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Studying the Thermodynamic Characteristics of Anodic Alumina

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Abstract—We report on the complex scanning electron microscopy, X-ray diffraction, energy-dispersive X-ray spectroscopy, and differential thermal analysis study of the composition, structure, and thermodynamic characteristics of a porous alumina membrane.

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INTRODUCTION

One of the most widespread methods for forming one-dimensional nanomaterials is based on using the appropriate matrix (template). It is most frequently proposed to use matrices (membranes) with blind or through nanochannels (nanopores). Porous anodic alumina (PAA) membranes fabricated by two-stage anodizing of aluminum preforms (plates or foil) in an aqueous solution of oxalic acid are the most popular templates used in experiments [1].

Most studies in this direction focus upon fabricating nanostructure arrays, including carbon nanotubes (CNTs) [2, 3] and magnetic or semiconductor nanothreads and nanodots [4–7]. In these studies, one of the conditions of synthesis is high temperature, e.g., in chemical vapor deposition (CVD) [8] and physical vapor deposition (PVD) [9]. In other cases, high-temperature heat treatment (annealing) is required [10].

After the chemical functionalization (modification) of the inner pore surface, the PAA can be used to fabricate chemical sensors [11] and catalysts [12]. However, the possibilities of the application of the PAA in gas separation [13], ultrafiltration [14], and separation of biomolecules with molecular masses close to each other [15] have been intensively studied.

The diversity of the possible applications of the PAA matrices has stimulated thorough investigations of their physicochemical properties using different techniques. Comparative analysis of the techniques for studying the thermal properties of the PAA and PAA-based nanocomposites showed that differential thermal analysis (DTA) is the best method for studying their thermodynamic characteristics [16]. Being relatively simple to implement, this method yields reliable information about the temperature behavior of samples in a wide temperature range according to a specified program and is sufficiently sensitive to study nanomaterials.

In addition, the practical interest of researchers in this direction is focused on the fact that incorporation of different nanoelements in a chemically and thermally inert alumina matrix is one of the ways of enhancing their stability. Therefore, it is important to study the thermodynamic properties of the PAA membranes in different media.

This work is aimed at complex investigations of the composition, structure, and thermodynamic characteristics, in particular, the specific features of the first-order phase transitions (crystallization), in the PAA membranes fabricated by us.

EXPERIMENTAL

To conduct the experiments, we fabricated free, bounded PAA-based membranes (PAA membranes). The bounding around the periphery was made for the simplicity of manipulations with a large-area membrane.

The initial material was an aluminum foil (99.995%) with a thickness of ~100 μm used for cutting standard substrates 60 × 48 mm in size. Double-sided electrochemical anodic oxidation of the Al substrate (stage 1) was performed at a temperature of 15°C in a 0.5 M solution of oxalic acid ($H_2C_2O_4$) at a constant anodizing voltage of 50 V for 25 min (the primary oxide thickness was ~10 μm). After selective chemical etching of the formed Al_2O_3 oxide in a mixture of 0.5 M of phosphorous acid and 0.2 M of chromium acid, the substrate was coated with a chemically stable lacquer (CSL); one substrate side was coated continuously and the other, along the periphery. Then, the Al substrate was subjected to one-sided electrochemical anodizing (stage 2) at 15°C in a 0.5-M solution of

Table 1. XRD PAA elemental composition in region 1

Element	mass %	at %
C	7.86	12.90
O	43.19	52.17
Al	48.05	34.33
P	0.20	0.14
S	0.18	0.12
Cl	0.52	0.34
Sum	100.00	100.00

oxalic acid at a constant anodizing voltage of 50 V for 125 min (the oxide thickness was 50 μm). The PAA membrane fabrication was described in more detail in [17].

The topography of the surface and transverse cleavages of the experimental samples was studied by scanning electron microscopy (SEM) on Philips XL 30 S FEG and Hitachi S-4800 microscopes and atomic force microscopy (AFM) on a Nanotop NT-206 facility (Mikrotestmashiny, Belarus) and a Solver P47H (NT-MDT Co., Russia) microscope.

The experimental data were processed using the Surface Explorer Document (SED) program package. The SED method allows studying the microstructure using a series of images with different scales, which cover the entire size range of the structural elements contained in a sample. The analysis provided information about the size and shape of the structural elements.

The phase composition of the experimental samples was examined by X-ray diffraction (XRD) analysis on a DRON-2 X-ray diffractometer in CuK_α radiation at a wavelength of $\lambda = 0.154056$ nm.

Chemical analysis of the elemental composition of experimental samples was performed on a scanning electron microscope with an energy-dispersive X-ray spectroscopy (EDX) attachment at an accelerating voltage of 15 kV (QUANTAX 200 microanalyzer for scanning electron microscopes (Bruker, Carl Zeiss AG)).

The DTA and thermogravimetric 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 50–80 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), as well as in an inert atmosphere at an argon flow rate of 50 mL/min. The temperature ranged from room temperature to 1000°C and the heating rate ranged within 10–20 deg/min.

RESULTS AND DISCUSSION

Study of the Structure and Composition of Al_2O_3 (PAA) Porous Matrices

Figure 1 shows the SEM images of a free PAA membrane with a thickness of 50 μm 70 × 70 mm (Figs. 1a, 1b), the reference sample of the same thickness 48 × 60 mm in size (Fig. 1c), and an AFM image of the PAA matrix with blind pores (Fig. 1d). The reference membrane consists of six identical samples 15 × 20 mm in size.

The membranes shown in Fig. 1 were fabricated by two-stage anodic oxidation and have a thickness of 50 ± 2 μm and a pore diameter of 55 ± 5 nm. The inset in Fig. 1b shows a profile of the membrane's back side after aluminum etching and removal of the barrier layer at the bottom of the pore.

Figure 2 shows AFM profiles (Fig. 2a) and SEM images (Fig. 2b) of the front surface of the PAA matrices.

According to the presented data, the obtained membranes have uniform geometrical sizes both on the surface and in the middle (along the cleavage) of the sample.

Using a JEOL JSM-6390A scanning electron microscope, we obtained the membrane's cleavage images (Fig. 3a) and scanned the sample in region 1 (Figs. 3b, 3c). According to the results of the PAA's (amorphous Al_2O_3) elemental composition, the sample contains, along with the main elements (Al and O), the impurities caused by the ability of electrolyte anions to incorporate in the oxide pore walls at the formation stage. The obtained quantitative EDX data are given in Table 1.

The contrast color-coded images of the main material elements (distribution maps) illustrate the phase contrast variation, i.e., the elemental distribution over the scanning region. According to the EDX images, the oxygen content is higher on the surface than in the bulk of the oxide. The ratio between the numbers of oxygen atoms and aluminum atoms deep in the oxide is 1.5, which corresponds to the atomic ratio in the stoichiometric Al_2O_3 oxide, whereas on the surface this ratio is over 2.