

Studying of Kinetic Legitimacies of Nanosize Aluminium Films Oxidizing Process

E.P. Surovoi and N.V. Borisova

*Kemerovo State University, 6, Krasnaya str., Kemerovo, 650043, Russia
Phone: +8(3842) 58-06-05, Fax: +8(3842) 58-38-85, E-mail: epsur@kemsu.ru*

Abstract – By gravimetric, spectrophotometric and microscopic methods is established, that the transformation degree and weight change of aluminium are determined by initial aluminium thickness ($d=2\text{--}200\text{ nm}$), temperature ($373\text{--}600\text{ K}$) and thermal processing time ($1\text{--}140\text{ min}$) during atmospheric corrosion. It is established, that changes of transformation degree and aluminium film weights are connected to aluminium oxide formation on their surface. A limiting stage of nanosize aluminium film corrosion process is aluminium ion diffusion to border of oxide layer surface with an environment.

1. Introduction

Studying of the nature and legitimacies of the processes proceeding at thermal action in aluminium and on its surface, is obviously necessary as for the solution of group of scientific problems, in particular, transpiring of a degree of a generality of the processes proceeding on boundary between metal, oxide and an environmental atmosphere, and in connection with necessity of development of essentially new materials for solid-state microelectronics. Aluminium and its alloys due to a complex of the positive properties have found wide application in various areas of a science, technique, and the industry. On latitude, aluminium and its alloys application take the second place after steel and cast iron. In the capacity of structural materials, aluminium and its alloys are used in rocketry, aircraft industry, motor industry, shipbuilding and instrumentation technologies, in building, in constructions of railway and tram paths [1–3]. In the electro-technical industry, aluminium is applied to manufacturing wires and cables [4]. The thin aluminium layers “clarified” by oxide are applied to manufacturing heat-reflecting coats [5]. Making of contacts of aluminium with light-sensitive materials results to change of photosensitivity last [6, 7]. However, aluminium is reactive and at engagement with a surrounding medium is exposed to atmospheric corrosion with formation of a protecting Al_2O_3 aluminium oxide film, which safely protects metal from the further oxidizing [1–3, 8, 9]. In last years it proved, that atoms of aluminium formed clusters [10]. And, clusters from 13, 23, and 37 aluminium atoms have valence shells with one empty vacancy. It is known, that shells of halogens – fluorine, chlorine, bromine, iodine, and astatine are those. Expansion of application ranges of alumin-

ium telescopes new scientific and technical problems lifts requirements to properties of products from aluminium and its alloys [11–16].

In the present work results of operation, directed on finding-out of the nature and laws of processes proceeding in requirements of an atmosphere in nanosize aluminium layers depending on its thickness, temperature and thermal action time.

2. Objects and research techniques

Samples for examinations plotted a method of a thermal vacuum evaporation ($2 \cdot 10^{-3}\text{ Pa}$) by drawing thin ($2\text{--}200\text{ nm}$) aluminium layers on substrates from a glass, using a vacuum universal post “VUP-5M”. In the capacity of an evaporator used the floating troughs manufactured of molybdenum by thickness $d = 3 \cdot 10^{-4}\text{ m}$. The optimal distance from a floating trough – evaporator to a substrate makes $8\text{--}9\text{ cm}$. As substrates glasses served glasses from photoplates with thickness of $1 \cdot 10^{-3}\text{ m}$ and the area $(2\text{--}4) \cdot 10^{-4}\text{ m}^2$ which subjected to pretreatment in concentrated hydrogen nitrate, glasses served in a solution of potassium bichromate in concentrated sulfuric acid, in boiling soap water, washed out in distilled water and dried [17, 18]. Handled substrates optically are transparent over the range $300\text{--}1100\text{ nm}$. Thickness of aluminium films is determined by spectrophotometric (spectrophotometer “Shimadzu UV-1700”), microscopic (interference microscope “MII-4”), ellipsometric (laser ellipsometer “LEF-3M”) and gravimetric methods (crystal vibrator) [1, 17–19]. The gravimetric method of quartz microweighing sets up on definition of increment of mass (Δm) per unit surfaces of the crystal vibrator (thickness $h = 0.1\text{ mm}$) after drawing on it of aluminium film. Resolution of the instrument at thermostabilisation of resonators at a level $\pm 0.1\text{ }^\circ\text{C}$ made $\Delta m = 1 \cdot 10^{-8}\text{--}1 \cdot 10^{-9}\text{ g/cm}^2$. Medium film thickness after weighing counted by the formula

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

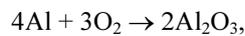
where Δm is the increment of mass of the crystal vibrator after drawing aluminium film; F_f is the film area on a substrate; ρ_m is the unit weight of the put substance [17, 18].

Samples seated on heated up to the relevant temperature ($373\text{--}600\text{ K}$) a ceramic plate and subjected to heat treatment within $1\text{--}140\text{ min}$ in drying case “Memmert BE 300” in atmospheric conditions. Recording of effects before explored sample heat treat-

ment carried out by gravimetric, microscopic and spectrophotometric (over the wave length range of 190–1100 nm) methods.

3. Results and discussion

Earlier [17–20] as a result of the systematic examinations of optical properties of thin aluminium layers put on glass substrates, up to, in process and after heat treatment in atmospheric conditions it stated, that absorption and reflection spectra of aluminium films essentially depend on their thickness, temperature and time of heat treatment. For identification of a yield of nanosize Al layers interaction with the fissile ingredients of a surrounding medium a series of experience on the complete oxidizing of aluminium films with use of the crystal vibrator has been carried out. According to the equation of reaction



it was necessary to expect, that at the x g complete oxidizing of aluminium up to Al_2O_3 the incremental value of mass will make $8/9x$.

Observed data are given in the table. From the table it is visible, that oxidizing reaction of different thickness nanosize aluminium films in an explored interval of heat treatment temperatures proceeds in the stoichiometric relationships relevant to Al_2O_3 formation. Kinetic curves of thermal conversion degree $\alpha = f(\tau)$ for aluminium films obtained by results of evaluations on increment of mass of resultant of reaction are given at 373 K in Fig. 1.

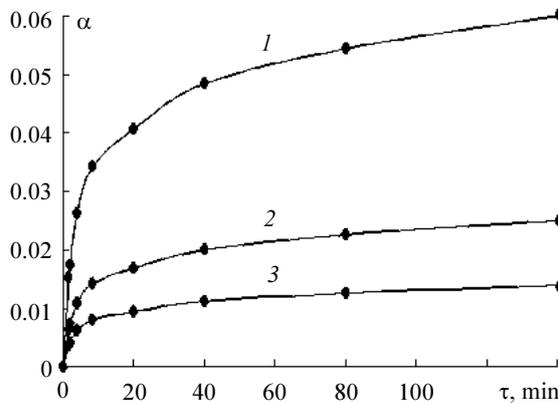


Fig. 1. Dependence of fractional conversion of aluminium films on their initial thickness, calculated on increment of mass of resultant of reaction at 373 K: 1 – 38; 2 – 92; 3 – 164 nm

For transpiring legitimacies of passing of process of an oxidizing (using observed data of absorption and reflection spectra of different thickness aluminium films before heat treatment at different temperatures) kinetic dependences of fractional conversion $\alpha = f(\tau)$ have been designed and built at various wavelengths. The following approach has been applied for build-up of kinetic curves in coordinates $\alpha = f(\tau)$. On the basis of the analysis of absorption and reflection spectra of aluminium and Al_2O_3 films for build-up of kinetic curves $\alpha = f(\tau)$ picked a gamut of wavelength of $\lambda = 400\text{--}900$ nm in which aluminium film have the considerable uptake, and Al_2O_3 uptake can be neglected (on the different data breadth of forbidden region of Al_2O_3 makes $E \geq 3.5\text{--}9.5$ eV [10, 17–20]). Optical density (A_{samp}) of aluminium film depends on heat treatment time and at fixed time of heat treatment will develop of optical density, connected with presence of aluminium (A_{Al}) and aluminium oxide ($A_{Al_2O_3}$) layers:

$$A_{samp} = A_{Al} + A_{Al_2O_3}.$$

If to mark out through α a degree of thermal conversion of aluminium films in aluminium oxide, at wave length (for example, $\lambda = 590$ nm), the relevant spectral area in which limits aluminium absorbs, and aluminium oxide practically does not absorb light [10, 14, 17–20], current optical densities of aluminium (A_{Al}) and aluminium oxide ($A_{Al_2O_3}$) films can be presented in the following view:

$$A_{Al} = A_{Al}^1 (1 - \alpha),$$

$$A_{Al_2O_3} = A_{Al_2O_3}^1 \cdot \alpha,$$

where $A_{Al}^1, A_{Al_2O_3}^1$ are the limiting optical density of aluminium and aluminium oxide layers at $\lambda = 590$ nm. In a summary it is received the following expression for a degree of thermal conversion of aluminium film in aluminium oxide:

$$A_{samp} = A_{Al}^1 (1 - \alpha) + A_{Al_2O_3}^1 \cdot \alpha,$$

$$\alpha = (A_{Al}^1 - A_{samp}) / (A_{Al}^1 - A_{Al_2O_3}^1).$$

As a result of machining absorption spectra it stated, that the degree of thermal conversion of aluminium films depends on tentative thickness, temperature and heat treatment time, and kinetic curves $\alpha = f(\tau)$

Table. Theoretical and experimental values of increment of mass of oxidized aluminium films for a case of Al_2O_3 formation

T, K	Initial frequency of the resonator, Hz	Frequency after drawing Al film, Hz	$d(Al), nm$	Frequency at $\alpha = 100\%$, Hz	Experimental difference of frequencies for $\alpha = 100\%$, Hz	Theoretical difference of frequencies for $\alpha = 100\%$, Hz
373	7999612	7999098	38	7998642	456	457
373	7999524	7998279	92	7997173	1106.5	1106.5
373	8000953	7998734	164	7996760	1974	1973
423	7999266	7999022	30	7998495	365	361
423	7999721	7999274	80	7997675	964	962
423	7999651	7999069	196	7994654	2345	2357.5

for aluminium films of the various thickness, obtained by results of quartz microweighing and measuring of absorption spectra (Figs. 1 and 2), practically coincide.

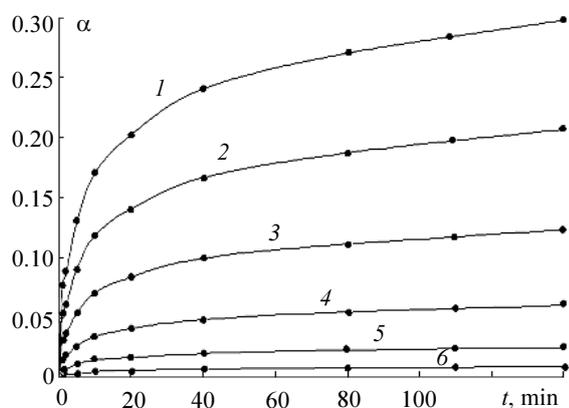


Fig. 2. Dependence of fractional conversion of aluminium films on thickness at 373 K: 1 – 7; 2 – 11; 3 – 19; 4 – 38; 5 – 92; 6 – 219 nm

It has been marked, that the degree of thermal conversion in accordance with magnification of heat treatment time increases. Diminution of aluminium film thickness results in magnification of thermal conversion degree in all an explored interval of temperatures ($T = 373\text{--}573\text{ K}$).

In Figs. 2–4, kinetic curves of fractional conversion of aluminium films are given depending on tentative thickness at 373, 423, and 573 K, accordingly.

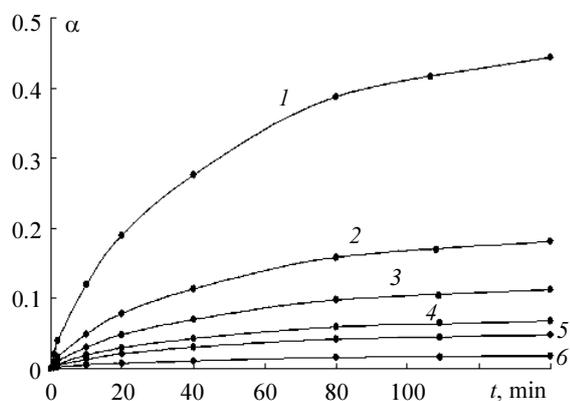


Fig. 3. Dependence of fractional conversion on thickness of aluminium films at 423 K: 1 – 8; 2 – 19; 3 – 30; 4 – 50; 5 – 71; 6 – 195 nm

The magnification of heat treatment temperature at stationary thickness of aluminium films results in increment of thermal conversion degree.

It is known [1, 2], that one of the basic requirements describing ability of educated initial layer of interaction yields of a surrounding medium ingredients with metal to apply the brakes the further oxidizing of metal, is continuity of a received oxide layer.

The formed oxide layer will interfere with infiltration of the agents participating during an oxidizing in reaction chamber, and thus to apply the brakes its fur-

ther propagation. According to Pilling and Bedvorts measure which for aluminium makes 1.28 [1, 2], it was necessary to expect formation of the continuous oxide layer, considerably braking the further passing of oxidizing process, and, as investigation, in a theoretical case [21] – the parabolic law of an oxidizing process of aluminium films, limited by diffusion of Al^{3+} ions through oxide layer to its surface (Al^{3+} ionic radius makes 0.5 \AA , and Al atomic radius – 1.43 \AA) [1, 2, 8, 9]:

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

where L is the film thickness; τ is the oxidizing time; k is the kinetic oxidizing constant; A is the integration constant.

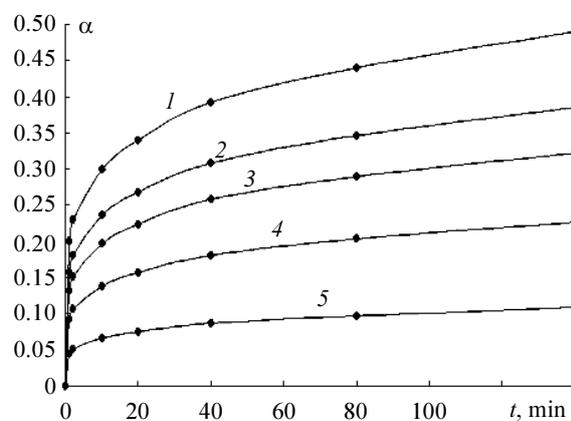


Fig. 4. Dependence of fractional conversion of aluminium films on thickness at 573 K: 1 – 21; 2 – 26; 3 – 32; 4 – 45; 5 – 94 nm

In an assay value of kinetic dependences of fractional conversion it set, that at heat treatment of aluminium films by thickness of 2–200 nm in atmospheric conditions in an interval of temperatures 373–573 K within 140 min kinetic curves of an oxidizing of aluminium films are well featured within the framework of the parabolic law.

The incipient state of an oxidizing of metals considers chemisorption of oxygen (as a rule, in the nuclear shape) on a metal surface, and after formation of several lattice constants of oxide – on oxygen – oxide interface [21]. And, on a surface of aluminium films continuous oxide layers are shaped.

Oxide layers on aluminium have ionic crystalline structure [1, 2], having ionic and, to some degree, electronic conductivity.

Therefore with the major basis it is necessary to expect, that corrosion process of aluminium films will be applied the brakes by diffusion through a aluminium oxide film not aluminium atoms (1.43 \AA), and ions (0.5 \AA) and mobile electrons (between points of the lattice) which further propagation will be retarded gradually at magnification of oxide layer thickness [1, 2].

References

- [1] N.D. Tomashov, *Theory of corrosion and protection of metals*, Moscow, AN USSR, 1960, p. 592.
- [2] G.T. Bachvalov, *Protection of metals against corrosion*, Moscow, Metallurgiya, 1964, p. 288.
- [3] *The brief chemical encyclopedia*, Vol. 1, Moscow, Sov. Encyclopedia, 1961, p. 1263.
- [4] V.I. Striha and E.V. Buzaneva, *Principal physics of reliability of metal – semiconductor contacts in an integronics*, Moscow, Radio and Communication, 1987, p. 254.
- [5] A.V. Spiridonov, *Building Materials* **7**, 4 (1998).
- [6] I.Z. Indutnyj, M.T. Kostyshin, O.P. Kasjarum, V.I. Minko, E.V. Mihajlovskaja, and P.F. Romanenko, *Photoboosted interactions in metal – semiconductor structures*, Kiev, Naukova dumka, 1992, p. 240.
- [7] E.P. Surovoi, S.M. Sirik, and L.N. Bugerko, *Chem. Phys.* **19**, 22 (2000).
- [8] P. Kofstad, *Diversion from stoichiometry. Diffusion and electric conductivity in prime metals oxides*, Moscow, World, 1975, p. 399.
- [9] *An oxidizing of metals*, Moscow, Metallurgiya, 1969, p. 448.
- [10] D.E. Bergeron, P.J. Roach, A.W. Castleman, and S.N. Khanna, *Sci.* **307**, 231 (2005).
- [11] *Technology of thin films*, Moscow, Sov. Radio, 1977, p. 664.
- [12] V.E. Minajchev, *Drawing of films in vacuum*, Moscow, Vyssh. Shkola, 1989, p. 110.
- [13] V.B. Lazarev, V.V. Sobolev, and I.S. Shaplygin, *Chemical and physical properties of prime metal oxides*, Moscow, Nauka, 1983, p. 239.
- [14] M.M. Gurevich, *Photometry*, Leningrad, Energoatomizdat, 1983, p. 272.
- [15] V.A. Afanasjev, *Optical measurings*, Moscow, Vyssh. Shkola, 1981, p. 229.
- [16] M.I. Epstein, *Measurings of optical radiation in electronics*, Leningrad, Energoatomizdat, 1990, p. 256.
- [17] N.V. Borisova, E.P. Surovoi, I.V. Titov, *Materials Technol.* **7**, 16 (2006).
- [18] E.P. Surovoi, S.V. Bin, and N.V. Borisova, I.V. Titov, *Materials Technol.* **4**, 23 (2007).
- [19] E.P. Surovoi, I.V. Titov, and L.N. Bugerko, *Materials Technol.* **7**, 15 (2005).
- [20] N.V. Borisova and E.P. Surovoi, *Corrosion: materials, protection* **6**, 13 (2007).
- [21] P. Barre, *Kinetics of heterogeneous processes*, Moscow, Mir, 1976, p. 400.