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PECULIARITIES OF RADIATION OXIDATION OF ALUMINUM SURFACE IN CONTACT WITH WATER

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The peculiarities of the oxidation process and the dynamics of the formation of oxide nanostructures on the surface of aluminum and water at room temperature and under the influence of radiation were studied by IR reflection-absorption spectroscopy, radiothermoluminescence and atomic-force microscopy. The role of intermediate surface-active particles in the dynamics of changes in the process of aluminum oxidation in the absorbed dose range of 0.5…120 kGy is considered. It is established that the formation of nanostructured films is dominated by molecular oxygen and other oxygen-containingion radicals generated by gamma-irradiation. It is shown that the radiation modification of the surface leads to a change in the morphology and topography of the surface state and is accompanied by the formation of oxide nanostructures whose defectiveness is determined by the irradiation time. A possible mechanism for the radiation oxidation of aluminum in the Al/ads. H_2O system is discussed.

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]. 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. The formation of a nanosystem plays a decisive role in radiation-stimulated processes of water on the surface of metals. The study of the initial stage of formation and formation of oxide nanolayer is of fundamental importance for solving the problems of surface passivation and predetermines the course of the corrosion process [2–4].

At the same time, a comprehensive study of the process of radiation oxidation of the surface of metals is of fundamental importance in radiation material science from the point of view of the safety of nuclear and nuclear reactors. Metallic aluminum is a promising radiation material. Despite the fact that numerous experimental and theoretical studies have been devoted to his study, some questions remain open and unresolved [5, 6].

In the present work, the features of the radiation oxidation of the aluminum surface in contact with water at room temperature and under the influence of gamma-radiation are studied.

EXPERIMENTAL PART

Aluminum plates with dimensions of 20x10x2 mm, were obtained by stage-by-stage pressing of cylindrical Al granules with a diameter of 3 and a height of 6 mm using a special mold designed for optical studies. The resulting plates had a smooth polished surface with R = 0.80…0.85 in the IR (λ = 15…2.2 μm) wavelength region. Twenty samples with identical reflection coefficients for comparative parallel experiments of radiation oxidation in the aluminum-adsorbed water system (Al/ads. H_2O) were prepared by the methods of radiothermoluminescence (RTL) and IR reflectance-absorption spectroscopy (IRRAS). The IR reflection spectra at the drop of linearly polarized radiation on samples at an angle $\varphi = 88°$ were measured in the region 2000…650 cm^{-1} (Specord 71 IR) at room temperature and under the influence of gamma-radiation [7]. From the IR reflection spectra, the optical densities of the absorption bands and their ratios of stretching vibrations of the Al-O-groups in the initial and processed samples were determined.

The samples were irradiated with γ-quanta on an isotope ^{60}Co source with a dose rate $d\Phi_\gamma/dt$ = 0.80 Gy/s. Radiation oxidation in the Al/ads. H_2O heterosystem was carried out at room temperature (T = 300 K). The absorbed dose varied in the range of Φ_γ = 0.5…120 kGy.

RTL curves were obtained in the temperature range 80…500 K at a warming-up rate of 0.08 K/s. For RTL analysis, the samples were further irradiated with a dose of 10 kGy at 77 K.

The thickness of the oxide films was from 8 nm to 0.25 μm. The small thicknesses of oxide films were estimated by the Stromeyer formula [8], applied to X-ray-photoelectron spectra.

On the atomic force microscope (AFM) Nano Educator SZMU-15, the initial surfaces of metallic aluminum plates and the changes occurring on the surface of these samples after radiation treatment at room temperature and under the action of γ-quanta are traced.

RESULTS AND ITS DISCUSSION

The formation of a surface oxide film in the radiation oxidation of aluminum in contact with water was monitored by IR reflection spectra in the range ν ~ 1200…650 cm^{-1}. Fig. 1 shows the changes in the absorption band of the valence vibration of the Al-O bond as a function of the contact time of aluminum with water (τ) during the radiation oxidation of Al. 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 film 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 [9]. In the case of thin films (d = 8 nm) at the contact time τ = 1 min we detected a band with a maximum at 1010 cm^{-1}, which refers to Al_2O_3 and characterizes the valence vibration of Al-O.

Thickening of the oxide film from 8 nm to 0.25μm, or an increase in the contact time up to 1 min. Up to τ = 5 hours, this band shifts from 1010 to 950 cm^{-1} (i. e. by 60 cm^{-1}) and to its broadening (half-width $\nu_{1/2}$ increases by 50 cm^{-1}). The wide diffuse maximum of the Al-O vibration band is characteristic of amorphous and polycrystalline structures and confirms the in homogeneities of relatively thick oxide films [4, 10].

In order to clarify and determine the role of relaxing intermediate-active particles, in particular, oxygen hole centers and other oxygen-containing groups in the dynamics of the oxidation process in contact with water, we used the RTL-method for the first time.

It is assumed that the main role in radiation oxidation is played by surface oxygen holes generated by γ-irradiation and capable of migrating into the volume interacting with the metal atoms constituting it. The mechanism of this process is presumable and requires rigorous experimental evidence.

Irradiation of γ-quanta at 77 K temperature of radiation-oxidized aluminum plates in contact with water leads to the appearance of a number of RTL peaks at temperatures of 170, 220, and 320 K (Fig. 2, curve 1). A low-temperature peak at T = 170 K with an activation energy E_a = 0.38 eV can be associated with the thermally stimulated luminescence of chemisorbed oxygen. According to [11], an oxygen peak in the 150…170 K region due to dissolved oxygen and other oxygen-containing gases was also detected during the radiation excitation of thermoluminescence in polymers. The intensity of the peak with a maximum at 170 K strongly depends on the time of contact of aluminum with water at γ-irradiation in the system Al/ads. H_2O, from the thickness of the radiation-oxidized film. With an increase in this thickness from 8 nm to 0.25 μm, the intensity of the peak increases by a factor of ~ 6 and another peak appears at T = 175 K with an activation energy E_a= 0.42 eV. The asymmetric peak at T = 220 K also splits into two relatively narrow peaks, with the peak at 320 K virtually unchanged (see Fig. 2, curves 2, 3).

Apparently, a narrow peak at T = 175 K is associated with the thermally stimulated adsorboluminescence of the molecular oxygen product of the radiation-heterogeneous decomposition of water at surface-localized hole centers of the O^- type [12].

In favor of this is evidence of the luminescence of the peak at 175 K after additional adsorption of dried O_2 in the cell with the system under study and its quenching after prolonged evacuation of this system at a temperature $T \geq 773$ K. The emission of electrons accompanied by emission in the visible region of the spectrum during the adsorboluminescence of oxygen on aluminum was also observed by the authors of [12]. The absorption of oxygen at hole centers in aluminum oxide (Al_2O_3) was also observed by electron paramagnet resonance (EPR) (cold signal g = 2.009), photo- and thermal desorption and thermoluminescence [13].

Peaks at T = 195 and 230 K with activation energies E_a = 0.50 and 0.65 eV belong to aluminum hydroxides. The formation of various hydroxides is confirmed by IR reflection spectra (see Fig. 1). A diffuse peak with a maximum at ~ 320 K, with an activation energy E_a = 0.8…1.0 eV, is due to the thermally stimulated luminescence of chemisorbed oxygen and other oxygen-containing groups (OH^-) on surface electronic F^+ and F-centers.

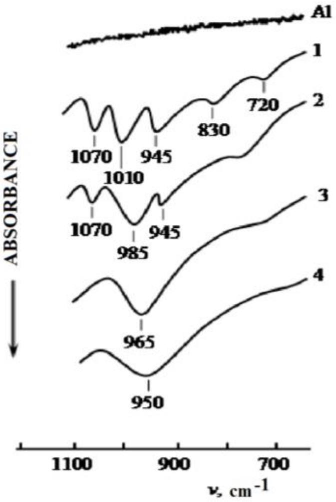

Fig. 1. The change in the absorption band of the stretching vibration of the Al-O bond as a function of the contact time of aluminum with water at a radiation (T = 300 K, $d\Phi_\gamma$ = 6.67 Gy/s) oxidation, τ = 1 min (1); 10 min (2); 5 h (3), and 18 h (4)

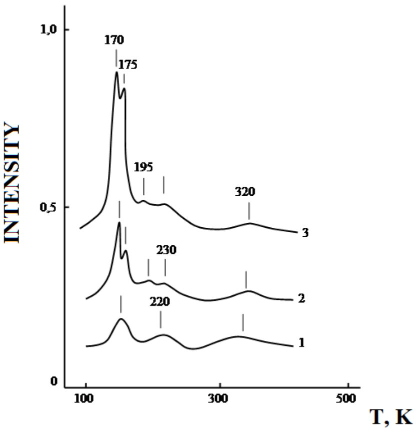

Fig. 2. Changes in the RTL curves of oxide films as a function of the time of contact of aluminum with water during the radiation oxidation of Al: τ = 1 min (1); 10 min (2), and 5 h (3)

The observed features of the manifestation of the multicomponent structure of the RTL oxygen peak in the region of 100…250 K (for relatively thick nonuniform oxide films) are related both to the inhomogeneity of the hole centers themselves and to the fact that radiation-adsorbed oxygen can be on the surface in different states (O^-_{ads}, O_{2ads}, OH^-_{ads}, etc.). It should be noted that with the thickening of the oxide film, radiation-stimulated adsorption of oxygen occurs already at the Al-Al_2O_3 interface. Therefore, the increase in the intensity of the oxygen peak of RTL with increasing oxide film thickness should be attributed to an increase in the density of surface defect states in the near-surface oxide layer of Al_2O_3, and hence, the probability of oxygen adsorption at these centers.

Radiation modification of the surface leads to a change in the morphology and relief of the near-surface state. Therefore, it seems interesting to microscopically study the morphology and topography of the surface of radiation-oxidized aluminum plates at room temperature and under the influence of γ-quanta. Three-dimensional (3d) surface AFM 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. As the AFM investigations have shown, 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. As an example, in Figs. 3 and 4 show three-dimensional (3d) surface images and their histograms of aluminum samples before (a) and after radiation oxidation at room temperature (T = 300 K) (b, c). As can be seen from three-dimensional images, the surface of the original sample is characterized by the presence of a thin oxide film (d = 8 nm) with a high degree of defectiveness (see Fig. 3,a). The nanoparticles are evenly distributed and have a depth of 60 nm. Radiation oxidation leads to a change in the surface state of aluminum (see Fig. 3,b,c). The surface is smoothed out and the nanoparticles have a depth of 30 nm.

As the histograms of the AFM 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 (see Fig. 4,a).

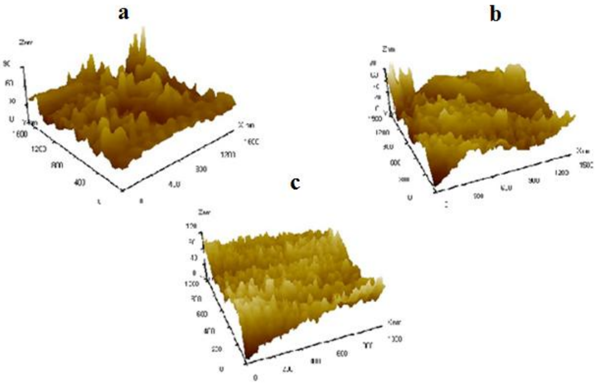

Fig. 3. Three-dimensional (3d) images of the surface of the initial (a) and radiation-oxidized Al at times of contact with water of 10 min (b) and 5 hours (c)

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.

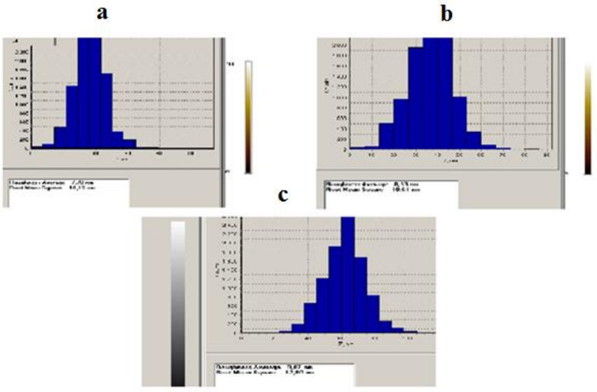

Fig. 4. The histograms of the surface of the initial (a) and radiation-oxidized Al at times of contact with water of 10 min (b) and 5 h (c)

Further increase in the irradiation time τ (corresponding to an increase in the thickness of the oxide film from 8 to 250 nm) from 10 min to 5 h leads to the formation of nanoclusters with a size ~ 2 times on the aluminum surface as compared to the initial samples. At the same time, a continuous oxide layer forms on the surface of Al.

The mechanism of oxidation of aluminum in the presence of water under the action of γ-radiation can be represented as follows: under the action of γ-radiation on the surface of Al, active states S* (ions, localized charges, etc.) are formed and secondary electronic radiation (e_{sec}).

$$Al \xrightarrow{\gamma} S^*, e_{BT}. \qquad (1)$$

Their interaction with water leads to the excitation of H_2O molecules.

$$H_2O \xrightarrow[S^*]{e_{BT}} H_2O_S^*, \qquad (2)$$

where H_2O_s* is the excited adsorbed state of water molecules.

On the surface-active states of S*, water molecules are excited through the complexation stages and further transfer of excitation energy of the complex to H_2O molecules. Then the decay of excited states of water molecules occurs along a homogeneous mechanism [14] and is accompanied by the formation of intermediate (OH, OH^-, O, H, H^+, H_2O^+) and gaseous (H_2, O_2) decomposition products. Intermediate active particles can interact with the surfactant states of Al and form Al-H hydrides and Al-OH aluminum hydroxides [15].

The formation of surface hole centers (oxygen holes) occurs according to the scheme:

$$\text{Al-OH} \rightarrow \text{Al-O-Al} + H_2O, \qquad (3)$$

$$Al^+ + H_2O \rightarrow Al^+O^- + H_2. \qquad (4)$$

The hole centers formed by the formula (4) migrate into the volume and interact with the bulk atoms of aluminum. The presence of oxygen during radiation oxidation accelerates the oxidation process.

According to the calculation, the yield of molecular hydrogen $G(H_2)$ in the Al/ads. H_2O heterosystem with allowance for the total absorbed dose of γ-radiation under the conditions of our experiments is $G(H_2)$ = 2.25 molec./100 eV. It should be noted that the hydrogen yield for a homogeneous phase (in the absence of aluminum) is $G(H_2)$ = 0.40 molec./100 eV [14].

CONCLUSION

The complex study of the process of oxidation of the aluminum surface in contact with water at room temperature was carried out using OAS-, RTL-, and AFM-methods. The possibility of using the RTL-method for studying the radiation oxidation of aluminum in the Al/ads. H_2O system is shown. It is shown that the radiative decomposition of water in an Al/ads. H_2O heterosystem is accompanied by the formation of an oxide film on the Al surface. The PTL peaks are recorded in the temperature range 100…250 K with activation energies E_a = 0.38…0.65 eV, which are associated with the thermally stimulated adsorption and chemiluminescence of oxygen and its groups at surface-localized centers under γ-irradiation. It was found that the surface oxygen hole centers generated by γ-irradiation and chemisorbed oxygen play a major role in the formation of oxide films. The formation of oxide films by the change in the absorption band of the stretching vibration of the Al-O bond ($\nu = 950\ cm^{-1}$) is monitored by IR reflection spectra as a function of the time of contact of aluminum with water. According to the AFM studies (3d surface images and their histograms), it is established that the radiation modification of the surface relief is accompanied by the formation of oxide nanostructures whose defectiveness is determined by the irradiation time. The possible mechanism of aluminum oxidation in the Al/ads. H_2O system is discussed.

REFERENCES

1. V. Gorbachev, L.G. Spitsyna. *Physics Semiconductors and Metals*. M.: “Metallurgy”, 1982, 336 p.
2. V.P. Grigoriev. Protection of metals from corrosion // *Soros Educational Journal of Chemistry*. 1999, p. 42-48.
3. P.G. Borzyak, Yu.A. Kulyupin. *Electron processes in island films*. Kiev: “Naukova dumka”, 1980, 239 p.
4. G.G. Bondarenko, A.P. Korzhavy, I.P. Gashchenko, V.P. Marin. Oxide films on the metal surface: the current state of research and problems of practical use // *Proceedings of the VI Scientific and Technical Conference*. M.: INTERMATIC, 2008, 21–23 September, p. 170-176.
5. N.N. Gadzhieva. Oxidation and accumulation of H_2 in the aluminum water system under the radiation-thermal action *// Journal of Applied Spectroscopy*. 2005, v. 72, N 4, p. 471-477.
6. N.N. Gadzhieva. Radiation oxidation of aluminum in contact with water // *Journal of Metal Protection*. 2007, v. 43, N 4, p. 413-417.
7. N.N. Gadzhieva, A.N. Rimikhanova, A.A. Garibov. Study of radiation-stimulated adsorption and radiolysis of water on the aluminum surface by the OAS method // *Izvestiya NAS Azerbaijan. Series of Physics of Technical and Mathematical Sciences*. 2004, N 5, p. 120-125.
8. V. Demange, J.W. Anderegg, J. Ghanbiya, et al. Surface oxidation of Al-Cr-Fe alloys characterized by X-ray photoelectron spectroscopy *// J. Applied Surface Science*. 2001, v. 173, p. 327-338.
9. V.A. Dubovitsky, A.V. Chekanov, S.A. Vozchikova. Comprehensive diagnostics of inorganic compounds from the infrared absorption spectrum // *Chemical Physics*. 2004, v. 23, N 5, p. 90-100.
10. A.A. Davydov.Education and degradation of oxide films on beryllium // *Problems of Atomic Science and Technology*. *Series “Physics of Radiation Effects and Radiation Material Science”*. 2010, N 2, p. 39-49.
11. V.N. Kuleshov, V.G. Nikolsky. *Radiothermoluminescence of Polymers*. M.: “Nauka“, 1991, 223 p.
12. I.N. Ogorodnikov. *Electron excitations, luminescence and radiation defects in wide-band nonlinear opticalcrystals:* Avtoref. of doctor of physical science. Yekaterinburg, 2004, 46 p.
13. V.N. Kuznetsov, A.A. Lisachenko. On the nature of optical absorption induced by UV irradiation of γ-Al_2O_3 in oxygen // *Kinetics and Catalysis*. 1991, v. 32, N 1, p. 222-225.
14. A.K. Pikaev. *Modern radiation chemistry. Radiolysis of gases and liquids*. M.: “Nauka”, 1986, 433 p.
15. N.N. Gadzhieva, A.N. Rimikhanova, A.A. Garibov, Sh.S. Ismayilov. Investigation of the radiation oxidation of aluminum in the aluminum-water system by the methods of electrical conductivity and infrared spectroscopy // *Problems of Atomic Science and Technology. Series “Physics of Radiation Effects and Radiation Material Science” (91)*. 2007, N 6, p. 36-39.

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ОСОБЕННОСТИ РАДИАЦИОННОГО ОКИСЛЕНИЯ ПОВЕРХНОСТИ АЛЮМИНИЯ В КОНТАКТЕ С ВОДОЙ

Н.Н. Гаджиева

Методами ИК отражательно-абсорбционной спектроскопии, радиотермолюминесценции и атомно-силовой микроскопии изучены особенности процесса окисления и динамика формирования оксидных наноструктур на поверхности алюминия с водой при комнатной температуре и при радиационном воздействии. Рассмотрена роль промежуточных поверхностно-активных частиц в динамике изменений процесса окисления алюминия в области поглощенной дозы 0,5…120 кГр. Установлено, что при формировании наноструктурных пленок основную роль играют молекулярный кислород и другие кислородосодержащие ион-радикальные группы, генерированные гамма-облучением. Показано, что радиационная модификация поверхности приводит к изменению морфологии и рельефа поверхностного состоянии и сопровождается формированием оксидных наноструктур, дефектность которых определяется временем облучения. Обсужден возможный механизм радиационного окисления алюминия в системе Al/адс. H_2O.

ОСОБЛИВОСТІ РАДІАЦІЙНОГО ОКИСЛЕННЯ ПОВЕРХНІ АЛЮМІНІЮ В КОНТАКТІ З ВОДОЮ

Н.Н. Гаджиєва

Методами ІЧ відбивно-абсорбційної спектроскопії, радіотермолюмінесценції і атомно-силової мікроскопії вивчені особливості процесу окислення і динаміка формування оксидних наноструктур на поверхні алюмінію з водою при кімнатній температурі і при радіаційній дії. Розглянута роль проміжних поверхнево-активних часток у динаміці змін процесу окислення алюмінію у області поглиненої дози 0,5…120 кГр. Встановлено, що при формуванні наноструктурних плівок основну роль відіграють молекулярний кисень та інші кисневоскладові іон-радикальні групи, генеровані гамма-опроміненням. Показано, що радіаційна модифікація поверхні призводить до зміни морфології і рельєфу поверхневого стану і супроводжується формуванням оксидних наноструктур, дефектність яких визначається часом опромінення. Обговорено можливий механізм радіаційного окислення алюмінію в системі Al/адс. H_2O.