The influence of thermal annealing on structural properties of Ni nanotubes

A.L. Kozlovskiy[a,b,*], D.I. Shlimas[a,b], I.E. Kenzhina[a,b], M.V. Zdorovets[a,b,c]

[a] Institute of Nuclear Physics, Almaty, 050032, Kazakhstan
[b] Gumilyov Eurasian National University, Astana, 010000, Kazakhstan
[c] Yeltsin Ural Federal University, Yekaterinburg, 620002, Russia

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ABSTRACT

The paper presents the results of studying the structural properties of Ni nanotubes affected by thermal annealing. Scanning electron microscopy, X-ray phase analysis and energy dispersive analysis were used to investigate the microstructure. An increase in the annealing temperature is found to lead to a change in the main crystallographic characteristics (unit cell parameter, crystallite size) and the appearance of new phases in the structure. The change in microarrays in the structure as a result of thermal annealing is of a two-stage nature: the first stage is characterized by an improvement in the crystal structure as a result of annealing defects; the second stage is characterized by an increase in micro-displacements in the crystal structure due to the appearance of two phases-the nickel oxide compound NiO_2 and γ-Ni, whose contribution increases with the annealing temperature. At the same time, the formation of new phases in the crystal structure leads to a partial amorphization of the structure and the formation of outgrowths on tubes surface. The obtained knowledge can be applied to supplement the theory of thermal stability of nanostructures, as well as to assess their applicability in modern materials science.

1. Introduction

An important requirement for nanostructured materials and devices based on them is an increase in operational characteristics, chemical and thermal stability and resistance to external influences. All this has an essential role in the lifetime of nanostructured materials [1–5]. In connection, one of the vital tasks is the study of the evolution of physical-chemical properties, corrosion resistance and the processes of degradation of nanomaterials structure as a result of directional modification through thermal treatment, irradiation with ionizing radiation, etc. [6–8]. The existence of numerous defects, residual stresses, non-equilibrium phase states in nanostructures leads to the formation of excess free energy, while the external action on the nanostructure can start the processes of recrystallization, relaxation and segregation, leading to changes in nanostructures or degradation [7–9]. From this point of view, new knowledge of the stability of nanostructures to external influences is of great importance, both for fundamental and applied research, which basing the development of methods for determining the reliability of nanostructures and assessing their applicability [10–15]. The problem of thermal stability of nanostructures includes various aspects, such as the effect of temperature on the size and shape of crystallites, oxidation and degradation processes, interactions with the environment and external influences, phase transitions and transformations. Heat transfer in nanostructured materials is carried out by mechanics analogous to the mechanisms of classical thermophysics. But dimensional effects can significantly change the kinetics of heat transfer can the basic regularities [16,17]. Also, the study of processes of heat exchange and stability of nanostructures to thermal heating is very crucial for solving the following problems: 1) control of thermal generation in nanostructured devices; 2) heat transfer and energy conversion; 3) controlled phase transformations, etc. Unlike macroobjects, for nanostructures, the classical features of heat transfer processes can be violated. For example, thermal conductivity can be ballistic, phase transitions can occur at lower temperatures, etc. [18,19]. One of the important factors affecting the violation of classical heat transfer laws is size effects. The influence of such effects is well known for nanostructured materials [20,21]. The size effects include changes in the spectrum of elementary excitations of carriers and energy carriers, boundary effects and sinks of defects, grain growth. According to [21–23], one of the main processes occurring in nanomaterials during thermal annealing is grain growth. The author claims that the process of grain growth in nanostructures takes place through a rotational mechanism. And with a decrease in grain size, this mechanism begins to increasingly prevail over the process of co-operative homogeneous displacement, which is more typical for the coarse-grained structure of materials. Also, in his work [17], another

important factor affecting the changes in properties during the annealing process is indicated by phase transformations. Due to the non-equilibrium conditions for obtaining nanomaterials in their crystal structure, a large content of supersaturated solid solutions and unusual crystalline phases can be observed which can have a significant effect on the thermal stability of nanostructures [18–25]. Today, the theory of stability of nanostructures as a result of heat treatment and heat transfer processes has been examined in detail for carbon nanostructures of various geometries [26–30], nanoparticles based on iron oxides [31,32], in which phase transitions associated with changes in morphology and structural properties. However, for metal nanostructures as nanotubes or nanowires, these processes are not consecrated very much. In connection with which it is interesting to study phase transformations and the change in the crystal structure as a result of heat treatment in an oxygen-containing medium. The choice of medium is due to the potential use of nanostructures in microelectronic devices that are capable of heating during operation, while they are not protected from the influence of the external environment. The choice of nickel as a material for the production of nanostructures is due to its physical-chemical properties, as well as its wide field of practical application such as photovoltaics, catalysis, magnetic carriers, biomedicine, and targeted delivery of drugs [33–40]. The most detailed review of the methods of production and potential areas of practical application of nickel nanostructures is presented in [41], which indicates promising areas of application of nickel nanostructures in the field of targeted delivery, and also reflects the main ways of modifying nanostructures surface to improve physical and chemical properties.

2. Experimental part

Ni nanotubes synthesis was carried out by electrochemical deposition in the pores of template matrices based on polyethylene terephthalate of the Hostaphan® type manufactured by Mitsubishi Polyester Film (Germany). The thickness is 12 μm, and a pore density is 4×10^7 cm^2 at diameters of 380 nm. Electrochemical deposition was carried out in potentiostatic mode with a potential difference in the interval from 1.75 V using the following electrolyte: NiSO$_4$ × 6H$_2$O (100 g/l), H$_3$BO$_3$ (45 g/l), C$_6$H$_8$O$_6$ (1.5 g/l) at an electrolyte temperature of 25 °C. The cathode was a layer of 10 nm thick gold deposited on one side of the polymer template by magnetron sputtering in a vacuum. With such Au layer thickness, the pores remained open, and nanostructures growth began at the points of contact of gold with the electrolyte. The deposition process was monitored chronoamperometrically using an Agilent 34410A multimeter.

Studying of structural characteristics and elemental composition of obtained nanostructures before and after irradiation was performed using a scanning electron microscope "Hitachi TM3030" with a microanalysis system "Bruker XFlash MIN SVE" with an accelerating voltage of 15 kV. X-ray diffraction analysis (XRD) was done on a D8 ADVANCE ECO diffractometer (Bruker, Germany) using CuKα radiation. In order to identify phases and study the crystal structure, the software BrukerAXSDIFFRAC.EVAv.4.2 and the international ICDD PDF-2 database were used.

The thermal annealing of obtained nanotubes in polymer matrix was carried out in the temperature range from 100 to 600 °C in steps of 100 °C for 1 h in an oxygen-containing atmosphere in a muffle furnace Nabertherm LE 4/11/r6.

3. Results and discussion

Fig. 1 presents SEM images and EDS spectrum of investigated nanostructures samples.

As can be seen from the presented data, the synthesized nanostructures are hollow nanotubes whose height coincides with the thickness of the template matrix of 12.0 ± 0.1 μm, the diameter of nanotubes corresponds to pore diameters of 380 ± 10 nm. The

nanotube diameters were 170 ± 5 nm. The wall thickness was 105 ± 2 nm. Also, the determination of diameters d of pores of template matrices and the internal diameters of nanotubes in PET templates was carried out by the manometric method of determining the gas permeability. This method is based on measuring the molar density of the air flow Q as a function of the pressure difference Δp in the closed chamber on both sides of the template, which varied in the range from 0.008 to 0.020 MPa in steps of 0.004 MPa. The diameters d were determined in accordance with the Fick law from the relation [42]:

$$Q = \frac{nd^3}{6l}\sqrt{\frac{2\pi}{RTM}}\Delta p,$$

where l is the thickness of the template (the length of nanotube), R is the universal gas constant, M is the air molar mass, n is the pore surface density (the fluence of irradiation of PET films when template obtaining), and T is the temperature. The resulting average value of the pore diameter of PET template was 378 ± 10 nm. The average value of the inner diameter of nanotubes, determined by the same method, was 166 ± 7 nm for all investigated samples. The obtained values of diameters are in good agreement with the data obtained as a result of SEM studies of template matrices and nanotube diameters. Fig. 1c shows a TEM image of nanostructures, which confirms that synthesized nanostructures represent hollow structures along the entire length. According to elemental analysis data, the initial samples are single-component nanotubes consisting of nickel. Impurities of oxide and carbide compounds are not detected.

One of the crucial factors in the heat treatment of nanomaterials is the change in electronic states, the restoration of the crystal structure, and phase transformations. In this case, heating can lead to an irreversible change in the electro-physical parameters of initial material [43–46]. X-ray phase analysis method was used to assess the effect of heat treatment on the change in structural properties and phase composition. Fig. 2 shows X-ray diffraction patterns of Ni-nanotubes before and after heat treatment. All diffractograms of investigated samples had low-intensity peaks, which are characterized by X-ray diffraction on nanoscale objects (broadening of diffraction lines, low intensities).

Analysis of X-ray diffraction patterns made it possible to establish that the initial samples are polycrystalline structures with a fcc phase, a cubic syngony of the spatial group Fm-3m (225).

A change in the intensity and diffraction peaks shape with increasing processing temperature is observed as a result of the thermal action. Thermal annealing can lead to an increase in the thermal motion of atoms in the crystal lattice, which leads to a change in diffraction peaks intensity. The thermal motion is characterized by the Debye-Waller factor (1) [47]:

$$e^{-2M} = \frac{I_t}{I_0} \tag{1}$$

where I_t and I_0 are the final and initial intensity of peaks in the diffractogram. Fig. 3a shows the diagram of the change in the Debye-Waller factor value as a result of thermal annealing. The change in the magnitude of the thermal motion of atoms leads to a change in the value of the mean square displacement of atoms from their places. As a result, when the displacement is large enough, the atoms can leave equilibrium positions and begin to migrate along the crystal lattice, thereby creating additional defects in the structure. Formed voids can be filled with impurity atoms resulting in, structure deformation and the formation of oxide phases. The total mean square displacement of atoms can be calculated using formula (2) [47]:

$$B = \frac{M}{\left(\sin\frac{\theta}{\lambda}\right)^2} \tag{2}$$

where M is the Debye-Waller factor, θ is the diffraction angle, λ is the X-ray length (1.54 Å). Fig. 3b shows the results of calculations of the change in the mean square displacement of atoms as a result of thermal