

Oxidizing of Nanosize Lead Films¹

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Abstract – By gravimetric, microscopic and spectrophotometric methods it set, that as a result of heat treatment in an interval of temperatures 423-573 K within 1–90 min in atmospheric conditions thickness, mass, absorption and reflection spectra of lead films ($d = 5\text{--}135\text{ nm}$) considerably change. Changes of absorption spectra, thickness and masses of lead films are bound to lead (II) oxide formation on their surface.

1. Introduction

Lead, alloys and linkings on its bottom due to a complex of the positive properties (plasticity, low melting point, rust resistance, etc.) have found wide application in various fields of a science, technique, industry [1-5]. However lead is thermodynamic labile in atmospheric conditions [1-3, 10]. Dissociation tension of lead (II) oxide at $T \geq 423\text{ K}$ enough low ($\sim 3.1 \cdot 10^{-38}\text{ atm}$) and consequently at engagement with a surrounding medium lead is exposed to atmospheric corrosion [1].

Effects of examinations of the processes proceeding in requirements of an atmosphere in nanosize lead films of various thicknesses depending on temperature and time of thermal action in-process presented.

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 ($5\text{--}135\text{ nm}$) lead films on glass substrates, using vacuum universal post "VUP-5M". In the capacity of an evaporator used the floating troughs manufactured of molybdenum [6, 9]. Thickness of lead films is defined by spectrophotometric, microscopic and gravimetric methods [6]. The gravimetrical method of quartz microweighing sets up on definition of mass increment (Δm) per unit surfaces of the crystal vibrator (thickness $h = 0.1\text{ mm}$) after drawing of lead film on it. Resolution of the instrument made $\Delta m = 1 \cdot 10^{-8}\text{--}1 \cdot 10^{-9}\text{ g/cm}^2$ at thermostabilisation of resonators at a level $\pm 0.1\text{ }^\circ\text{C}$.

Samples are subjected to heat treatment in drying case "Memmert BE 300" during 1–90 min in atmospheric conditions in temperature interval 423–573 K. Registration of effects is carried out by gravimetric, microscopic and spectrophotometric (spectrophotometer "Shimadzu UV-1700") methods.

3. Effects and their discussion

As a result of the examinations of optical properties of lead films put on glass substrates, up to, in process and after heat treatment in atmospheric conditions it stated, that absorption and reflection spectra of lead films before heat treatment essentially depend on their thickness.

In Fig. 1, absorption spectra of lead films of different thickness are given.

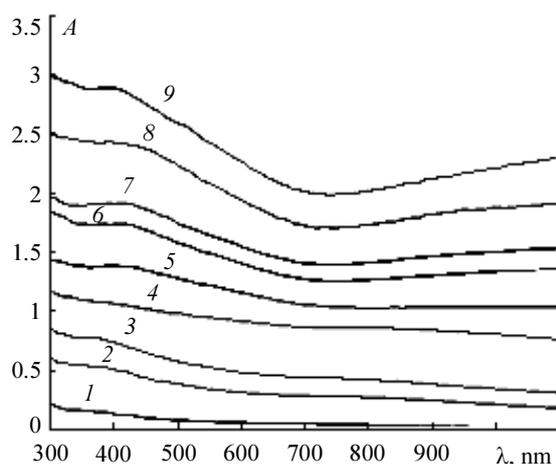


Fig. 1. Absorption spectra of lead films of various thickness: 1 – 5; 2 – 17; 3 – 25; 4 – 50; 5 – 60; 6 – 77; 7 – 86; 8 – 110; 9 – 135 nm

It is visible, that in an explored gamut of wavelengths on spectral absorption curves for all explored samples it is possible to bleed characteristic strips for lead [3, 6, 9]. In accordance with diminution of lead film thickness characteristic strips for lead gradually cease to be displayed on spectral absorption curves. For lead films by thickness ($d < 5\text{ nm}$) structureless absorption and reflection over the range $\lambda = 190\text{--}1100\text{ nm}$ are observed. The reflection factor (R) of luminous flux falling on a normal line to an even surface of a solid body from empty space (air), is [7, 8]

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

where n and k are the refraction and absorption factors.

Absorption and deflecting coefficients and as consequence, a reflection factor substantially depend on

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wavelength of an incident light [7, 8]. For chemically pure lead at $\lambda = 589 \text{ nm}$ $n = 2.01$, $k = 3.48$ [8], and $R = 0.62$. To this value of a reflection factor correspond lead film of thickness more than 85 nm.

From the equation follows, that if in a fixed spectral gamut the solid body does not capture light the reflection factor will depend only on value of refraction index. Figuring, that a main product of lead is lead (II) oxide at heat treatment which refractivity makes 2.535–2.71 depending on modification [2], a reflection factor for PbO should make quantity ≈ 0.19 – 0.21 .

Thus, at thermal transpiration on a surface of lead films is shaped lead (II) oxide layer and in accordance with diminution of thickness optical properties of lead films all in the greater degree (at film thickness less than 14 nm practically completely) are defined by presence of PbO film on their surface. Changes of absorption and reflection spectra, thickness and weights of lead films after heat treatment largely depend on tentative thickness of lead films, temperature and heat treatment time. In Fig. 2, absorption spectra of lead films by thickness $d_{\text{pb}} = 50 \text{ nm}$ before heat treatment at 523 K are given.

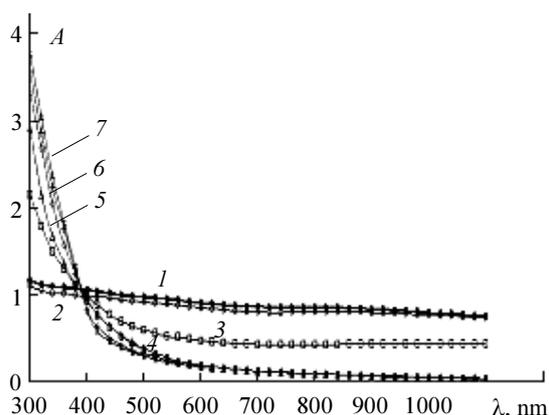


Fig. 2. Absorption spectra of lead film with thickness $d_{\text{pb}} = 50 \text{ nm}$ before heat treatment at $T = 523 \text{ K}$: 1 – 0; 2 – 2; 3 – 5; 4 – 10; 5 – 20; 6 – 30; 7 – 60 min

It is visible, that heat treatment results in essential changes of a view of absorption spectra of samples. We shall note that apparent changes are not additive in a viewed spectral gamut of wavelengths. Alongside with diminution in the $\lambda = 380$ – 1100 nm interval and magnification in the interval of $\lambda = 300$ – 380 nm of sample of optical density are shaped an absorption spectrum of new substance.

Rated on a long-wavelength threshold of absorption [in coordinates $k \sim (E_v - E_i)^{0.5}$] which is at $\lambda \approx 430 \text{ nm}$, the optical breadth of a forbidden region of formed substance makes $E \approx 2.9 \text{ eV}$. Received value of breadth of a forbidden region of substance well coincides with breadth of a forbidden region of lead (II) oxide [10]. Therefore, the guess has been made, that the main product of lead film interaction

with ingredients of a surrounding medium at heat treatment is lead (II) oxide.

At magnification or diminution of temperature at which heat treatment was carried out, legitimacies of change of absorption spectra irrespective of initial thickness of lead films are conserved, diminution of optical density is observed. At equal initial thickness of lead films with magnification of temperature increment of effects of optical density change are observed. In accordance with magnification of thickness of lead films (down to 135 nm) at a heat treatment stationary temperature (in the interval 423–573 K) is observed serial diminution of effects of optical density change in all an explored spectral gamut.

For transpiring legitimacies of passing of lead film interaction process with the fissile ingredients of a surrounding medium (using observed data of absorption and reflection spectra of lead films of different thickness 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 for build-up of kinetic curves in coordinates $\alpha = f(\tau)$ has been applied. On the basis of the analysis of absorption and reflection spectra of lead and PbO films received in the present work for build-up of kinetic curves $\alpha = f(\tau)$ has been chosen a gamut of wavelength of $\lambda = 400$ – 900 nm in which lead film have the considerable absorption and PbO absorption can be neglected.

Degree of lead film thermal conversion in lead (II) oxide have been determined

$$\alpha = (A_{\text{pb}}^1 - A_{\text{samp}}) / (A_{\text{pb}}^1 - A_{\text{pbO}}^1),$$

where A_{samp} is the optical density of lead film; A_{pb}^1 , A_{pbO}^1 are the limiting optical densities of lead and lead (II) oxide films at $\lambda = 750 \text{ nm}$.

True (caused by light absorption in substance) value of optical density

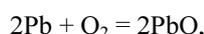
$$A_{\text{samp}} = A + \lg(1 - R).$$

It stated that the thermal conversion degree of lead films depends on tentative thickness, temperature and heat treatment time. Irrespective of initial thickness of lead films in accordance with magnification of heat treatment time the degree of thermal conversion increases. Diminution of thickness of lead films results in magnification of a degree of thermal conversion in all an explored temperature interval ($T = 423$ – 573 K). The magnification of heat treatment temperature at a stationary thickness of lead films results in increment of thermal conversion degree. In Fig. 3, kinetic curves of fractional conversion of lead films ($d_{\text{pb}} = 50 \text{ nm}$) at various temperatures are given.

With magnification of heat treatment temperature the mass fraction of the formed lead (II) oxide is incremented.

By comparison of lead (II) oxide masses, measured at different times and temperatures of heat treat-

ment under condition of the complete an oxidizing of lead films of different thickness and designed on the equation



their satisfactory concurrence is established.

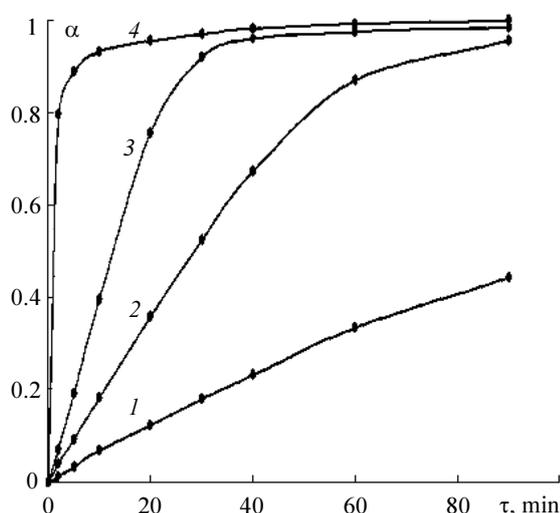


Fig. 3. Dependence of fractional conversion of lead film ($d_{\text{pb}} = 50 \text{ nm}$) from temperature: 1 – 423; 2 – 473; 3 – 523; 4 – 573 K

Heat treatment results in magnification of thickness of lead (II) oxide films. In Fig. 4, kinetic curves of the thickness change of lead (II) oxide formed on lead films surface ($d_{\text{pb}} = 78 \text{ nm}$), presented at various temperatures.

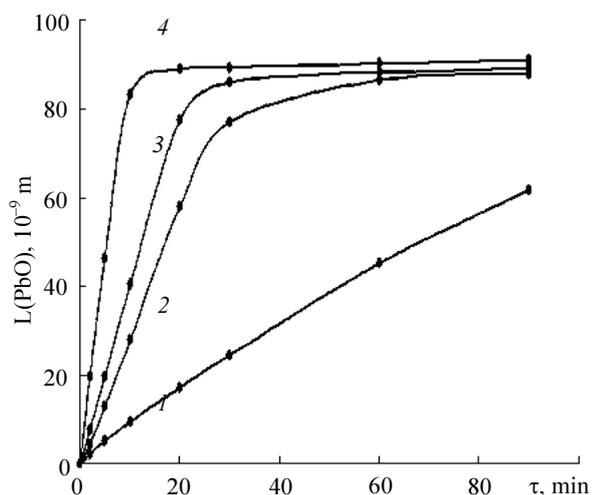


Fig. 4. Dependence of thickness of lead (II) oxide from heat treatment time at various temperatures ($d_{\text{pb}} = 78 \text{ nm}$): 1 – 423; 2 – 473; 3 – 523; 4 – 573 K

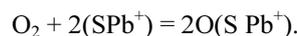
It is visible, that in accordance with magnification of temperature the considerable and enough sharp incremental value of lead (II) oxide already at small times of heat treatment is observed. And velocity of an incremental value of lead (II) oxide the more, than less lead film thickness.

At 423 and 473 K temperatures $\alpha = f(\tau)$ kinetic curves of Pb films ($d = 50 \text{ nm}$) are well featured within the framework of the parabolic law [$\lg \alpha = f(\lg \tau)$]. At 523 and 573 K temperatures initial sections of $\alpha = f(\tau)$ kinetic curves for Pb films ($d = 50 \text{ nm}$) are practically linear and with magnification of heat treatment time are featured within the framework of the logarithmic law [$\alpha = f(\lg \tau)$].

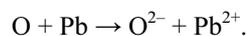
According to representations [1, 10, 11] propagation of thin films as a result of interaction of a solid body with a gaseous fluid is bound to processes of a chemical adsorption of gases (or their ingredients) on a solid body surface, “nucleuses” formation on a surface, and after formation of several lattice constants and conduction of ions of a different sign and electrons in generated layer of new substance (or substances).

During a chemical adsorption [12] particles which are taking place in the adsorbed state, differ by the nature from the relevant molecules in a gas phase, representing not molecules, and separate parts of these molecules which conduct self-contained existence on a surface. We guess, that at O_2 chemical adsorption mobile electrons (in PbO lattice built from Pb^{2+} and O^{2-} ions, to a mobile electron corresponds Pb^+ state, and to a loose electron defect – O^- state, vagabonding on Pb^{2+} and O^{2-} regular ions) of lead (II) oxide lattice (in accordance with approach of oxygen molecule to PbO surface) all in the greater degree are localized about those points on a surface (S Pb^+) to which the oxygen molecule comes nearer.

Thus between oxygen atoms and PbO surface there are the communications provided with localized electrons (S Pb^+) and hardened in accordance with approach of oxygen molecule. Communication between oxygen atoms gradually relaxes. In a summary atoms of oxygen appear the bound with PbO surface:



Necessary for chemisorbed oxygen atoms ionization electrons if thickness of an oxide layer less 5 nm, can tunnel from metal through lead (II) oxide layer [1, 10, 11]



The lead (II) oxide layer formed during reception of lead films will interfere with travel of Pb^{2+} ions (radiuses of lead atom and Pb^{2+} make 1.74 and 1.21 Å accordingly) and, thus, to apply the brakes lead interaction with oxygen.

One of requirements [1, 10, 11], describing ability of lead (II) oxide to apply the brakes process of interaction, is continuity of lead (II) oxide film. According to Pilling and Bedvorts measure, which for lead makes 1.31 [1], it is necessary to expect formation of a continuous oxide layer. Because of enough high electronic mobility and low speed of a motion of lead ions in Pb–PbO system there is a potential. This potential creates an electric field in PbO layer, which boosts

a motion of Pb^{2+} ions to an exterior oxide surface. Thus, it agrees [10, 11] depending on type of admittance of an oxide layer (in a theoretical case) cubic and parabolic laws of propagation of thin oxide layers can be implemented.

When PbO film thickness less 5 nm an electric field (on estimates [10, 11] electric field strength makes 10^6 – 10^7 V/cm) capably to wrest ions from metal and to transpose them through oxide layer. Thus, growth rate of an oxide layer will be defined by pull out velocity of lead ions from lead, and experimental data in a temperature dependence of heat treatment are featured within the framework of the linear or revertive logarithmic law.

On visual, growth rate of lead oxide on a surface of lead films with thickness $d = 50$ nm at temperatures more 523 K will be defined by pull out velocity of Pb^{2+} ions from lead, and at temperatures less 523 K will be defined by diffusion rate of lead ions through an oxide layer (a limiting stage of process is diffusion of lead ions through lead oxide layer to an exterior surface) which further propagation will be retarded in accordance with magnification of thickness of PbO film.

Diffusion rate of Pb^{2+} ions, in turn, will be proportional to electric field strength. Ions of oxygen (O^{2-}) in surface fields of lead (II) oxide create new clusters. Thereof in PbO surface fields there is a deficiency of points of the lattice engaged in cations, i.e., cationic vacancies (V_c^{2-}) which presence facilitates travel of Pb^{2+} cations from metal to an exterior surface of Pb–PbO system are shaped.

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