

MODIFICATION OF ANODIC ALUMINA BY LASER IRRADIATION DURING ANODIZING

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I. INTRODUCTION

Anodic oxide films of aluminum (AOFA) and other valve metals are promising materials for creation of functional materials [1, 2]. In the present work, irradiation of a pulsed N₂ laser was employed to possibly modify of morphological parameters and optical properties of porous alumina during the anodizing.

II. MATERIALS AND METHODS

The initial experimental samples were 1.1 μm thick Al layers (99.99%) sputtered in vacuum on polished silicon plates. Anodizing was carried out in galvanostatic mode, in a stirred citric acid solution ($j_a = 3.9 \text{ mA}\cdot\text{cm}^{-2}$) for 13 min. Temperature of the electrolyte was kept in the range of 20–22°C. Anodizing was carried out in a specialized PTFE electrochemical cell with a horizontal sample and a tantalum cathode and a protective ring, providing an anodization area of 1.54 cm². The studied samples were irradiated during anodic polarization with a pulsed N₂ laser (LGI-21) with a Gaussian energy distribution through a quartz lens and directed normally to the sample and electrolyte surface. The laser beam had a wavelength of 337 nm, a pulse frequency of 100 Hz, a pulse duration of 10 ns, and an intensity of 5 kW.

Surface morphology and composition of the AOFAs was examined by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and Auger electron spectroscopy (AES), respectively.

The samples surface was observed in a SEM Hitachi S-4800 operated at 10–15 kV, after over coating the specimens with a thermally evaporated 3 nm thick gold layer. AES surveys were registered using a PHI-660 spectrometer after 1 min sputtering of the specimen's surface layer with argon ions with an energy of 3 keV. FTIR spectra of AOFAs were registered with a Thermo Nicolet Nexus IR-spectrometer with a wave number range of 4000 cm⁻¹ to 400 cm⁻¹ and a resolution of 2 cm⁻¹, after 128 scans using a Deuterated Tri Glycine Sulfate (DTGS) detector.

III. RESULTS AND DISCUSSION

The optical image of the experimental AOFA sample and FTIR spectra are shown in Figure 1 a, b, respectively. As can be seen in Figure 1 a, the irradiated area looks lighter compared to the unirradiated area. It is noteworthy (Figure 1 b) that the IR transmittance of the AOFA in the irradiated area (curve 1) is also significantly higher than in the unirradiated area (curve 2).

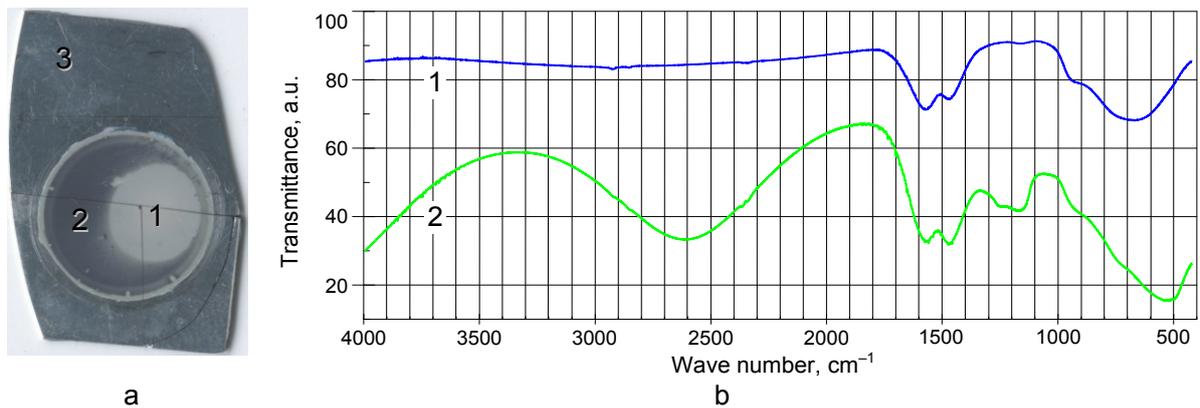


Figure 1. Optical image of the experimental sample: 1 — irradiated area, 2 — unirradiated area, 3 — unoxidized aluminum (a); FTIR-spectroscopy: curve 1 — irradiated area, curve 2 — unirradiated area (b)

As seen in Figure 1 b, the intensity of the absorption bands near 1570 and 1470 cm^{-1} , which characterize the stretching vibrations of C-O, is markedly higher in the non-irradiated part (curve 2), which suggests a decrease in the incorporation of electrolyte derivatives in the presence of a high electric field into the structure of growing aluminum oxide. The wide absorption band in the $1000\text{--}400\text{ cm}^{-1}$ range, due to the bending vibrations of Al-O, also becomes significantly more intense in the unirradiated area. Moreover, additional absorption bands at 2750 , 1250 , and 1150 cm^{-1} are detected in the IR spectrum of the non-irradiated oxide film. The identification of the new absorption bands is ambiguous.

Two assumptions arise: that these bands are due to nitrogen-containing groups, or the maximum in the region of 2750 cm^{-1} may be due to the presence of C-H-groups. The final elucidation of the origin of the new bands is especially interesting if we consider that nitrogen could only be present in the anodizing electrolyte in the form of N_2 dissolved from the atmosphere.

Figure 2 shows SEM images of experimental sample surfaces and AES surveys of sample surfaces. SEM images show no significant differences in the morphology of the both anodized surfaces. Auger-electron analysis revealed increased carbon content in the unirradiated area. At the same time, nitrogen was not detected. Consequently, we can attribute the detected absorption band in the region of 2750 cm^{-1} to C-H-groups.

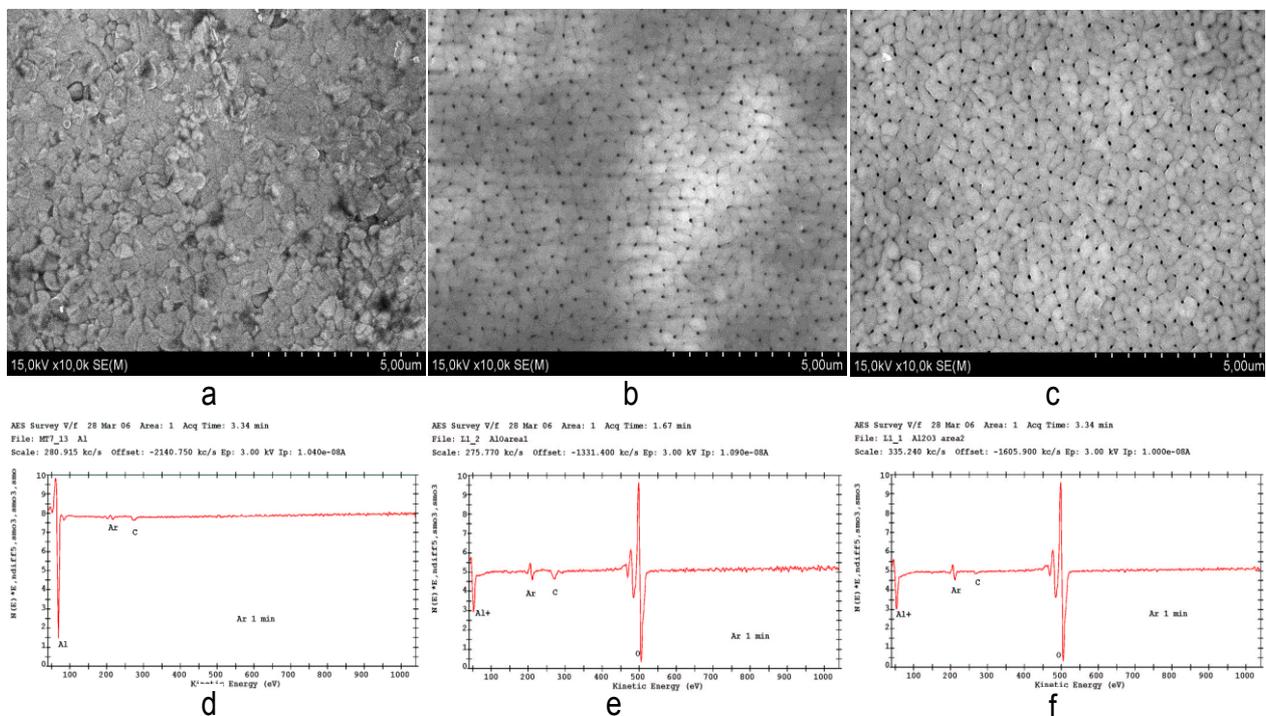


Figure 2. SEM images of experimental sample surfaces: unoxidized aluminum (a), unirradiated area (b), and irradiated area (c); AES surveys of sample surfaces after 1 min Ar^+ sputtering: unoxidized aluminum (d), unirradiated area (e), and irradiated area (f)

IV. CONCLUSIONS

Irradiation with a pulsed N₂ laser beam employed during anodic oxidation of aluminum in a citric acid electrolyte was found to significantly affect optical properties of porous alumina oxide, providing no significant changes in its morphological parameters. The combination of anodizing and laser techniques enables it to modify functional properties of AOFA without introducing morphological defects.

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