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Influence of media with different acidity on structure of FeNi nanotubes

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Abstract. A detailed analysis of the structure features of FeNi nanotubes exposed at environment with different acidity is carried out. It is demonstrated that the exposure of the nanostructures in the environment with high acidity causes the structure deformation, leading to sharply increasing of the presents of oxide phases and partial amorphization of nanotubes walls that determined the rate of FeNi nanotubes destruction. It was established that the evolution of the crystal structure parameters concerned with appearance of oxide phases and with formation of disorder regions as a result of oxidation processes.

1 Introduction

Nowadays, precise attention is paid to nanostructured materials, which in the future will take their place in practically all fields of science and technology: from magnetic recording devices to sensors and carriers of drugs [1-3]. An alloy of iron and nickel is one of the unique materials for practical applications, due to its physical-chemical properties [4-7] . The composition of alloy strongly influences on such properties [8].

One of the essential criteria for evaluating the potential application of magnetic nanotubes is their reactivity as well as rate of oxidation and destruction in environment with different value of acidity (pH). Oxidation process lead to evolution of the crystal structure parameters, Fe : Ni ratio, presence of amorphous phase and the material destruction. These processes can produce changes in target magnetic and electrical properties, which are critical for micro- and nanoelectronic applications.

The information about the changes occurring in FeNi nanostructures during holding in environments with different acidity is fragmentary. In this paper, the dynamics of FeNi nanotube degradation in environment with different acidity is considered. An analysis of the change in structural properties is carried out. Morphology and structural properties were

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investigated using scanning electron microscopy, energy dispersive and X-ray diffraction analysis.

2 Experimental part

The synthesis of FeNi nanotubes was conducted in the pores of the polyethylene terephthalate (PET) ion-track membranes with a thickness of 12 μm, with pore density 4×10^{7} cm^{-2} and diameters of 400 nm. The cathode during deposition was a 10 nm thick gold layer, which was deposited by magnetron sputtering in a vacuum. With this thickness of the Au layer, the pores remained open, and the growth of the nanostructures began at the points of contact of gold with the electrolyte.

Electrochemical deposition was carried out at a potential of 1.75 V using an electrolyte: $FeSO_4\times6H_2O$ (20 g/l), $NiSO_4\times6H_2O$ (100 g/l), H_3BO_3 (45 g/l), $C_6H_8O_6$ (1.5 g/l) at temperature of 25 °C, the pH of the electrolyte solution was 3. The deposition process was monitored chronoamperometrically using an Agilent 34410A multimeter.

Three aqueous solutions were chosen to study the reactivity with different values of the hydrogen index, ranging from pH=1 (strongly acid environment) to pH=7 (neutral environment). The most common chemical reagent used to reduce the high pH of aqueous solutions is hydrochloric acid. A gradual increase in the concentration of hydrogen ions in solutions was achieved due to the use of slightly concentrated (0.01 M/l) hydrochloric acid. Value of pH was monitored with pH meter (Hanna Instruments HI2210-02).

The nanotubes were taken out from the polymer template by dissolving it in an alkaline solution for conduction of experiment. 9 M/l solution of sodium hydroxide was used to dissolve the film. Pure nanotubes were placed in prepared aqueous solutions with different pH values. The time range was 1, 5, 10 and 20 days. At the end of each time interval, changes in the structure and morphology of nanotubes were investigated.

Characterization of structural features was conducted by scanning electron microscopy method (SEM, Hitachi TM3030), energy dispersive analysis (EDA, Bruker XFlash MIN SVE), X-ray diffraction analysis (XRD, Bruker D8 ADVANCE) using Cu K_{α} radiation.

3 Results and discussion

Typical SEM image of FeNi nanotubes obtained by the template synthesis are shown in Figure 1.

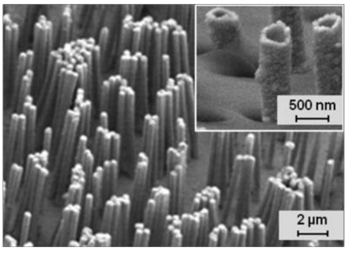

Fig. 1. SEM images of pristine FeNi nanotubes (nanotubes taken out from the PET templates).

From SEM microphotographs it is seen that the nanotubes are isotropic and cylindrical, with a length of 12 µm and an outer diameter of 400 nm, which corresponds to the pore size of the initial template. The effect of environment acidity on the crystal structure of FeNi nanotubes was studied using EDA and XRD. Pristine FeNi nanotubes composition was Fe : Ni = 20： 80 (permalloy).

Based on the EDA the composition of FeNi nanotubes after exposure in media with different pH was provided (Table 1).

Table 1. Composition of the FeNi nanotubes, bases on EDA, %.

Time, days	pH=1			pH=5			pH=7		
	Fe	Ni	O	Fe	Ni	O	Fe	Ni	O
0	21	79	0	21	79	0	21	79	0
5	18	77	5	20	77	3	21	79	0
10	15	75	10	18	75	7	20	78	3
15	13	71	16	16	73	11	18	75	7
20	10	68	22	14	70	16	15	73	12

To understand the changes occurring in the structure of nanotubes, XRD analysis was performed. Based on the analysis of the change in intensity and shape of XRD peaks (Figure 2), as well it is possible to assume of structure amorphization and partial nanotubes degradation in acidic environment.

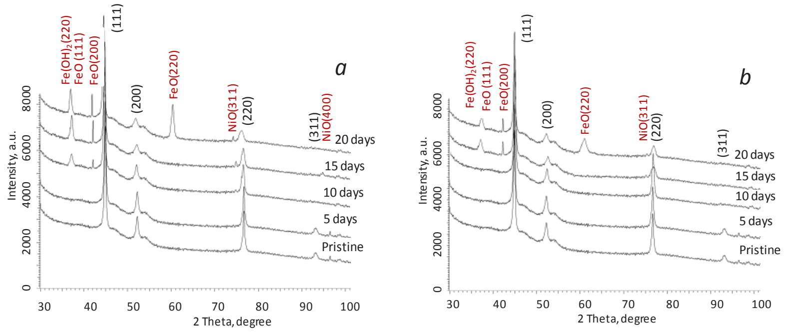

Fig. 2. XRD patterns of FeNi nanotubes exposed in media with various acidity: a) pH=1, b) pH=5.

On the diffractograms for aggressive environment, there are iron hydroxide ($Fe(OH)_2$) and oxide (FeO) for the 10th day, and for environment with pH=5 for the 15th day. Also, there are nickel oxide (NiO) phase with Miller indices (311) and (400). At the same time, as the exposition time in solutions increases, a decrease in the intensity of the peaks characteristic for the FeNi phase is observed, while the intensity of peaks of $Fe(OH)_2$ and FeO phases increases. Based on the analysis of the shape of the peaks, the contributions of various phases to the crystal structure of the nanotubes were obtained during the oxidation process. The results of the assessment of contributions are presented in Table 2.

Table 2. Phase state of the FeNi nanotubes, bases on analysis of XRD patterns, %.

Time, days	pH 1				pH 5				pH 7			
	FeNi	FeO	$Fe(OH)_2$	NiO	FeNi	FeO	$Fe(OH)_2$	NiO	FeNi	FeO	$Fe(OH)_2$	NiO

0	100	-	-	-	100	-	-	-	100	-	-	-
5	100	-	-	-	100	-	-	-	100	-	-	-
10	91	6	2	1	100		-	-	100	-	-	-
15	86	9	3	2	94	3	2	1	100	-	-	-
20	77	15	5	3	88	7	3	2	100	-	-	-

As can be seen from the presented data, the formation of hydroxide phase $Fe(OH)_2$, oxide phase FeO begins on the 10th day, when the oxygen content in the structure of nanotubes exceeds 10%. At the same time, for nanotubes in neutral environment, the presence of oxide phases is not detected. However, the appearance of oxygen is observed by EDA (Table 1) as well. Probably the oxide phase is formed only on the nanotubes surface.

The crystallinity degree was estimated by decreasing the integrated intensity of diffraction peaks automatically with using of software BrukerAXSDIFFRAC.EVAv.4.2. X-ray diffraction patterns were processed by the required number of symmetric pseudo-Voigt functions, it made possible to determine the FWHM of the registered lines, which is necessary for further calculations. The degree of crystallinity, which characterizes the fraction of regularly packed molecules with respect to the number of disordered molecules, i.e. the ratio of crystalline (S_{cr}) and amorphous (S_{am}) phases in polymer (relative degree of crystallinity),%, was determined on the basis of equation:

$$\text{Crystallinity} = \frac{S_{cr}}{S_{cr} + S_{am}} * 100\%$$

Reduction of the integrated intensity of the diffraction peaks, observed in the analysis of diffractogramms, corresponds to a decrease in the degree of crystallinity of the study samples.

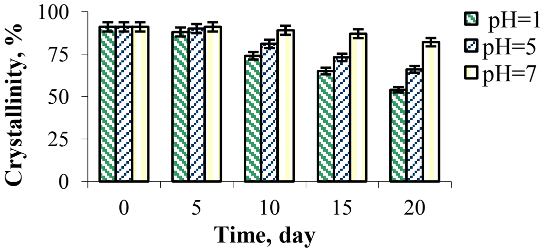

Fig. 3. Diagram of the changes in the FeNi nanotubes crystallinity degree exposed in media with various acidity.

From the presented data, for an environment with pH=1, a decrease in the degree of crystallinity from 91% to 65% for the pristine sample is observed at the 15th day and 54% for the 20th day, and for an environment with pH=5, a decrease in the degree of crystallinity to 73% for the 15th day and 66% on the 20th day. It was found that partial destruction of the structure due to the formation of oxide compounds on the surface of nanotubes and subsequent corrosion processes can cause structural failure, leads to a high degree of structure amorphization and decreases the degree of crystallinity below 70%. In turn, for samples in an environment with pH=7, an insignificant decrease in the degree of crystallinity is observed. The results, obtained by XRD analysis are in a good correlation with EDA. For nanotubes, exposed in media with pH=1, the outgrowths on surface were detected. According to the results of EDA, a high concentration of iron oxides was observed in the outgrowths, which indicates the oxide structure of the growths. On the 15th and 20th day, an increase in the number of outgrowths is observed that cause amorphization of nanotubes surface, which is confirmed by the results of these changes in the degree of crystallinity. For environment with pH=5 and pH=7 and according to the EDA, the appearance of oxygen in the structure is observed on the 5th day for pH=5 and for the 10th day for pH=7. However, according to XRD, oxide compounds in the crystal structure appear on the 15th day for the environment with pH=5. The presence of small impurities of oxygen on the 5th day is due to the oxidation of the surface layer of nanotubes.

4 Conclusion

The synthesis and study of the physical and chemical properties of nanotubes based on the Fe : Ni alloy (permalloy) synthesized in the pores of PET membranes were carried out. Investigation of the dependence of structural and morphological parameters of nanotubes allowed to evaluate the degree of crystallinity, and also to establish the dynamics of crystal structure amorphization in environment with different pH. On the basis of the analysis of the structure change dynamics, an increasing of oxides phases in the structure with an increasing of nanotubes exposition time in solutions with different acidities was shown. For example, when nanotubes were kept in environment with pH = 1 for the 10th day and in environment with pH 5 for the 15th day, the iron oxide (FeO) and iron hydroxide ($Fe(OH)_2$), as well as nickel oxide (NiO) were established. Most of the oxides were concentrated in the near-surface layers and were localized in the form of outgrowths mainly on the surface of the amorphized oxide phase. Conversely, when samples were held in environment with pH 7, even at the maximum exposure time, only a slight decrease in the degree of crystallinity was observed. The nickel and iron oxide compounds were not found. It should be mentioned that understanding of the degree of nanotubes degradation in different environments could make it possible to significantly clarify the terms of FeNi nanotubes applicability without any special processing, such as covering with protection coats.

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