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# Effect of Laser Treatment and Hydrophobization on the Corrosion-Electrochemical Behavior of Aluminum

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**Abstract**—The effect of laser treatment of aluminum samples on the properties of the surface hydroxide oxide layer is studied. It is shown that treatment in air leads to an increase in the thickness of the oxide layer and the almost complete disappearance of hydroxide forms, which results in deterioration of the protective properties of this layer due to its higher defectiveness and porosity. It is found that the optimal treatment regime for aluminum, the surface of which is covered by an oxide layer with a significant fraction of hydroxides, is laser irradiation in an inert argon gas medium with small (1–2 vol %) oxygen content. Laser treatment leads to the formation of a protective surface layer that effectively inhibits the anodic dissolution of aluminum in a model corrosion medium, borate buffer solution at pH 7.4. It is shown that the initial hydroxide oxide film and the oxide film formed during laser treatment processing are hydrophilic, that is, they are well moistened with water. The surface treatment of aluminum in the initial state and after laser irradiation with a solution of vin-yltriethoxysilane (VTES) leads to the formation of a hydrophobic adsorption layer and a significant decrease in the currents of anodic dissolution. Using X-ray photoelectron spectroscopy, it is shown that silane adsorption occurs both with the participation of silicon atoms and carbon atoms of an alkene bond. The hydrophobic layer of adsorbed silane on the laser-treated surface has a greater thickness and has a higher inhibiting effect on the anodic dissolution of aluminum than in the case of the initial aluminum surface.

*Keywords:* aluminum, laser treatment, alumina, hydrophobization, protective layer **DOI:** 10.1134/S2075113320030065

# **INTRODUCTION**

Despite the high chemical activity, aluminum and its alloys often exhibit fairly high corrosion resistance, which is associated with spontaneous formation of a hydroxide oxide film on the surface [1–4]. It is known [5, 6] that, although this film provides corrosion protection, it also has pores and other defects that occur mainly at the sites of formation of aluminum hydroxides owing to the fact that the Al–OH bond formed during hydration of aluminum oxide has lower strength than Al–O bond in the case of non-hydrated oxide [5–7]. Nevertheless, chemical oxidation of aluminum-based alloys, as well as electrochemical anodizing, is widely used to form sufficiently resistant oxide and hydroxide layers, including decorative ones [1, 2, 4, 5, 8–13].

Upon thermal exposure, aluminum hydroxide transforms into more stable  $Al_2O_3$  oxide with varying

structures, and the conversion of surface hydroxide to a relatively anhydrous oxide and the formation of a more effective protective film can be achieved by using various techniques of high-energy surface treatment [14, 15]. One of the effective techniques for improving the functional properties of the surface of metallic materials, including anticorrosive ones, is the treatment of materials by laser irradiation [16-19]. So, for example, in [20], it was shown that scanning an aluminum surface with a spontaneously formed film of aluminum oxides and hydroxides by pulsed laser irradiation leads to the formation of a fairly dense passive film consisting mainly of anhydrous aluminum oxide. Such a surface film more effectively reduces currents of anodic dissolution of samples in the passive-state region.

At the same time, it should be noted that the surface layer formed under different regimes and consisting of anhydrous alumina, although more effectively suppressing anodic dissolution currents, has a significant drawback, as it is hydrophilic, that is, it can be moistened with water. Regardless of the crystallographic modification of the oxide, the contact of aluminum oxide with water or its vapor may result in a thermodynamically favorable  $Al_2O_3$  hydration process, in which the loss of free energy of spontaneous hydration of 1 mol of oxide is ~245 kJ [1].

Water adsorption can be considered as the first stage of hydration of surface alumina and its subsequent local transformation into hydroxide [5–7]. In this case, the oxygen of the oxide gradually turns into hydroxyl groups, which are less strongly bound to aluminum. The formation of hydroxide forms of aluminum, which are less effective in terms of protective properties, is confirmed by the analysis of the Pourbaix diagram for the Al–H<sub>2</sub>O system [21].

The purpose of this work was to study the corrosion-electrochemical behavior of aluminum with a laser-modified oxide layer and the possibility of using surface hydrophobization to increase the corrosion resistance of aluminum.

## MATERIALS AND METHODS

Samples of aluminum (99.9 wt %) in the form of plates  $10 \times 10 \times 2$  mm in size were treated with thin sandpaper (P2000, grain size 5–7 µm, GOST R 52381-2005), washed with distilled water, and degreased with ethanol before the experiment. Previously, the current collector wires were soldered to the back of the samples for connection to a potentiostat.

Some of the samples remained in the initial state (series of samples no. 1), which ensured the presence of a spontaneously formed hydroxide oxide layer on the surface.

A series of samples no. 2 was subjected to shortpulse laser treatment using a fiber-optic pulsed ytterbium laser with a wavelength of 1.065  $\mu$ m, which allowed varying the irradiation power, pulse repetition rate, and the rate of scanning the surface with a laser beam over fairly wide ranges. The samples were treated in air, in a vacuum, or in a gas medium with a controlled composition.

Preliminary experiments on determining the most effective laser treatment regimes revealed that the maximum decrease in the density of anode currents in a model corrosion medium is observed during treatment in an argon medium with a residual oxygen concentration of ~1–2 vol %. The specific power of the laser irradiation was 4.539 × 10<sup>10</sup> W/cm<sup>2</sup>, the pulse repetition rate was 20 kHz, and the rate of scanning the surface with the laser beam was 400 mm/s.

To impart hydrophobic properties, the samples were immersed in a solution of vinyltriethoxysilane (VTES) in distilled water at an additive concentration of 1 g/L for 60 min. Vinyltriethoxysilane

CH<sub>2</sub>=CHSi(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> is one of the silanes produced industrially according to TU 6-09-14-1670-82. The unsaturated (alkene) bond of the vinyl fragment of VTES includes labile  $\pi$ -bond electrons that impart adsorption activity to unsaturated compounds. The adsorption activity in a VTES molecule may be characteristic of silicon and oxygen atoms. After treatment in the VTES solution, the samples were dried in air.

Samples in the initial state after VTES treatment were designated as samples no. 3 and those after laser treatment and treatment with the VTES solution were designated as samples no. 4. Five samples were prepared for each treatment variant. Three samples from each series were studied using a potentiostat, their hydrophobicity was studied using the fourth sample, and the composition of their surface was determined on the fifth sample from X-ray photoelectron spectra (XPS).

The corrosion-electrochemical properties of the samples were studied by the electrochemical method in the potentiodynamic anodic polarization mode using an EcoLab 2A-100 potentiostat in a three-electrode electrochemical cell at room temperature ( $20 \pm 2^{\circ}$ C) under natural aeration. A borate buffer solution with pH 7.4 was used as a background electrolyte, a saturated silver chloride electrode was used as a reference electrode. and a platinum electrode was used as an auxiliary one. All potentials E were measured relative to a saturated silver chloride reference electrode; density I was determined by the visible (geometric) surface of the electrodes. Before electrochemical studies, all nonworking surfaces of the samples were varnished. The measurements were made from a stationary potential with a sweep speed of 2 mV/s. In the polarization measurements repeated three times under identical conditions, the current differences at these potentials did not exceed 5%.

The surface composition was studied by the XPS technique [22] using a SPECS spectrometer in Al  $K_{\alpha}$  radiation (hv = 1486.6 eV) with layer-by-layer etching of the surface by argon ions with an energy of 4 keV and a current density of 30  $\mu$ A/cm<sup>2</sup>. The rate of etching the surface layers was ~1 nm/min. The experimental spectra were processed using the CasaXPS software package. The relative error in determining the concentration of elements was  $\pm 5\%$  of the measured value.

The hydrophobicity of the samples was determined by measuring the wetting angles of the surface with water according to the standard technique [23]. One drop of distilled water in a volume of 1 mL was applied to the surface of the sample and photographed after holding it for 5 min while strictly keeping the sample in the horizontal position, which was checked by the laser level, at a constant temperature of 20°C. The obtained images were processed by a computer using special software with sufficient accuracy of determining wetting angles. The confidence interval of the measured values of the wetting angle was  $\pm 1'$ .

#### **RESULTS AND DISCUSSION**

As a result of exposure to short pulses of laser irradiation with high power density, thin surface layers are quickly heated to temperatures above 3000°C [17, 18], so the natural hydroxide oxide layer of aluminum is dehydrated and aluminum oxide Al<sub>2</sub>O<sub>3</sub> melts, disperses in the thin surface layer, and dissolves in the near-surface layer of the metal (aluminum) matrix, which leads to better protective properties of the surface layer. Under these conditions, small concentrations of residual oxygen are also involved in the formation of aluminum oxides. As a result of high-speed cooling, the surface layer of aluminum does not have time to reach equilibrium, which leads to the formation of a number of solid solutions of aluminum oxides in metal aluminum. Thus, laser treatment results in the formation of a thin and dense nanostructured film up to 30 nm thick, which is characterized by a nonequilibrium structural state, the absence of large crystals of aluminum and its oxide, high continuity, and good adhesion to the base metal. It should be noted that the hydroxide oxide film of natural origin was  $\sim 10$  nm thick.

It was shown previously [20] that, at a higher irradiation power with a lower frequency and scanning speed, the formed surface layer, although reaching thickness of  $\sim$ 30 nm, reduces the anode current to a lesser extent than in the optimal treatment conditions in our experiments. Preliminary experiments have shown that, under various laser treatment conditions in air, a thicker but probably more friable coating is formed, which negatively affects its protective properties.

The anode polarization curves shown in Fig. 1 were obtained by summing and averaging the results of parallel measurements. The polarization curves were recorded up to the transpassivation potentials. Given the fairly high density of the protective passivated layer and low electrical conductivity, the breakdown potential  $E_{\rm br}$  can be taken as the transpassivation potential. The values of the breakdown potential and the anode current density in the passive-state region at E = 500 mV were taken as quantitative indicators of corrosion resistance. It should be noted that, at this potential, all electrodes are in a passive state.



**Fig. 1.** Potentiodynamic curves of aluminum samples in borate buffer solution with pH 7.4. The numbers of the curves correspond to those in Table 1.

As follows from Fig. 1 and Table 1, samples no. 4 exhibit the best corrosion resistance. So, for example, if the sample in the initial state has a breakdown potential  $E_{\rm br} = 800$  mV, then after laser treatment it increases to 1150 mV. The current in the passivation region also decreases markedly. Treatment of the initial sample with the VTES solution reduces the anode current by more than an order of magnitude and significantly increases the breakdown potential (Fig. 1, curve 3). The best results are achieved by treating a sample subjected to laser irradiation with the VTES solution, for which, at the same current density in the passivation region as for sample no. 3, the breakdown potential increases to  $E_{\rm br} = 3000$  mV.

The obtained results suggest that the enhancement of the anticorrosive properties of aluminum after treatment with the VTES solution is associated with the higher hydrophobicity of the surface due to the formation of an adsorption layer, which contains VTES particles. According to [23, 24], the larger the wetting angle (acute angle between the surface of the material and the drop of water on top of it), the higher the hydrophilicity of this surface. The surface is considered hydrophilic when the wetting angle is less than

Al sample	Laser irradiation	VTES solution treatment	Corrosion resistance properties	
			anode current at potential of 500 mV, $\mu$ A/cm <sup>2</sup>	transpassivation potential, mV
1	_	_	32	800
2	+	—	22	1150
3	—	+	2	1200
4	+	+	2	3000

Table 1. Characteristics of corrosion resistance of Al specimens after various kinds of treatment



**Fig. 2.** Wetting angles of the surface of the samples of aluminum. The number of the image corresponds to the sample number (Table 1).

 $90^{\circ}$  and hydrophobic, that is, non-wettable with water, when the contact angle is more than  $90^{\circ}$ . As follows from Figs. 2.1 and 2.2, the surfaces of both the initial aluminum sample having the hydroxide oxide protective film of natural origin and the sample after laser treatment without subsequent hydrophobization are hydrophilic and their angle of wetting with a drop of water is  $61^{\circ}38'$  and  $61^{\circ}47'$ , respectively.

After exposure of the aluminum samples in the initial state and after laser treatment in the VTES solution, the wetting angles are 94°18′ and 94°22′, respectively; that is, the surface becomes hydrophobic (Figs. 2.3 and 2.4). Following [24], it can be assumed that VTES molecules (as well as other hydrophobizing agents) during adsorption (in our case, on the surface of aluminum with oxide or mixed hydroxide oxide layers) block surface oxygen atoms or hydroxide groups possessing



**Fig. 3.** Al2*p* XPS spectra obtained from aluminum samples in the initial state (1) and after treatment in a controlled gas atmosphere (2): (a) after 1 min of etching the surface with argon ions (etching depth  $\sim 1$  nm); (b) after 10 min of etching (etching depth  $\sim 10$  nm).

affinity for water molecules, which leads to deterioration in the wettability of the surface. This allows us to conclude that the increase in the corrosion resistance of aluminum is actually largely due to the hydrophobization of its surface.

According to the XPS data (Fig. 3), the surface of the initial aluminum (spectra 1) is covered with a spontaneously formed oxide layer up to 10 nm thick. At a depth of  $\sim$ 1 nm, almost all aluminum is oxidized to Al<sub>2</sub>O<sub>3</sub>, while at a depth of  $\sim$ 10 nm a pronounced peak of unoxidized metallic aluminum is observed. Thus, the surface of the initial aluminum is coated with a thin protective oxide layer that has a sharp boundary with the base metal.

After laser treatment, the thickness of the oxide film increases to 30 nm, and as the depth of the analyzed layer increases, its aluminum oxide content gradually decreases, which indicates nonstoichiometric oxide states of aluminum in the surface layer, the composition of which changes smoothly (gradientwise) with increasing depth. It can be assumed that a smooth change in the composition of the surface laver and the absence of a sharp interface will increase the adhesion of this layer to the substrate. It should also be noted that the bonding energy  $E_{\text{bond}}$  corresponding to the maximum of the Al2p peak characterizing the oxidized state of aluminum in sample no. 2 almost completely matches the reference value for  $Al_2O_3$ . In the case of sample no. 1, the spectrum is somewhat blurred and slightly shifted toward higher binding energies, which can be attributed to the partial hydration of the initial oxides of natural origin.

The XPS spectra shown in Fig. 4 suggest that the Si2*p* binding energy is 102-102.6 eV, which is significantly less than the corresponding value for silicon dioxide, but much larger than in the case of a chemical





**Fig. 4.** Si2p XPS spectra of the samples after soaking in the VTES solution: (a) the initial sample; (b) the sample after laser treatment.

bond of silicon directly with the metal. According to [22], the values of  $E_{bond}$  (Si2p) obtained for samples nos. 3 and 4 are characteristic of complex organic molecules that include C, H, O, and Si, as well as Si–O–Me bonds, which suggests that, in the studied surface films of these samples, silicon forms a chemical bond with aluminum through the oxygen atom of aluminum oxide. Considering that the intensity of the silicon signal on the laser-treated sample is higher than on the initial aluminum, it can be argued that the laser-treated aluminum surface is coated with a thicker and denser protective VTES film.

The XPS spectra of carbon *C*1*s* recorded after treating the surface with VTES exhibit a two-component peak. The maximum at  $E_{bond} = 285-286$  eV corresponds to the C–H bond characteristic of organic compounds, and the maximum at  $E_{bond} = 288$  eV corresponds to the carbon in the composition, for example, of the [Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>] fragment. This indirectly indicates the possibility of the formation of a bond of alkene carbon with the surface.

The data obtained suggest that the VTES molecules, upon adsorption interaction with oxides on the surface of aluminum, form a multicenter adsorption complex that preserves the individual hydrophobic properties of VTES, which leads to hydrophobization of the surface.

The presented results showed the possibility of embedding VTES particles into the surface layer of oxides and, consequently, enhancing their protective properties. The protective properties of the surface layer are also enhanced in the case of the VTES solution treatment of aluminum in the initial state, without laser irradiation; however, the effect of VTES in this case was less than when treating the aluminum irradiated with the laser.

## CONCLUSIONS

Using X-ray photoelectron spectroscopy, it has been shown that the spontaneously formed protective oxide layer on the surface of aluminum is at least 10 nm thick and consists of both aluminum oxide and its partially hydrated forms. Measurements of the wetting angle showed that this layer is hydrophilic.

Pulsed laser irradiation of the aluminum surface in an argon medium with the residual content of 1-2 vol %oxygen leads to a noticeable increase in the thickness of the hydroxide oxide layer, mainly consisting of anhydrous aluminum oxide.

Measurements of the wetting angle of the lasermodified surface of aluminum showed that the resulting modified surface film is hydrophilic, and its protective (passivation) properties are better than those of the initial hydroxide oxide layer.

The treatment of aluminum with the VTES solution enhances the hydrophobic properties of the surface, as a result of which the currents of anodic dissolution of aluminum are reduced. The greatest inhibiting effect on the corrosion process is achieved when the laser-modified surface is treated with VTES. The XPS data show that the formation of the adsorption binding of VTES with the aluminum surface involves silicon atoms and, possibly, carbon atoms of the alkene bond.

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#### CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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