

Study of Formation of Oxide Nanostructures on the Surface of Radiation-oxidated Aluminum

Gadzhieva N.N.

Institute of Radiation Problems of National Academy of Sciences of Azerbaijan AZ 1141 Baku, B.Vahabzadeh st., 9.

Abstract: Reflection IR spectroscopy, atomic force microscopy (AGM), and electrophysical measurements were used to investigate the formation of surface oxide nanostructures during the radiation oxidation of metallic aluminum in contact with water. It is revealed that the radiation modification of the surface relief is accompanied by the formation of oxide nanolayers, the defectiveness of which is determined by the irradiation time. It is shown that the formation of oxide nanolayers in the region of absorbed dose (0.5-120 kGy) occurs in three stages, which is accompanied by a decrease in electrical conductivity by 5 orders and an increase in the thickness of the oxide layer by an order of magnitude. The role of surface intermediate-active particles in the formation of oxide nanostructures is considered.

Keywords: Aluminum; radiation; oxidation; nanostructure; absorption; IR-spectroscopy; AGM microscopy and electrophysical measurements

1. Introduction

The surface layer of metals is in a special physico-chemical state. It is largely saturated with structural defects (vacancies, dislocations, impurities) and its properties differ from the bulk properties^[1-5]. Therefore, the special state of the near-surface layers can influence the kinetics of various processes, including diffusion, adsorption, and radiolysis of water molecules. Contact and interaction of water with the surface of metals leads to their change and is accompanied by the formation of an oxide layer. At the same time, a Me-MeO heterosystem is formed on the surface, which plays a decisive role in radiation-stimulated water processes on the surface of metals. The study of the initial stage of formation of surface oxide nanolayers is of fundamental importance for solving the problems of surface passivation and predetermines the course of the process of radiation corrosion^[4,6-7].

Among the reactor materials, metallic aluminum is the most promising^[1-5]. It seems important to clarify and determine the role of the relaxing intermediate-active water decomposition particles in the heterogeneous Al / ads.H₂O system under the action of γ -radiation. In order to solve these problems in a complex manner, we used the detection method based on the measurement of the electrical conductivity of a metal, which makes it possible to control the behavior of chemisorbed particles by studying its electrophysical properties and the IR spectroscopic method, which simultaneously allows the formation of oxide nanolayers^[8-10]. The change in the relief and morphology of the surface before and after the radiation oxidation of aluminum was controlled by the AGM microscopy method. The application of these methods allows obtaining a package of new data and information on the formation of oxide nanostructures on the surface of radiation-oxidized aluminum in contact with water under the action of γ -radiation.

2. Experiment Part

Aluminum plates measuring 20x10x2mm³ were investigated as objects. AD-00 aluminum plates were obtained by step-by-step pressing of cylindrical Al granules with a diameter of 3 and a height of 6 mm by means of a special mold

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designed for optical studies.^[6] The plates had a smooth surface with $R = 0.80 \pm 0.05$ in the mean IR wavelength region ($\lambda = 15\text{-}2.2 \mu\text{m}$). Twenty samples with the same R values were prepared for conducting parallel experiments on the electrical conductivity and IR spectra of reflection of aluminum plates before and after radiation oxidation in an aluminum-water system at room temperature.

To eliminate impurity contamination, the samples were treated with solvents (ethyl alcohol, acetone) and washed with distilled water. Samples were pre-dried at room temperature in argon. For dehydroxylation of the surface and complete purification from organic contaminants, the samples were placed in quartz cells and additional heat treatment was carried out at 673 K in a vacuum of $P = 10^{-6}$ Pa for 6 hours. Adsorbate was unsaturated vapors of bidistilled water, from which foreign gases were removed by repeated freezing in a trap with liquid nitrogen followed by evacuation. Adsorption of H_2O was studied by the method described in^[9,10].

Radiation oxidation in the Al / ad. H_2O heterosystem was carried out at room temperature ($T = 300\text{K}$). The samples were irradiated on an isotope ^{60}Co source with a dose rate $d\Phi_\gamma / dt = 1.03 \text{ Gy/ s}$. The absorbed dose determined by the ferrosulfate dosimeter was varied within the $\Phi_\gamma = 0.5\text{-}120 \text{ kGy}$ ^[11].

The thickness of the oxide Al films was 8 to 250 nm. The small thicknesses of the oxide layers were estimated by the Stormier formula^[12] for X-ray photoelectron spectra, and relatively large thicknesses were determined by gravimetric method.

The infrared reflection spectra at the drop of linearly polarized radiation on the sample at an angle close to the sliding angle ($\varphi = 88^\circ$) were measured on a Specord 75IR spectrophotometer (Carl Zeiss, Germany) in the 2000-650 cm^{-1} region at room temperature using a special optical device (Shimadzu, Japan). To this end, a quartz cell with a CaF_2 window was developed and fabricated, making it possible to obtain spectra of adsorbed water and to follow the changes resulting from its decomposition under the action of γ -radiation^[6].

Measurements of the resistivity (ρ) of aluminum plates before and after radiation oxidation were conducted by a four-probe point contact method at constant current and room temperature^[13]. The calculations used the averaged values for which the influence of geometric dimensions was taken into account.

The initial surfaces of aluminum plates and the changes occurring on the surface of these samples after radiation treatment at room temperature under the influence of gamma quanta are traced on an atomic force microscope (Nanoeducer of SZMU-L5 of NT-MDT RF). Three-dimensional (3d) surface AGM images and histograms (curves of distribution of surface images in sizes) before and after radiation oxidation were obtained in order to reveal the dynamics of morphological changes in the surface.

3. The Discussion of the Results

Infrared reflection spectra before (1) and after radiation oxidation of aluminum in contact with water under the influence of γ -radiation (curves 2 -4) at room temperature are presented in fig. 1. The formation of surface oxide nanolayers was monitored in the frequency range $\nu \sim 1200\text{-}650 \text{ cm}^{-1}$. The bands with maxima of 1070 and 945 cm^{-1} observed by us should be attributed to the valence vibration of Me-OH, where several aluminum atoms act as Me. The bands with maxima of 1010, 830 and 720 cm^{-1} can be attributed to the stretching vibrations of the Al-O surface oxide layer formed on the aluminum surface as a result of radiation interaction with water. The maxima at 830 and 720 cm^{-1} refer to Al-O groups bound to tetrahedrally and octahedrally coordinated aluminum atoms, respectively.^[6] In the case of thin layers ($d = 8 \text{ nm}$), we observed a band with a maximum at 1010 cm^{-1} , which refers to Al_2O_3 and characterizes the valence vibration of Al-O.

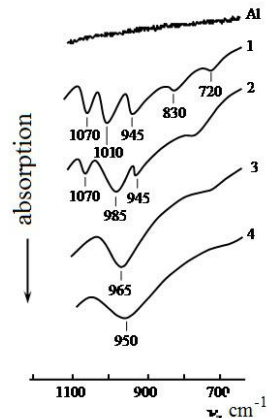


Figure 1; The change in the absorption band of the valence vibration of the Al-O bond as a function of the time of contact of aluminum with water at the radiation oxidation ($d\Phi_\gamma / dt = 1.03 \text{ Gy} / \text{s}$) of Al, $\tau = 5 \text{ min}$ (1), 10 min (2), 5 h (3) and 18h (4).

The dynamics of the formation of oxide nanolayers shows that an increase in the contact time of aluminum with water under the influence of γ -radiation from 5 min to 18 hours (or the absorbed dose of Φ_γ from 0.5 to 120 kGy) leads to a shift in the maximum of the Al-O valence vibration band from 1010 to 950 cm^{-1} and its broadening (half-width $\nu_{1/2}$ is increased by 50 cm^{-1}). The thickness of the nano layer increases from 8 to 250 nm.

The wide diffuse maximum of the Al-O vibration band for polycrystalline structures and indicates the heterogeneity of relatively thick oxide nanolayers^[6]. It is known that irradiation can create microstructural inhomogeneities (MH) in a metal.^[4] It is possible that these MH lead to a significant inhomogeneous broadening of the Al-O vibration band of the oxide nanolayer obtained by radiation oxidation of Al-O in contact with water.

As the AGM studies show, the radiation modification of the surface relief is accompanied by the formation and formation of oxide nanostructures, the defectiveness of which is determined by the irradiation time. As an example, in figures 2 and 3 show three-dimensional (3d) surface images and their histograms of aluminum samples before (a) and after radiation oxidation at room temperature ($T = 300\text{K}$) (b, c). As can be seen from the three-dimensional images, the surface of the initial sample is characterized by the presence of a thin oxide film ($d = 8 \text{ nm}$) with a high degree of defectiveness (Fig. 2a). The nanoparticles are evenly distributed and have a height of 60 nm. Radiation oxidation leads to a change in the surface state of aluminum (Fig. 2b, c). The surface is smoothed and the nanoparticles have a height of 30 nm.

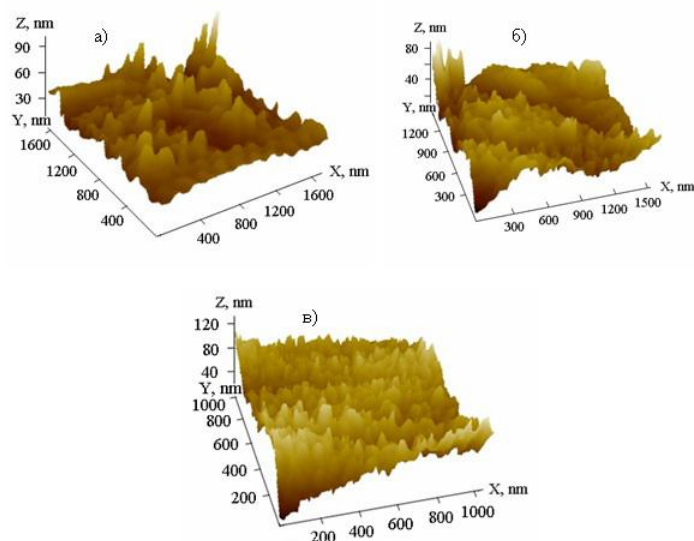


Figure 2; Three-dimensional (3d) images of the surface of the initial (a) and radiation-oxidized Al at times of contact with water of 5 min (b) and 18 hours (c).

As the histograms of the AGM images of the surface of the original aluminum show, nanoparticles predominantly with sizes of 25-50 nm (the number is 2200 units) participate in the formation of a thin oxide film (Fig. 3a).

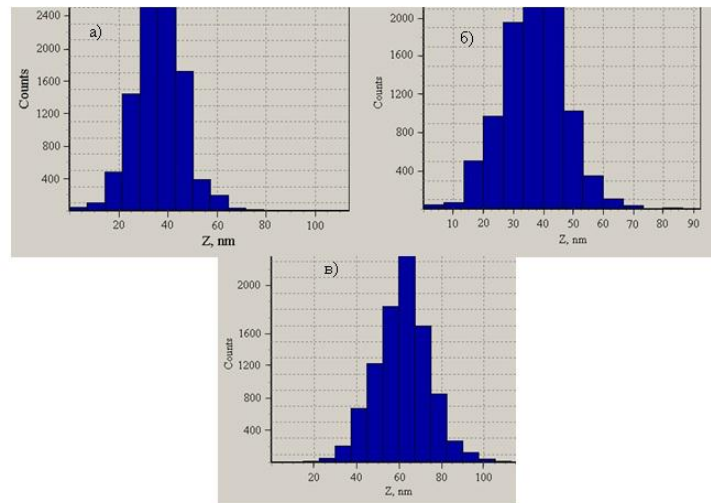


Figure 3; Histograms of the surface of the initial (a) and radiation-oxidized Al at times of contact with water of 5 min (b) and 18 hours (c).

The histogram of the surface of a radiation-oxidized aluminum plate is characterized by a region of distribution of nanoparticles with a size of 30-45 nm (the number is 2000 units). In both cases, a symmetric Gaussian distribution of nanoparticles is observed in size.

A further increase in the irradiation time τ (corresponding to an increase in the thickness of the oxide layer from 8 to 250 nm) from 5 minutes to 18 hours leads to the formation of nanoclusters with a size ~ 2 times on the aluminum surface compared to the initial samples. At the same time, a continuous oxide nanolayer is formed on the surface of Al.

The logarithmic dependence of the surface resistivity of aluminum plates (ρ) on the absorbed dose of γ -irradiation (Φ_γ) in the coordinates was studied for the purpose of revealing the kinetic regularities of the oxidation of the aluminum surface in the Al/ads.H₂O system under the action of γ -radiation at room temperature ($T = 300\text{K}$) $\lg\rho \sim f(\lg\Phi_\gamma)$, which is shown in Fig.4. As can be seen from Fig. 4 (curve 1), the kinetic curve is characterized by the presence of three linear regions described by the power-law dependence $\rho \sim \Phi_\gamma^n$ and indicates a three-stage flow of the aluminum oxidation process in the region of absorbed dose $\Phi_\gamma = 0.5\text{-}120\text{ kGy}$ in the heterosystem Al/ad.H₂O. At the same time, the values of the exponent n , defined as the slope of these lines, are close to 0.5 (for the absorbed dose of $\Phi_\gamma \leq 30\text{ kGy}$, region I), 0.15 (for the absorbed dose $30 < \Phi_\gamma \leq 90\text{ kGy}$, region II) and 2.2 (for the absorbed dose of $90 < \Phi_\gamma < 120\text{ kGy}$, area III), respectively. Moreover, the transition from the first region to the third is accompanied by an increase in the resistivity (or a decrease in the electrical conductivity) of aluminum plates by ~ 5 orders of magnitude.

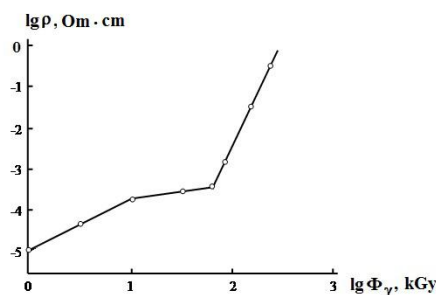


Figure 4; The logarithmic dependence of the resistivity of aluminum on the absorbed dose of γ -irradiation in the Al / ads.H₂O system during radiation oxidation ($T = 300$, $d\Phi_\gamma / dt = 1.03\text{ Gy/s}$).

The observed feature of the kinetic curve of the radiation oxidation of aluminum is apparently due to the formation of a thin oxide nanofilm with a thickness of 8-12 nm (oxygen atoms are chemisorbed on the metal surface, stage I), a chemisorption sublayer of the dissolved oxygen layer (stage II, where the tangential oxygen mobility can be neglected, a thin oxide nanolayer in the subsurface region greatly complicates the introduction of oxygen atoms into the volume and the metal-oxide yield is completely screened and the thickness of this layer changes and amounts to ~15-20 nm), as well as the formation of a continuous intrinsic oxide nanolayer as a result of the introduction of oxygen atoms and the migration of oxygen hole centers to the volume either from a defective surface or from internal traps along the grain boundaries (the thickness of the oxide layer increases by almost an order of magnitude and reaches a value of 250 nm, stage III).

It should be noted that the three-stage course of the process of radiation oxidation of aluminum in contact with water in the region of the absorbed dose $\Phi_\gamma \sim 0.5-120$ kGy was also observed in the study of the kinetics of oxidation from the dose dependence of the intensity of the thermo-exposure curve of chemisorbed oxygen at a temperature of 170 K using the method of radiothermoluminescence (RTL) [8,14]. Radiation-chemisorption passivation of the metal was detected at the values of the absorbed dose of $40 \leq \Phi_\gamma \leq 90$ kGy, which corresponds to the second stage.

It is assumed that at the I and II stages of the oxidation process, the surface-chemisorption intermediate-active particles OH^- and H^+ also affect the surface electrical conductivity of aluminum. Apparently, in the second stage of the oxidation process, activated hydrogen ions (H^+) partially emit into the subsurface layer of aluminum, resulting in the formation of s-atoms [13]. This leads to a slowing of the growth rate of resistance, depending on the absorbed dose of γ -irradiation. A further increase in the absorbed radiation dose is accompanied by an increase in the thickness of the oxide layer and the formation of r-atoms [13], which in turn causes a strong increase in the resistance of aluminum. The competition for the formation of s and r atoms causes a different manifestation of the dependence of the resistance of aluminum on the absorbed dose of γ -irradiation at different stages of the oxidation process.

4. Conclusion

Reflection IR spectroscopy, atomic force microscopy (AGM), and electrophysical measurements were used to perform a complex study of the formation of surface oxide nanostructures during the radiation oxidation of metallic aluminum in contact with water at room temperature. The dynamics of formation of oxide nanolayers was controlled by the change in the absorption band of the valence vibration of the Al-O bond ($\nu = 950 \text{ cm}^{-1}$) as a function of the time of contact of aluminum with water from 5 minutes to 18 hours.

The initial surfaces of aluminum plates and changes occurring on the surface of these samples after radiation treatment at room temperature under the influence of gamma quanta are traced on an atomic force microscope. Three-dimensional (3d) surface AGM images and histograms were obtained in order to reveal the dynamics of morphological changes in the surface before and after radiation oxidation. As demonstrated by AGM studies, the radiation modification of the surface relief is accompanied by the formation of oxide nanostructures, the defectiveness of which is determined by the irradiation time.

On the basis of electrophysical measurements, in particular, according to the logarithmic dose dependence of the surface resistivity of aluminum, a three-stage oxidation process in the region of absorbed dose (0.5-120 kGy) was revealed. It is shown that the transition from the first stage to the third is accompanied by a decrease in the electrical conductivity by 5 orders of magnitude and an increase in the thickness of the oxide nano layer by an order of magnitude (from 8 to 250 nm). The role of surface relaxing intermediate-active particles in the dynamics of formation of oxide nanostructures is considered.

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