

# Chemistry

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## THERMAL TRANSFORMATIONS OF ALUMINIUM – ALUMINIUM OXIDE SYSTEMS IN NANOSIZE LAYERS

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*Aluminium film of more than 2 nm thick indicates, but less than 2 nm do not indicate characteristic absorption and reflection bands for aluminium in range  $\lambda=190\text{...}1100$  nm. By spectrophotometric, gravimetric and microscopic methods it is stated that thickness, mass and absorption, reflection spectrum of aluminium films ( $d=2\text{...}200$  nm) undergo considerable transformations as a result of heat treatment in an interval of temperatures 373...600 K during 1...140 min in atmospheric conditions. Kinetic curve of transformation degrees, change of thickness and weights of samples are shown to be satisfactorily described in the context of the logarithmic law. It is established that changes of absorption spectra, thickness and weights of aluminium films are connected with the formation of aluminium oxide on their surface.*

Aluminium is a silvery (white) metal, its alloys finding wide application in different branches of science, technology and industry due to a number of useful properties (plasticity, low density, low melting point, high reflectance, heat- and electrical conductivity and etc.). Aluminium and its alloys are used in rocket engineering, aircraft-, auto-, ship- and machine building, in construction engineering, in building of railroads and tramlines as construction materials [1–3]. In electrical engineering aluminium is employed to produce wires and cables [4]. Thin aluminium layers, «lighted» with oxides, are used in production of heat-reflective coatings [5]. According to the range of application aluminium and its alloys rank next to steel and cast iron. The contact of aluminium with light-sensitive materials leads to changes in photosensitivity of the latter [6, 7]. However, metal state of aluminium in atmospheric conditions is thermodynamically unstable [1–3, 8–10]. Aluminium is chemically active and when contacting with environment it subjected to atmospheric corrosion forming protective film of aluminium oxide  $\text{Al}_2\text{O}_3$ , which prevent metal from subsequent oxidation [1–3, 8–10]. Aluminium belongs to the group of base metals, which have a negative value of free energy in the course of ionization reaction even in the absence of oxygen [1–3]. The wide scope of aluminium application put forward new technical tasks, increase the requirements to the properties of aluminium products [11–16]. Study of nature and regularities of the processes occurring in heat interaction of aluminium and of its surface is thought to be necessary both for solution of some scientific problems, and, in particular, for revealing the degree of commonness in the processes taking place at the boundary of metal, oxide and environment, and owing to the necessity of development of radically new materials for semiconductor microelectronics.

In the given paper the results of a series of investigations directed to statement of the nature and the regularities of the processes taking place in nanosize layers of aluminium-aluminium oxide systems in atmospheric conditions depending on thickness of material, temperature and time of thermal action are presented.

### Objects and methods of research

Samples for investigation have been prepared by the method of thermal vacuum evaporation ( $2 \cdot 10^{-3}$  Pa) by means of application of thin (2...200 nm) layers of aluminium to glass substrate using universal vacuum station UVS-5M. As evaporators the troughs made of molybdenum of  $d=3 \cdot 10^{-4}$  m thick were used. The optimal distance from troughs-evaporator to the substrate was 8...9 cm.

Photoplate glasses of  $1 \cdot 10^{-3}$  m thick and area of  $2 \cdot 10^{-4}\text{...}4 \cdot 10^{-4}$  m<sup>2</sup> preliminary treated by aquafortis, solution of potassium dichromate, in concentrated sulphuric acid, in boiling soupsuds, washed in distilled water and dried served as substrates [17, 18] were used as a substrate. The treated substrates were optically transparent in the range of 300...1100 nm.

Thickness of aluminium films was defined by spectrographic, microscopic and gravimetric methods [1]. The gravimetric methods of quartz microweighing is based on determination of mass increment ( $\Delta m$ ) per unit of quartz resonator surface (of  $h=0,1$  mm thick) after application of aluminium film on it. Resolution capacity at resonators cure at the level of  $\pm 0,1$  °C amounted  $\Delta m=1 \cdot 10^{-8}\text{...}1 \cdot 10^{-9}$  g/sm<sup>2</sup>. Average thickness of film after weighing was calculated by the formula:

$$d_f = \Delta m / F_f \rho_m,$$

where  $\Delta m$  is mass increment of quartz resonator after film application,  $F_f$  is the film square on the substrate,  $\rho_m$  is the specific mass of applied substance [17, 18].

Samples were treated by heat in drying box «Memmert BE 300» and «SPT-200», in muffle furnace «Tulyachka-3П» in the temperature range 373...600 K. In this case the samples were placed on porcelain plate heated to appropriate temperature and treated by heat during 1...140 min. in atmospheric conditions. The effects before and after thermal treatment were registered by gravimetric, microscopic and spectrophotometric (in the range of wavelength 190...1100 nm, using spectrophotometer «Shimadzu UV-1700») methods.

### Results and discussion

As a result of investigations into optical properties of aluminium thin layers applied to glass substrates before, in the process, and after thermal treatment in atmospheric conditions, it has been, first of all, stated that absorption and reflectance spectra of aluminium films before thermal treatment depend sufficiently on their thickness. In fig. 1 and 2 absorption and reflectance spectra of aluminium films of different thickness in the range ( $d=2...200$  nm) are presented. It is evident that in the range of wavelength involved one can point out characteristic for aluminium bands (in particular, reflective minimum at  $\lambda \approx 840$  nm) on spectral absorption and reflectance curves for all samples involved [12–14]. As the thickness of aluminium films decreases, the characteristic aluminium bands cease gradually to appear on spectral absorption and reflectance curves. For aluminium films of  $d < 2$  nm thick structureless absorption and reflection in the range of  $\lambda = 190...1100$  nm is observed.

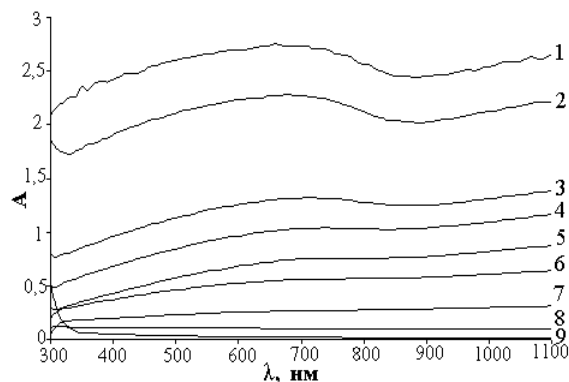


Fig. 1. Absorption spectra of aluminium films of 1) 200, 2) 165, 3) 92, 4) 71, 5) 50, 6) 38, 7) 19, 8) 8, 9) 2 nm thick

Reflection coefficient ( $R$ ) of light flux falling at a normal line to the flat surface of solid body from vacuum (air) can be presented through the refraction ( $n$ ) and absorption ( $k$ ) coefficients of solid body in the following form [14–16]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}.$$

Refraction and absorption coefficients and, consequently, reflection coefficient depend sufficiently on wavelength of falling light [14–16]. For chemically pure aluminium at  $\lambda = 589$  nm refraction and absorption coefficients amount 1,44 and 5,23 respectively [14]. Reflection coefficient is equal to  $R = 0,83$ . It is seen from fig. 2 that to this value of reflection coefficient correspond the aluminium films of 160 nm thick.

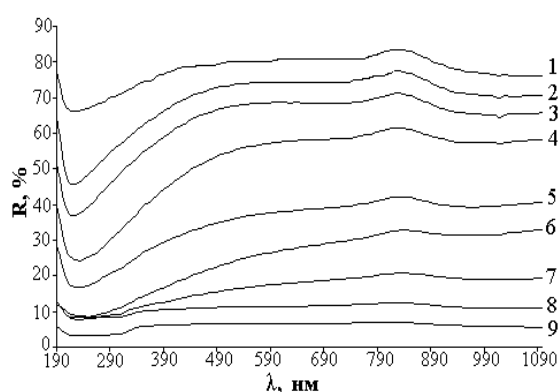


Fig. 2. Reflection spectra of aluminium films of: 1) 165, 2) 94, 3) 71, 4) 50, 5) 38, 6) 30, 7) 19, 8) 11, 9) 2 nm thick

It follows from the equation that if a solid body does not absorb light in a definite spectrum range, reflection coefficient will depend on just the value of refraction factor. Assuming that basic product in aluminium thermal treatment is aluminium oxide, the refraction coefficient of which amount 1,5...1,7 [3] depending on modification, the reflection coefficient for  $\text{Al}_2\text{O}_3$  should be  $\approx 0,04...0,07$  (4...7%). Thus (fig. 2), producing aluminium films by thermal evaporation method in vacuum (see above) a layer of aluminium oxide is formed on their surface and as the thickness decreases, optical properties of aluminium films are more and more (at the film of 2 nm thick completely) determined by  $\text{Al}_2\text{O}_3$  film on its surface.

As a result of storage as well as thermal treatment of aluminium films of different thickness in the temperature range ( $T = 373...600$  K) in atmospheric conditions absorption and reflectance spectra, thickness and weight of samples changes sufficiently. Moreover, the observed absorption and reflectance spectra changes, thickness and weight of samples after thermal treatment depend to a great extent on the initial thickness of aluminium films, temperature and time of thermal treatment. In fig. 3 the absorption spectra of aluminium films of  $d = 12$  nm thick before and after thermal treatment at 523 K are presented as an example.

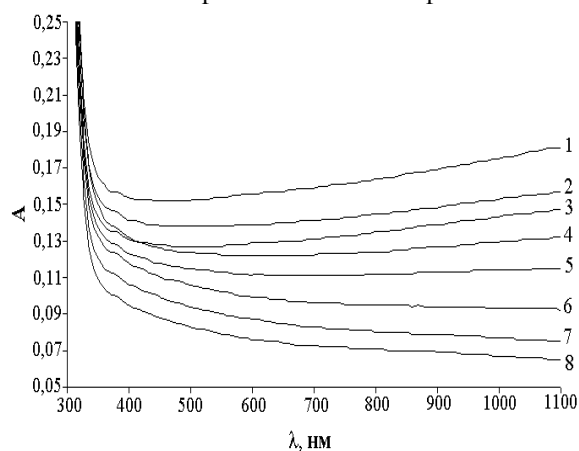


Fig. 3. Absorption spectra of aluminium film of 12 nm thick before and after preliminary thermal treatment at 523 K: 1) without thermal treatment, 2) 1, 3) 5, 4) 10, 5) 20, 6) 40, 7) 80, 8) 140 min

It is seen that thermal treatment results in sufficient transformations in the form of spectral curves of sample absorption. Note that the changes observed are not additive in the spectral range of wavelength involved. Along with decrease of sample optical density in the range  $\lambda=330\dots1100$  nm and increase in the range  $\lambda\leq 330$  nm the absorption spectrum of a new substance is formed. Estimated by long-wavelength threshold of reflection (fig. 2), which is at  $\lambda\leq 190$  nm, optical width of band gap of the substance formed amount  $E\geq 6,5$  eV. The obtained width value of substance band gap closely coincides with band gap width of aluminium oxide (according to different data  $E\geq 6,5\dots 9,5$  eV) [10]. Therefore, it was assumed that at thermal treatment of aluminium films the basic product of their interaction with environmental ingredients is aluminium oxide.

Increasing or decreasing the temperature at which there is thermal treatment, regularities of absorption spectrum transformations are retained independently on the initial thickness of aluminium films, and decrease in sample optical density is observed. At the same initial thickness of aluminium films with temperature increase the growth of transformation effects of sample optical density takes place. As the thickness of aluminium films increase (up to 200 nm) at constant temperature (in the range 373...600 K) of thermal treatment, a successive decrease in transformation effects of sample optical density all over investigated spectral range is observed.

To find out the regularities of the interaction process of aluminium films with active environmental ingredients (using the results of absorption and reflection spectra measurement of aluminium films of different thickness before and after thermal treatment of samples at different temperatures) kinetic dependencies of fractional conversion  $\alpha=f(\tau)$  were calculated and constructed at different wavelength. For construction of kinetic curves in  $\alpha=f(\tau)$  coordinates the following approach was applied. On the basis of analysis of obtained in the given work absorption and reflection spectra of aluminium films and  $\text{Al}_2\text{O}_3$  for construction of kinetic curves  $\alpha=f(\tau)$  the range of wavelength  $\lambda=400\dots 900$  nm, in which aluminium films have significant absorption, was chosen, but absorption of  $\text{Al}_2\text{O}_3$  can be neglected. Optical density ( $A_{\text{treat.}}$ ) of aluminium film depends on time of thermal treatment, but at definite time of thermal treatment it consists of optical density connected with the presence of aluminium layer ( $A_{\text{Al}}$ ) and aluminium oxide ( $A_{\text{Al}_2\text{O}_3}$ ):

$$A_{\text{sam}} = A_{\text{Al}} + A_{\text{Al}_2\text{O}_3}.$$

If we denote the degree of thermal transformations of aluminium films into aluminium oxide through  $\alpha$ , then at the wavelength (for example,  $\lambda=590$  nm – fig. 3), corresponding to spectral region within which aluminium absorbs, but aluminium oxide does not practically absorb light [10, 14], current optical densities of aluminium flowing optical films ( $A_{\text{Al}}$ ) and aluminium oxide ( $A_{\text{Al}_2\text{O}_3}$ ) can be presented in the following form:

$$\begin{aligned} A_{\text{Al}} &= A_{\text{Al}}^1(1-\alpha), \\ A_{\text{Al}_2\text{O}_3} &= A_{\text{Al}_2\text{O}_3}^1\alpha, \end{aligned}$$

where  $A_{\text{Al}}^1$ ,  $A_{\text{Al}_2\text{O}_3}^1$  is the limited optical density of aluminium layer and aluminium oxide at  $\lambda=590$  nm.

As a result we obtain the following expression for degree of thermal transformation of aluminium film into aluminium oxide:

$$\begin{aligned} A_{\text{sam}} &= A_{\text{Al}}^1(1-\alpha) + A_{\text{Al}_2\text{O}_3}^1\alpha, \\ \alpha &= (A_{\text{Al}}^1 - A_{\text{sam}}) / (A_{\text{Al}}^1 - A_{\text{Al}_2\text{O}_3}^1). \end{aligned}$$

It is known [14–16] that falling light wave from radiation source at normal line to the surface of some system undergoes mirror reflection, dispersion, absorption and transmission. Going through the boundaries of some media (air – aluminium oxide – aluminium – glass – air) with different refraction coefficients ( $n$ ), as it is in our case, summary specular reflected light wave ( $R$ ) is composed of several constituents:

$$R = R_1 + R_2 + R_3 + R_4,$$

where  $R_1$  is the specular reflected light wave from air-aluminium oxide boundary,  $R_2$  is the specular reflected light wave from aluminium oxide-aluminium boundary,  $R_3$  is the specular reflected light wave from aluminium-glass boundary,  $R_4$  is the specular reflected light wave from glass-air boundary.

Thus, spectrometer complete value of optical density measured in real conditions includes (at the minimum) some components

$$A = A_{\text{sam}} + A_{\text{ref.}} + A_{\text{scat.}},$$

where  $A_{\text{sam}}$  is the magnitude of sample optical density;  $A_{\text{ref.}}$  is the magnitude of optical density, conditioned by losses in light specular reflection by sample surface;  $A_{\text{scat.}}$  is the magnitude of optical density, conditioned by losses in light diffused scattering by sample surface.

In the course of special investigation it was stated that diffused scattering by aluminium film surface is negligible in comparison with specular reflection (see fig. 2) and, consequently,  $A_{\text{scat.}}$  can be considered  $\approx 0$ . Then

$$A = A_{\text{sam}} + A_{\text{ref.}}$$

$$\begin{aligned} A &= \lg I_{\text{fal.}} / I_{\text{trans.}} = \lg I_{\text{fal.}} - \lg I_{\text{trans.}}, \\ \lg I_{\text{trans.}} &= \lg I_{\text{fal.}} - A. \end{aligned}$$

coefficient of specular reflection  $R = I_{\text{ref.}} / I_{\text{fal.}}$ ;  $I_{\text{ref.}} = R \cdot I_{\text{fal.}}$ .

$$A_{\text{sam}} = \lg I_{\text{incom.}} / I_{\text{trans.}} = \lg I_{\text{incom.}} - \lg I_{\text{trans.}}$$

where  $I_{\text{fal.}}$ ,  $I_{\text{trans.}}$ ,  $I_{\text{ref.}}$ ,  $I_{\text{incom.}}$  is intensity of falling, transmitted, reflected and incoming into sample light.

$$\begin{aligned} I_{\text{fal.}} &= I_{\text{incom.}} + I_{\text{ref.}}, \\ I_{\text{incom.}} &= I_{\text{fal.}} - I_{\text{ref.}} = I_{\text{fal.}}(1-R). \end{aligned}$$

After simple transformations the final formula for calculation of true (caused by light absorption in substance) value of optical density is:

$$A_{\text{sam}} = A + \lg(1-R).$$

As a result of absorption spectra treatment it has been stated that the thermal fractional conversion of aluminium films depends on initial thickness, temperature and time of thermal treatment.

First of all, it was noted that the thermal fractional conversion grows as the time of thermal treatment increases. Decrease in thickness of aluminium film results in growth of thermal fractional conversion all over the investigated range of temperature 373...600 K. Increase in temperature of thermal treatment at constant thickness

of aluminium films leads to rise of thermal fractional conversion. It was stated that kinetic curves of fractional conversion at thermal treatment of aluminium films are adequately described in terms of the logarithmic law. In fig. 4 the kinetic curves of fractional conversion of aluminium films at 573 K depending on the initial thickness of samples are presented as an example.

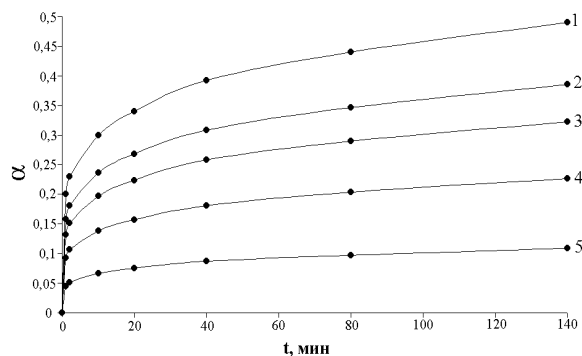


Fig. 4. Dependence of fractional conversion on thickness of aluminium films at 573 K: 1) 21, 2) 26, 3) 32, 4) 45, 5) 94 nm

In fig. 5 the kinetic dependences of mass changes in aluminium films owing to formation of aluminium oxide in the process of thermal treatment at 423 K are presented.

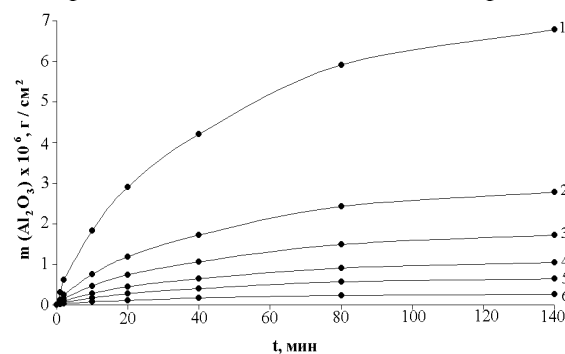
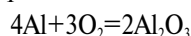


Fig. 5. Mass dependence of aluminium oxide on time of thermal treatment (423 K): 1) 8, 2) 19, 3) 30, 4) 50, 5) 80, 6) 195 nm

It is evident that during thermal treatment increase in sample mass is observed. Moreover, the less the initial thickness of aluminium films is, the more the intensity of oxidation process at constant temperature of thermal treatment. Increasing the temperature of thermal treatment raise the mass part of formed aluminium oxide. When compared the mass of aluminium oxide determined by the gravimetric method at different time and temperature of thermal treatment in the conditions of complete oxidation of aluminium films of different thickness and calculated by the equation of oxidation reaction



their satisfactory agreement is stated. This fact is an additional evidence of aluminium oxide layer forming in the process of thermal treatment of aluminium films.

Thermal treatment results in increase of aluminium oxide film thickness. In fig. 6 kinetic curves of thickness change of aluminium oxide formed on the aluminium film surfaces of different thickness at 523 K are presented.

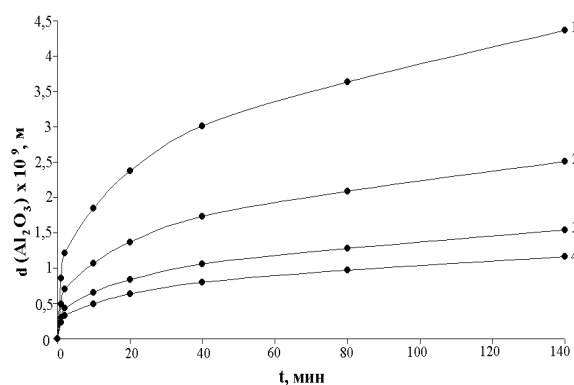


Fig. 6. Dependence of aluminium oxide thickness on time of thermal treatment (523 K): 1) 12, 2) 20, 3) 33, 4) 43 nm

It is seen that aluminium oxide thickness increases in the process of thermal treatment of aluminium films. At thermal treatment of aluminium films of different thickness at higher temperature significant and sharp growth of aluminium oxide is observed just at small time of thermal treatment. In this case the less the thickness of aluminium film is, the more the rate of growth in aluminium oxide is.

It is known [1, 2] that one of the main conditions characterising capacity of formed initial layer of interaction products of environmental ingredients with metal to retard further tarnishing is continuity of produced oxide film. The forming oxide film prevents from penetration of oxidation agents into reaction space and in this way retarding its further growth. According to the Pilling and Bedward criterion that amounts 1,28 for aluminium [1], formation of continuous oxide film retarding significantly further oxidation process should be expected and, consequently, in the ideal case – the parabolic law of oxidation process of aluminium films limited by ion diffusion  $\text{Al}^{3+}$  through oxide layer to its surface (ion radius  $\text{Al}^{3+}$  amounts 0,5 Å, but atomic radius is Al – 1,43 Å) [1, 2, 10]:

$$L^2 = K\tau + A,$$

where  $L$  is the film thickness,  $\tau$  is the oxidation time,  $K$  is the constant of oxidation rate,  $A$  is the integration constant.

Besides, according to the ratio of yield between aluminium and aluminium oxide [19, 20] as the thickness of oxide film increases on aluminium surface [21] absorption capacity of oxide film increases with respect to acceptor gas (air oxygen) independently of charge sign and cause for charging outer surface.

As a result of analysis of kinetic dependencies of fractional conversion, mass change and thickness of oxide layer it has been stated that at thermal treatment of aluminium films of  $d=2...200$  nm thick in atmospheric conditions in the temperature range (373...600 K) during 1...140 min. kinetic curves of aluminium film oxidation are adequately described in terms of the logarithmic law. Thus, on the surface of aluminium films continuous oxide films form as a result of chemical corrosion. The corrosion process can be retarded by diffusion of aluminium ions through oxide film (limiting stage of corrosion is diffusion of aluminium ions towards

the boundary of oxide layer surface and the medium), further growth of which will be slowed down while increasing thickness of oxide film [1, 2]. Efficient rate constants of limiting stage in corrosion process estimated

for aluminium films of different thickness amount  $k=2...8 \cdot 10^{-2} \text{ min}^{-1}$ .

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