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Investigation of the stability of nanostructures to degradation

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The paper presents the dependence of the degradation degree in various aggressive media and time in a medium. The greatest deterioration in crystallographic characteristics of nanostructures in corrosive media is observed on the day 10th, which is due to partial destruction of the crystal structure as a result of oxidation processes. Also, an increase in the oxygen concentration in the structure leads to an increase in disorder regions, amorphization, and subsequent destruction of samples.

Keywords: nanostructures; nanotubes; template synthesis; degradation processes; corrosion of nanomaterials.

Introduction

Corrosion and subsequent degradation processes are one of the main reasons for severe damage of the most functional materials and structures [1-3]. In turn, the use of nanostructures is accompanied by interaction not only with the environment, but also with aggressive media that can lead to a sharp increase in degradation processes of nanostructures [4-6]. In many devices, corrosion processes occur when the material contacts the electrolyte solutions. In this case, the corrosion of metals is due to the flow of conjugated electrochemical reactions, which lead to structure oxidation and subsequent degradation of materials. The degradation processes in nanomaterials have a specific character in connection with the non-equilibrium state of nanostructures [7,8]. In this case, the presence of a large number of grain boundaries and triple junctions should adversely affect nanomaterials stability to degradation. However, in some cases, a large number of the surface and near surface defects leads to the both protective films formation and surface passivation. As a result, barriers are created for the spread of corrosion processes and further degradation of nanomaterials. In this connection, the final result of the corrosion degradation directly depends on the kinetic features of the surface and electrochemical reactions, the physical-chemical properties of nanomaterials as well as the method of their production and modification [9-13]. Moreover, the nature of the corrosion degradation of nanostructured materials is non-trivial, as evidenced by the contradictory data from various studies [14-17]. Copper oxide CuO nanostructured materials have drawn great interest of several

research groups due their promising applications in electrocatalysis and micro-electronics [18-19]. Thus it is of great importance to study and understand their stability and possible degradation, which is very important for their successful and long-term practical application.

Experimental details

Track membranes were obtained of polyethylene terephthalate of "Hostaphan®" brand manufactured by Mitsubishi Polyester Film (Germany). The films were irradiated at DC-60 accelerator of heavy ions (Kazakhstan) with accelerated krypton ions with an energy of 1.75 MeV/nucleon and a fluence of 4×10^7 ion/cm². The membranes were etched according to the standard double-sided etching technique in a solution of 2.2 M NaOH at 85 ± 1 °C. The pore size according to gas porosimetry, and SEM was (380 ± 10) nm, the track length was 12 μ m.

Electrochemical synthesis in tracks of the template was carried out in potentiostatic mode at a voltage of 1.0 V. The electrolyte temperature was 25 °C. The composition of the electrolyte solution: CuSO₄ × 5H₂O (238g/l), H₂SO₄ (21g/l). The yield of copper by current from the sulfuric acid solutions of electrolytes is 100%. The growth of nanostructures was monitored by the chronoamperometry method with the "Agilent 34410A" multimeter. Since the template PET matrices are dielectric, a layer of gold with a thickness of no more than 10 nm, which is further a working electrode (cathode) during electrochemical deposition, was deposited to create a conductive layer by magnetron sputtering in a vacuum. By controlling the deposition time, the difference in the applied potentials, the electrolyte temperature, we can change the geometric parameters of synthesized nanostructures. All possible reactions associated with the synthesis process are listed below.



Copper sulfate dissociates into Cu⁺² and SO₄⁻² ions in the first stage of electrolysis. Then Cu⁺² ions are reduced near the cathode to Cu(s), and a layer is formed behind the wall layer of the nanostructures in pores, repeating the template geometry. Because of the change in concentration of H⁺ ions during the synthesis, the pH of the solution can vary, which leads to uneven filling of the pores. To control pH of the solution, sulfuric acid H₂SO₄ was used, acting as a buffer to maintain the pH. Investigation of structural characteristics and elemental composition of nanostructures obtained before and after irradiation was carried out using a scanning electron microscope "Hitachi TM3030" with a microanalysis system "Bruker XFlash MIN SVE" at an accelerating voltage of 15 kV. X-ray diffraction analysis (XRD) was performed on a D8 ADVANCE ECO diffractometer (Bruker, Germany) using Cu α radiation. The software Bruker-AXSDIFFRAC.EVA v.4.2 and the international ICDD PDF-2 database were used to identify the phases and study the crystal structure. Investigation of corrosion processes and nanostructures stability to degradation was carried out in 10% solutions of hydrochloric (HCl), sulfuric (H₂SO₄) and orthophosphoric (H₃PO₄)

acids in the time range from 1 to 10 days. The maximum residence time of nanostructures in solutions was limited to the maximum degree of samples destruction. At the stage of immersion nanostructures in acid solutions, the samples were taken off from the polymer template, by dissolving the template in a solution of 5 M NaOH at 50 °C for an hour, with vigorous stirring. Residues of the alkaline solution were neutralized in a 50% solution of acetic acid and deionized water.

Results and Discussion

Figure 1 shows SEM images of synthesized nanostructures released from polymer templates. As can be seen from the presented data, the resulting structures are hollow cylindrical nanotubes, 12 μm in length and 380 nm in diameter, which coincides with the pore diameter in the polymeric template.

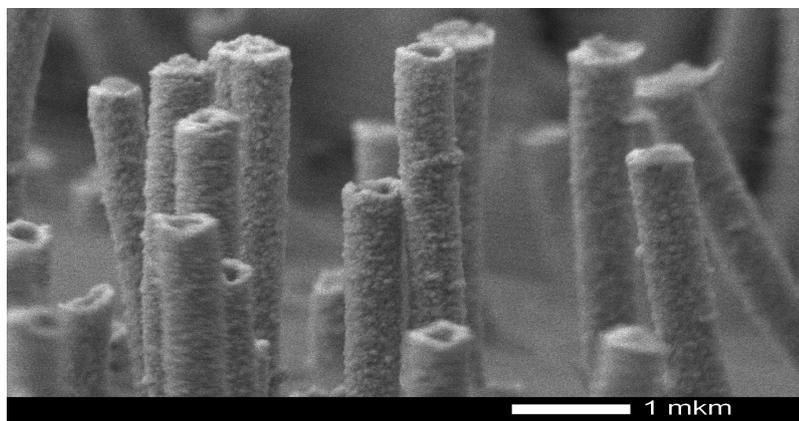


Figure 1. SEM image of synthesized nanostructures.

One of the important criteria for evaluating the potential application of nanotubes as elements of microelectronic devices is their reactivity and the oxidation rate and destruction in various acidic media. However, the degradation of materials can affect not only the deterioration of structural properties and morphology of nanomaterials surface, but also a decrease in the performance of nanostructures. Also, degradation processes can be slow, due to deterioration of the performance of the material during operation, and rapid, caused by external influences on the structure, such as irradiation, heating, corrosive media. In this case, as a rule, rapid degradation processes are spatially inhomogeneous and are associated with the presence of mobile defects in the structure [18, 19]. Figures 2 show the dynamics of surface morphology of Cu nanotubes after interaction with various aggressive media.

The discovery of Cu nanotubes in acids during one day leads to the formation of small outgrowths on the outer surface of walls and the formation of small porous inclusions. The increase in the time in acids up to 5 days leads to the formation of large porous inclusions, the average size of which is (30-50) nm. It is seen that the formation of porous amorphous inclusions on nanostructures surface is not homogeneous. An increase in the time of finding nanostructures in acids up to 10 days leads to a complete destruction of nanotubes walls and their destruction for samples in solutions of sulfuric and orthophosphoric acids. For samples in hydrochloric acid solution, an increase in the porosity of nanostructures walls due to the formation of amorphous inclusions is observed. The

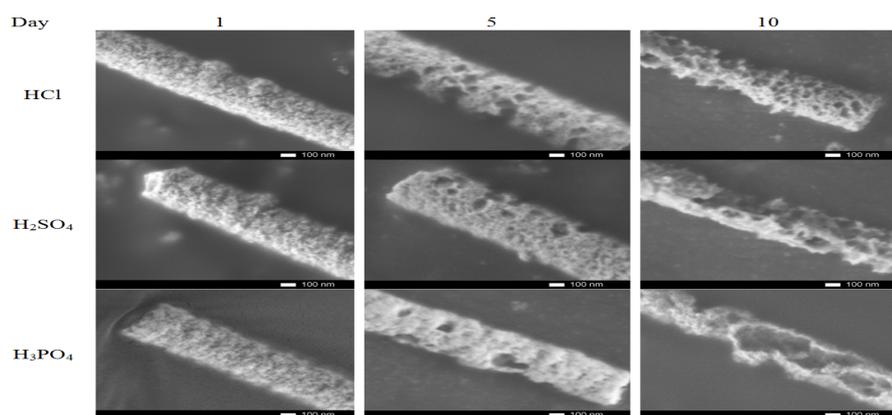


Figure 2. SEM images of Cu nanotubes after interaction with various aggressive media.

greatest degree of degradation is observed for samples in orthophosphoric acid, while porous inclusions are formed on nanotubes walls, the average size of which is (150 ± 180) nm.

The formation of porous inclusions can be due to a change in the elemental composition of investigated samples and the appearance of oxide compounds in the structure. Table 1 presents data on changes in the elemental composition of investigated samples before and after being in aggressive media.

Table 1.
Data changes in element composition.

Medium	Initial nanotubes			
	0 Day	1 Day	5 Day	10 Day
HCl	Cu ₁₀₀	Cu ₉₀ O ₁₀	Cu ₈₂ O ₁₈	Cu ₆₃ O ₃₇
H ₂ SO ₄	Cu ₁₀₀	Cu ₉₂ O ₈	Cu ₈₁ O ₁₉	Cu ₆₁ O ₃₉
H ₃ PO ₄	Cu ₁₀₀	Cu ₉₂ O ₈	Cu ₇₉ O ₂₁	Cu ₅₉ O ₄₁

From Table 1, it can be seen that the presence of oxygen in the structure of nanotubes is observed from 1st day. The oxygen concentration increases with increasing residence time in corrosive media. The XRD analysis method was used to determine the change in the crystal structure under the influence of aggressive media. Figure 3 shows the XRD patterns of Cu nanotubes after being in aggressive media.

For initial samples after the 1st day in aggressive solutions, peaks characteristic of copper oxide CuO with Miller (111) and (220) indices are found. However, an increase in the residence time in corrosive media with up to 5 and 10 days leads to an increase in peaks intensity of the oxide compound and a decrease in Cu peaks intensity. The formation of oxide compounds in the crystal structure under the influence of aggressive media can lead to a change in main parameters of the crystal lattice, a decrease in the degree of crystallinity due to the formation of amorphous inclusions, leading to a partial destruction of the structure. Figure 4 shows diagrams of the dependence of the change in the degree of crystallinity of nanotubes from the time in corrosive media.

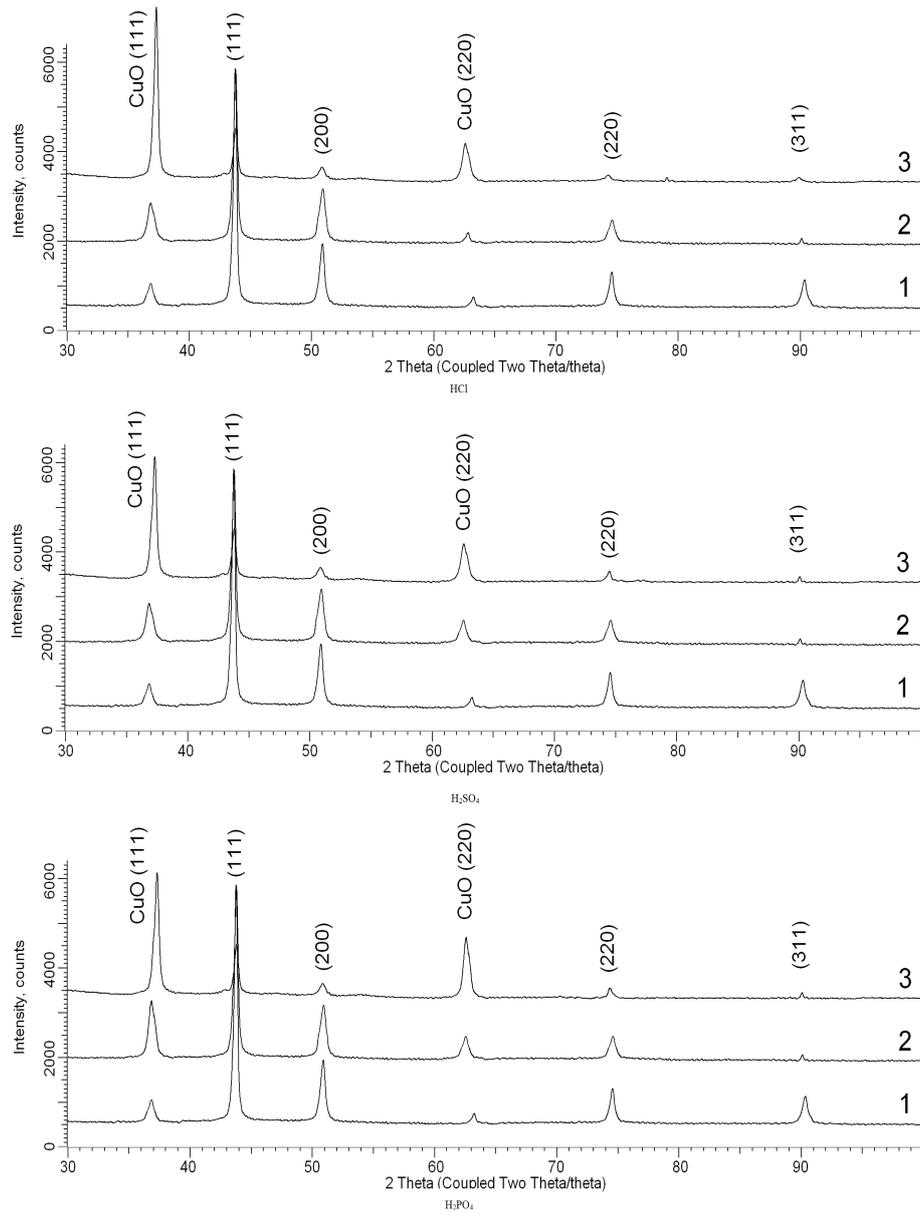


Figure 3. XRD patterns of Cu nanotubes after being in aggressive media: 1) 1 day; 2) 5 days; 3) 10 days.

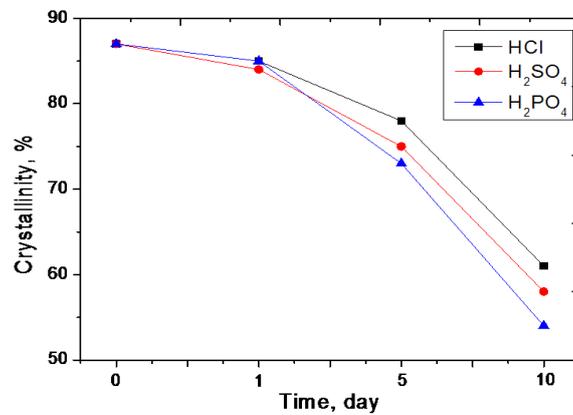


Figure 4. Diagrams of the dependence of the change in the degree of crystallinity of nanotubes from the time in aggressive media.

Conclusions

The paper presents the dependence of degradation degree in various aggressive media and time in a medium. The greatest deterioration in crystallographic characteristics of nanostructures is observed on the day 10th, which is due to the partial destruction of the crystal structure as a result of oxidation processes. However, an increase in the oxygen concentration in the structure leads to an increase in disorder regions, amorphization, and subsequent samples destruction.

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