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Original paper

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FORMATION OF ANTI-REFLECTION COATINGS BASED ON NANOSTRUCTURED ALUMINUM AND BARIUM TITANATE XEROGEL LAYER

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Abstract. The research has been carried out on the formation of anti-reflection coatings based on porous aluminum obtained by electrochemical anodic etching and a layer of barium titanate xerogel deposited on its surface. The thickness of the porous aluminum ranged from 15 to 100 microns. Analysis of the reflection spectra of the resulting structures showed effective anti-reflection properties of the formed coatings with a specular reflection coefficient of 0.25–2.50 % in the range of 200–1100 nm. The use of formed coatings with a low reflectance coefficient is possible in aircraft manufacturing, electronics and energy.

Keywords: electrochemical anodizing, porous aluminum, sodium chloride, barium titanate xerogel, anti-reflective properties.

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Introduction

Aluminum is the most common metal. In the earth's crust, aluminum is the third element after oxygen and silicon in prevalence. Aluminum-based alloys are widely used in aircraft manufacturing, electronics, and power engineering. This raises the problem of forming anti-reflective coatings on the aluminum surface. In particular, in aircraft manufacturing, such a problem arises when developing stealth technology; in microelectronics, anti-reflective coatings must be formed on the surface of aluminum films to suppress glare during photolithography operations; in power engineering, anti-reflective coatings are in demand in the manufacture of solar thermal collectors. Changing the reflection on the aluminum surface in combination with the application of luminescent films can also be used in the technology of protecting products from counterfeiting. To form anti-reflective coatings on the aluminum surface, it was proposed to use cone-shaped aluminum oxide nanostructures [1, 2], aluminum oxide nanoparticles obtained by laser ablation of aluminum targets [3], and aluminum nitride films [4]. However, all known methods for forming antireflective coatings on aluminum have limitations in terms of the level of optical signal absorption and the range of absorption wavelengths [1–5]. It should be noted that while the process of anodic porous oxidation of aluminum is being intensively studied [7–9], anodic porous etching of aluminum has not been sufficiently studied. Only a few reports are known about the etching process without studying the structure being formed.

This paper proposes a method for forming an antireflective coating on an aluminum surface based on nanostructured of aluminum followed by the application of a layer of $BaTiO_3$:Eu xerogel.

Experiment

Experiments on the formation of porous aluminum films were carried out on samples of aluminum foil 500 μm thick and 99.7 % pure with an area of 1 cm^2. A 1 % sodium chloride solution was used as an electrolyte.

After preliminary treatment of the aluminum foil surface with an alcohol-containing solution, porous aluminum was formed in a two-electrode electrochemical cell. The cell consists of a teflon cylinder, which is pressed against the anodized sample using a sealing rubber ring. The sample is located on a metal (aluminum) anode holder. To form porous aluminum, a titanium foil cathode was used, which was located inside the teflon cylinder. Anodization was performed in galvanostatic mode at a current density of J_f = 200 mA/cm^2. The anodization time ranged from 5 to 30 minutes.

Film-forming barium titanate sol containing europium was prepared using a previously developed technique based on glacial acetic acid (CH_3COOH) and acetylacetone ($CH_3COCH_2COCH_3$) in a volume ratio of 4:1 with the addition of titanium isopropoxide ($Ti(OC_3H_7)_4$), barium acetate ($Ba(CH_3COO)_2$) and europium acetate hydrate ($Eu(CH_3COO)_3 \cdot xH_2O$) [6]. The concentration of oxides in the resulting solution was 61.2 mg/ml barium titanate $BaTiO_3$ and 1.5 mg/ml europium (III) oxide Eu_2O_3. To obtain single-layer $BaTiO_3$:Eu samples, barium titanate sol was applied by centrifugation onto porous aluminum substrates, then the samples were dried in a drying oven at 200 °C for 10 min and then annealed at 450 °C for 30 min. Reflectance spectra were measured using an MS 122 spectrophotometer (PROSCAN Special Instruments, Belarus).

Research results and their discussion

As a result of the experiment, porous aluminum films with a thickness of 15 to 100 μm were formed (Fig. 1, *a*, *b*). The analysis shown in Fig. 1 of the obtained samples using a scanning electron microscope showed that the obtained films do indeed have a porous structure, the pore diameter varies from 0.8 to 2.0 μm, the minimum size of the aluminum “skeleton” is 50 nm (Fig. 1, *c*, *d*).

The results of X-ray spectral analysis of the formed porous films are shown in Fig. 2. It is evident from the figure that the porous film consists mainly of aluminum (83 at.%). The film also contains impurity elements - carbon (10 at.%) and oxygen (7 at.%).

The reflection spectra of the formed samples are shown in Fig. 3 and 4. Line 0 refers to the original substrate without anodization, lines 1, 2 and 3 – to the samples anodized for 5, 20 and 30 min, respectively, lines 4, 5 and 6 – to the samples anodized for 5, 20 and 30 min and coated with 1 layer of $BaTiO_3$:Eu xerogel. The reflection of the pure original aluminum substrate without anodization increases in the entire wavelength range from 6–7 % at 200 nm to 25 % at 940 nm.

Anodizing results in a significant decrease in reflectance. However, as with the original aluminum substrate, an increase in reflectance is observed in the range from 200 to 1100 nm. For the sample anodized for 5 min (Fig. 3, line 1), the reflectance increases from 2.5–3.0 % at 200 nm to 6.0–6.4 % at 1100 nm. For the samples anodized for 20 (line 2) and 30 min (line 3), the reflectance increases from 0.5 % at 200 nm to 1.1 % at 1100 nm. For the sample anodized for 5 min (line 4), the reflection decrease after the formation of the $BaTiO_3$:Eu xerogel layer is approximately 1–3 % over the entire wavelength range. The reflection increases from 1.5 % at 200 nm to 4.0 % at 1100 nm. For the samples anodized for 20 (line 5) and 30 min (line 6), applying the xerogel layer onto the porous aluminum substrate leads to a decrease in reflectance by approximately 2 times in the 200–300 nm range and reaches a minimum of ~0.2 % in the 200–225 nm range. For sample 5, the reflection decrease is approximately 0.1–0.3 % in the range from 350 to 1100 nm and reaches a maximum of up to 1 % at 1100 nm. For sample 6, the decrease in reflection is about 0.1–0.2 % in the range from 300 to 500 nm, from 500 to 1100 nm, the reflection values are almost the same as before the application of the $BaTiO_3$:Eu layer.

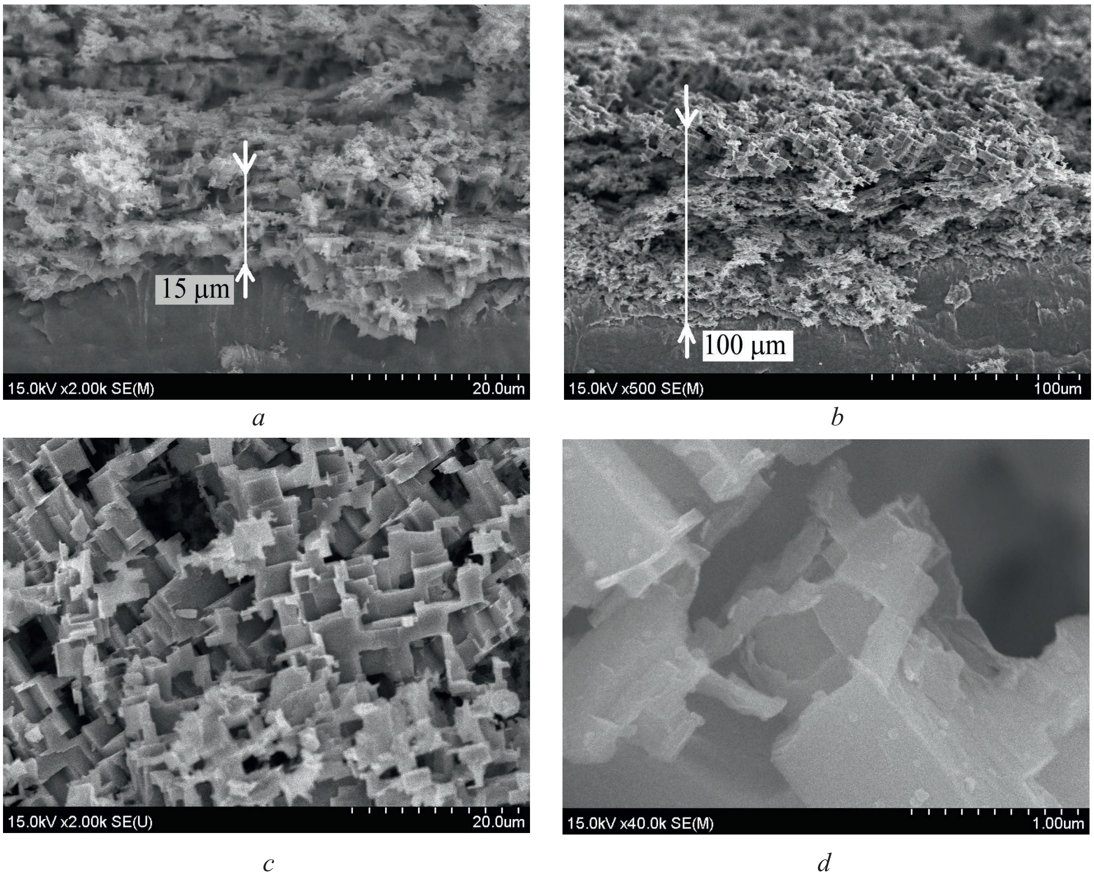
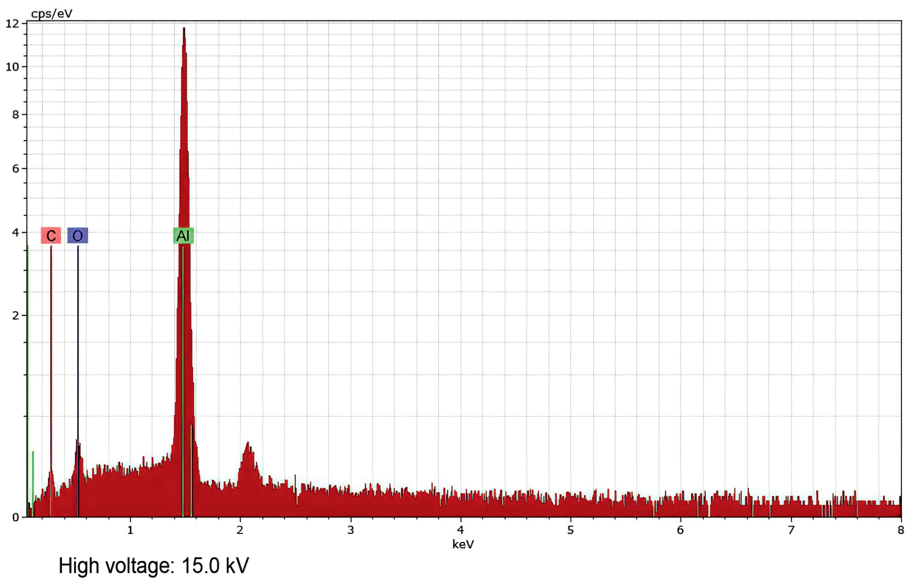


Fig. 1. SEM images of samples obtained in galvanostatic mode at different current densities in a 1 % aqueous solution of sodium chloride:
a, *b* – porous layer with a thickness of 15 and 100 μm, respectively;
c, *d* – cross section of the porous structure with magnification of 2 and 40 thousand times



El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
Al	13	K-series	58.96	90.75	83.21	2.8
C	6	K-series	3.14	4.83	9.96	1.4
O	8	K-series	2.87	4.42	6.83	0.9
		Total:	64.97	100.00	100.00	

Fig. 2. EDX analysis of porous aluminum films

Due to the scale limitation of Fig. 3, a number of lines on the graph are difficult to discern. Therefore, Fig. 4 shows the reflection spectra of the studied samples in the range of recorded reflection of 0.1–1.2 %, which allows us to see the differences in the obtained spectral characteristics.

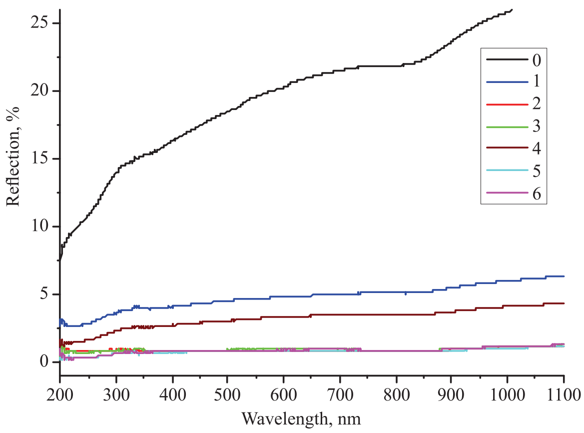


Fig. 3. Reflection spectra of porous aluminum samples obtained during anodization: 1, 2, 3 – for 5, 20 and 30 minutes, respectively; 4, 5, 6 – for 5, 20 and 30 minutes, respectively, with a deposited layer of $BaTiO_3$:Eu xerogel; 0 – sample of pure non-anodized aluminum

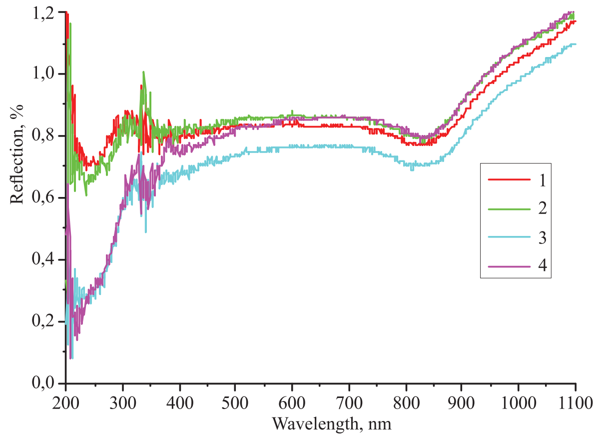


Fig. 4. Reflection spectra of aluminum samples obtained during the anodizing process, in the range of recorded reflection 0.1–1.2 %: 1, 2 – for 20 and 30 minutes, respectively; 3, 4 – for 20 and 30 min, respectively, with the deposited layer of $BaTiO_3$:Eu xerogel

Conclusion

1. A method for forming an antireflective coating on an aluminum surface is proposed, based on nanostructuring of aluminum with subsequent application of a layer of $BaTiO_3$:Eu xerogel. Films of porous aluminum with a thickness of 15–100 μm were obtained for the first time.

2. Formation of a porous layer on the aluminum surface by anodic etching leads to a significant decrease in reflection. Deposition of europium-doped barium titanate xerogel into porous aluminum also leads to a decrease in reflection.

3. It should be noted that the formed antireflective coatings can be used both in integrated electronics and in integrated optics. Control of the light signal using antireflective coatings during generation, propagation and registration of light in optical interconnections of integrated circuits is in demand in integrated optics, in particular in silicon photonics [10–17]. In addition, antireflective coatings on metal parts can find application in satellite systems for remote sensing of the earth, where it is necessary to prevent parasitic glare due to unwanted reflection of light from metal surfaces. When using the technology of forming anodized aluminum and luminescent coatings by the sol-gel method, it is possible to form areas on the aluminum surface that differ in luminescence intensity, which is of interest for the technology of forming luminescent images and protecting products from counterfeiting [18].

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Authors' contribution

The authors contributed equally to the writing of the article.

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