

Ionizing Radiation Effects in Ni Nanotubes

**D Shlimas^{1,2}, A Kozlovsky^{1,2}, A Shumskaya³, E Kaniukov^{*3}, M Ibragimova²,
M Zdorovets^{1,2} and K Kadyrzhanov¹**

¹L.N. Gumilyov Eurasian National University, Mirzoyan street, 2, Astana 010008, Kazakhstan

²Institute of Nuclear Physics, Ibragimov street, 1, Almaty 050032, Kazakhstan

³Scientific-Practical Materials Research Centre NAS of Belarus, P. Brovki street, 19, Minsk 220072, Republic of Belarus

*E-mail: Ka.Egor@mail.ru

Abstract. Polycrystalline nickel nanotubes with diameter of 380 nm and wall thickness 95 nm were synthesized by electrochemical method using PET track-etched membranes with thickness of 12 μm . A comprehensive study of the structural, morphological and electrical characteristics of Ni nanotubes irradiated with C^{+13} ions with energy 1.75 MeV/nucleon and fluence ranging from 10^9 to $5 \times 10^{11} \text{ cm}^{-2}$ was carried out. The ability of modification of structural parameters such as lattice parameter and the average size of crystallites and conductivity of Ni nanotubes by irradiation was shown.

1. Introduction

Nowadays, a huge attention is paid to nanostructures and one of the most promising of them is magnetic nanotubes (NTs). NTs are prospective for a wide range of its practical application: from drug delivery to the magnetic storage [1-4]. For the devices functioning at extreme conditions it is necessary to understand the influence of ionizing irradiation on the structure and electrical properties of them. It is well known that defect formation mechanism in irradiated nanostructures is different from the same processes in bulk materials [5]. Accordingly that, it is not possible to apply standard approaches for nanodimension systems. Unfortunately, nowadays only limited number of works are devoted to study of influence of various types of radiation on the structure and physical properties of nanoobjects [eg. 6, 7]. To improve the understanding of irradiation effect in this field, we present the results of studies of the structural and electrical properties of nickel NTs, which were treated by ionizing radiation.

2. Experimental

Track-etched membranes based on polyethylene terephthalate (PET) were used as templates with following dimensions: thickness of 12 microns, nominal pore diameter of 380 nm and a density of $4 \times 10^7 \text{ cm}^{-2}$. Electrochemical deposition in pours was carried out at voltage of 1.5 V in a potentiostatic mode. The electrolyte composition is $\text{NiSO}_4 \times 6\text{H}_2\text{O}$ (100,14 g/l), H_3BO_3 (45 g/l), $\text{C}_6\text{H}_8\text{O}_6$ (1,5 g/l). Control of the deposition was carried out by chronoamperometry using a multimeter Agilent 34410A.

Ionizing radiation effects in Ni NTs was studied on samples irradiated on cyclotron DC-60 with C^{+13} ions with energy 1.75 MeV/nucleon with fluence ranging from 10^9 to $5 \times 10^{11} \text{ cm}^{-2}$. Estimation of the appropriate irradiation energy was calculated in SRIM Pro 2013 program.



Characterization of structural features was carried out by scanning electron microscopy (SEM, Hitachi TM3030), energy dispersive analysis (EDA, Bruker XFlash MIN SVE) and X-ray diffraction (XRD, D8 ADVANCE) using Cu $K\alpha$ -irradiation. Determination of internal diameters of Ni NTs was carried out by determination of gas permeability method (Sartocheck® 3 Plus 16290) at a pressure in the range from 8 to 20 kPa [8]. Evaluation of electrical conductivity of NTs was carried out studying of current-voltage characteristics of samples using a current source HP 66312A and amperemeter 34401A Agilent. To provide SEM and EDA investigations of individual NTs templates were etched in 5M solution of sodium hydroxide at a temperature of 90°C during 60 minutes.

3. Results and Discussion

There are a lot of promising NTs synthesis techniques, but the simplest and cheapest one is electrochemical deposition in pores of templates from silicon, aluminum oxide, polycarbonate or polyethylene terephthalate [9-11]. Features of the electrodeposition of metals into the pores of track-etched membranes, as well as the stages of formation of the NTs are described in detail in [12-15]. Morphology of irradiated and non-irradiated NTs arrays were determined by SEM and gas permeation methods. Analysis of the SEM images showed that the nanostructure has tubular shape, their length is coincided with the templates thickness (12 microns) and NTs diameters correspond to pore diameter (380 nm, Figure 1). The results of experiments of gas permeability allow to calculate the inner NTs diameters which are ~ 190 nm, and the wall thickness is ~ 95 nm.

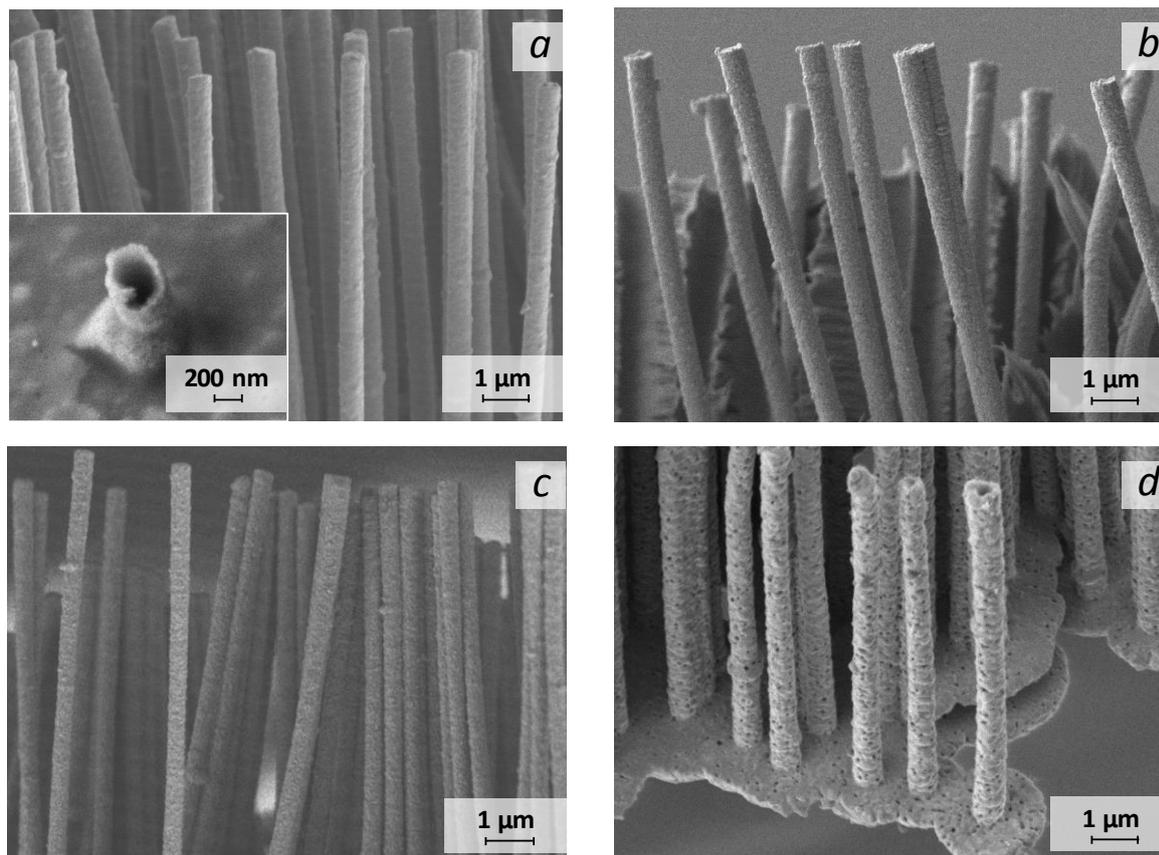


Figure 1. SEM microphotographs of Ni NTs: a) initial; b) irradiated at fluence $5 \times 10^{10} \text{ cm}^{-2}$; c) 10^{11} cm^{-2} ; d) $5 \times 10^{11} \text{ cm}^{-2}$.

Effect of irradiation of carbon ions with high energy leads to a modification of the NTs wall structure, herewith the size and number of defects would rise with increasing radiation fluence. This

fact is associated with multiple processes occurring during the interaction of ions with solids. For example, the interaction of the particles of high energy with solids lead to restructuring NTs walls by knocking out nickel particles and embedding of carbon particles. However, analysis of the SEM image shows the formation of vacancies and roughness on NTs surface take place only by irradiation with the maximum fluence (Figure 1d).

Determination of carbon presence in NTs structure was held by EDA. According to obtained data, the atomic ratio of nickel in the initial NTs sample is 100% (Figure 2a) and remains constant up to fluence of $5 \times 10^{10} \text{ cm}^{-2}$. Exceeding this fluence leads to registration in EDA spectra carbon peak ($K\alpha$ - series - 0.277 keV, Figure 2b). Future expanding of the fluence provides not only the increasing of carbon peaks intensity, but also changing in the intensities of Ni $K\alpha$ - series lines at 7,474 keV and $L\alpha$ - Series 0.849 keV, which caused by changes in the structure of NTs as a result of the interaction of carbon ions with the crystal lattice (Figure 2c-d).

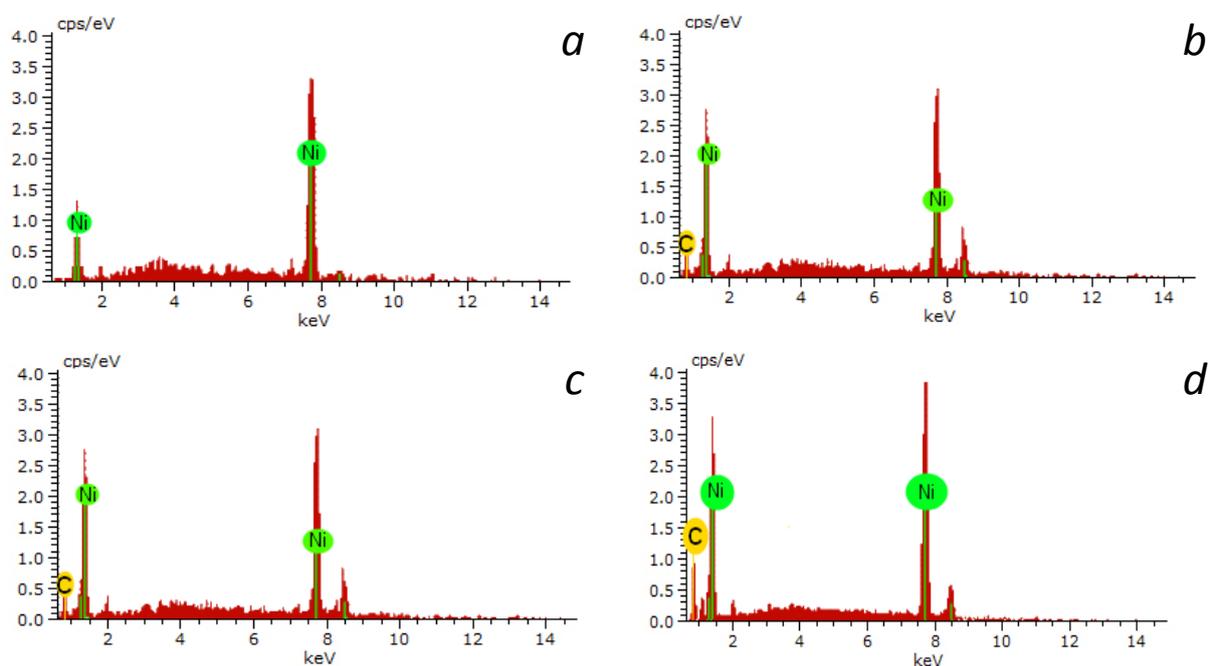


Figure 2. EDA spectra of Ni NTs: a) initial; b) irradiated at fluence $5 \times 10^{10} \text{ cm}^{-2}$; c) 10^{11} cm^{-2} ; d) $5 \times 10^{11} \text{ cm}^{-2}$.

Determination of the influence of ionizing radiation on the crystal structure was carried out by XRD (Figure 3). Analysis of the observed XRD peaks (111) (200) and (220) showed that the obtained NTs have a polycrystalline structure with a predominant crystallographic direction [111], typical for electrodeposited nickel nanostructures. At the same time, future increasing radiation fluence more than $5 \times 10^{10} \text{ cm}^{-2}$, the typical for nonstoichiometric carbides NiC_x peak with Miller indices (114) at $2\theta = 36.2^\circ$ appears on spectra. This fact confirms with the previously showed results of the EDA.

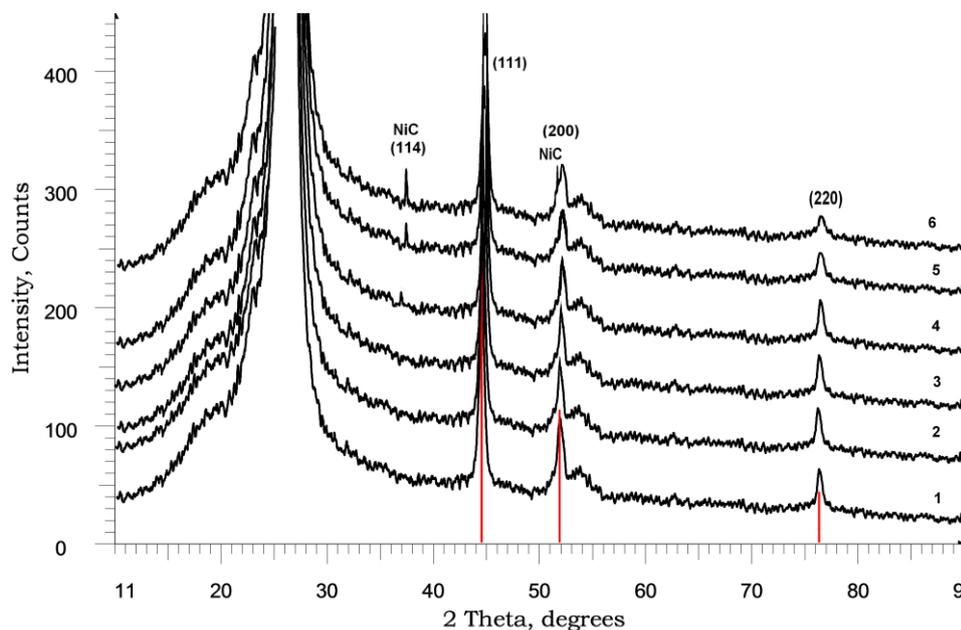


Figure 3. XRD spectra of Ni NTs in PET template at different irradiation regimes.
 1) initial;
 2) 10^9 cm^{-2} ;
 3) 10^{10} cm^{-2} ;
 4) $5 \times 10^{10} \text{ cm}^{-2}$;
 5) 10^{11} cm^{-2} ;
 6) $5 \times 10^{11} \text{ cm}^{-2}$.

It is worth to notice that on the every diffraction diagram of the samples broadening peaks typical for nanodimension objects are observed. Calculations of Ni NTs structural characteristics showed that both the original and irradiated samples have FCC structure with lattice parameter a , which is typical of the nickel, but different from the standard value. The results of a calculation and the average crystallite sizes are shown in table 1.

Table 1. Parameters of Ni NTs obtained at different irradiation regimes.

Irradiation fluence, cm^{-2}	a , Å	The average size of crystallites, nm
0 (initial)	$3,5223 \pm 0,0007$	$25,3 \pm 1,1$
10^9	$3,5190 \pm 0,0057$	$24,1 \pm 0,7$
10^{10}	$3,5173 \pm 0,0040$	$23,2 \pm 0,9$
5×10^{10}	$3,5160 \pm 0,0008$	$21,5 \pm 1,2$
10^{11}	$3,5157 \pm 0,0023$	$20,3 \pm 1,0$
5×10^{11}	$3,5244 \pm 0,0021$	$29,9 \pm 1,5$

To determine the influence of the irradiation conditions on the electrical properties (conductivity σ) of Ni NTs array in PET template were studied. The electrical conductivity was calculated by the formula:

$$\sigma = \frac{dI}{dU} \frac{l}{A},$$

where l – length of NTs, A – conducting surface area, dI/dU – tangent of the angle depending $I-U$. Graph of dependence σ from deposition potential is shown in figure 4.

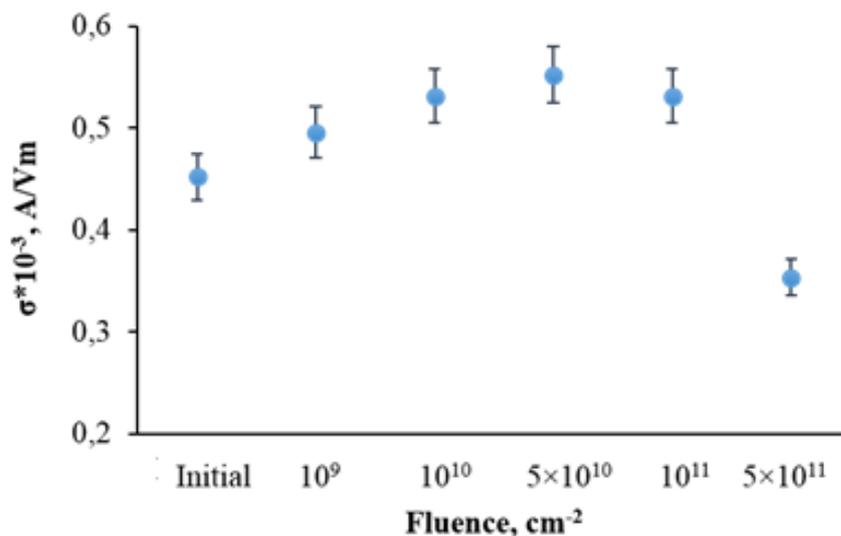


Figure 4. Dependence of Ni NTs conductivity on irradiation regimes.

The diagram of dependence of the conductivity on the radiation fluence has two parts. On the first part, from a zero to the fluence of $5 \times 10^{10} \text{ cm}^{-2}$ the conductivity slightly increases to a value on 20% more than the conductivity of the initial sample. On the second part of the diagram conductivity decreases sharply to value less on 23% than the non-irradiated sample. The growth of the conductivity on the first section, most likely related with the relaxation of defects of the NTs structure and the formation of less-defected wirings along the main NTs axis. At a fluence of $5 \times 10^{10} \text{ cm}^{-2}$ carbon in the form of carbides compounds accumulates appreciably in the structure (figures 2 and 3). The large quantity of carbon causes both the decreasing in the conductivity and the destruction of the wall structure, as is observed in figure 1d.

Conclusions

Nickel NTs with length of 12 microns, an external diameter of 380 nm and wall thickness about 95 nm were obtained by template synthesis method in the pores ion-track PET membranes. Modification of NTs structures was held on by irradiating by ions C^{+13} with energy of 1.75 MeV/nucleon and fluence ranging from 10^9 to $5 \times 10^{11} \text{ cm}^{-2}$.

It was shown that irradiation with fluences up to $5 \times 10^{10} \text{ cm}^{-2}$ led to decrease of the lattice parameter and the average crystallites size, which form the NTs walls. Together with that increasing in conductivity of samples on 20% more relative to non-irradiated structures was observed. At fluences higher than $5 \times 10^{10} \text{ cm}^{-2}$ accumulation of carbon in the structure of NTs in a form of a new phase - carbon carbide took place. Growing the amount of carbon led to degradation of the NTs structure and, consequently, to reduction of their conductivity.

Acknowledgments

The work was done within the №561 Project of the Ministry of Education and Science of the Republic of Kazakhstan approved on April 07, 2015.

References

- [1] Abedini A, Larki F, Saion E, Zakaria A and Hussein M Z 2012 *Radiat. Phys. Chem.* **81** 1653
- [2] Ayres V M, Jacobs B W, Englund M E, Carey E H, Crimp M A, Ronningen R M, Zeller A F, Halpern J B, He M-Q, Harris G L, Liu D, Shaw H C, and Petkov M P 2006 *Diam. Relat. Materi.* **15** 1117
- [3] Banhart F 1999 *Rep. Prog. Phys.* **62** 1181

- [4] Bid A, Bora A and Raychaudhuri A K 2006 *Phys. Rev. B* **74** 1
- [5] Ivanov L I and Platov Yu M 2004 *Radiation Physics of Metals and Its Application* (Cambridge, Cambridge International Science Publishing, UK)
- [6] Singh A K, Das B, Sen P, Bandopadhyay S K and Mandal K 2014 *IEEE Transaction on Magn.* **11** 2302104.
- [7] Kaur A and Chauhan R P 2014 *Radiat. Phys. Chem.* **100** 59
- [8] Kaniukov E, Kozlovsky A, Shlimas D, Yakimchuk D, Zdorovets M and Kadyrzhanov K 2016 *IOP Conf. Series: Materials Science and Engineering* **110** 012013
- [9] Coa G and Wang Y 2004 *Nanostructures and Nanomaterials—Synthesis, Properties, and Applications.* (Imperial College Press, London: Toh Tuck Link Ltd., Singapore)
- [10] Kaniukov E Yu, Ustarroz J, Yakimchuk D V, Petrova M, Terryn H, Sivakov V and Petrov A V 2016 *Nanotechnology* **27** 115305
- [11] Dalchiele E A, Marotti R E, Cortes A, Riveros G, Gomez H, Martinez L, Romero R, Leinen D, Martin F and Ramos-Barrado J R 2007 *Physica E* **37** 184
- [12] Kozlovsky A L, Meyrimova T Y, Mashentseva A A, Zdorovets M V, Kaniukov M V, Yakymchuk D V, Petrov A V and Kadyrzhanov K K 2016 *Chem. Bulletin of Kazakh National University* **3** 4
- [13] Kozlovskiy A L, Shlimas D I, Shumskaya E E, Kaniukov E Yu, Zdorovets M V, Kadyrzhanov K K 2017 Influence of electrodeposition parameters on structural and morphological features of Ni nanotubes *The Physics of Metals and Metallography* **2** (in press)
- [14] Shumskaya E E, Kaniukov E Yu, Kozlovskiy A L, Zdorovets M V, Rusakov V S, Kadyrzhanov K K 2017 Structural and physical properties of template-synthesized iron nanotubes *Physics of Solid State* **4** 766
- [15] Kozlovskiy A, Zhanbotin A, Zdorovets M, Manakova I, Ozernoy A, Kiseleva T, Kadyrzhanov K, Rusakov V and Kanyukov E 2016 *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* **381** 103