming a composite, annealing at a temperature below temperature of abnormal growth of grains, improves degree of crystallinity of the main phases of Ni nanocrystals with orientation (111) and (200). NWs in oxide do not collapse, and do not melt at short-term influence of high temperatures (up to 750 °C).

Acknowledgments

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