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RESEARCH ARTICLE

INFLUENCE OF THE NANOSTRUCTURE OF TANTALUM OXIDE ON THE FLARE CHARACTER OF ITS ELECTROLUMINESCENCEWITH ANODIC-ELECTROLYSIS FORMATION IN CHEMICALLY PURE WATER

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Abstract

Theoretical and experimental studies were carried out to identify the reasons for the flash nature of the combustion of electroluminescence (EL) of tantalum oxide (Ta_2O_5), formed in chemically pure (distilled) water during high-voltage anodization of 1700 s. Nonlinear growth of the Ta_2O_5 film during this time was established, and a polychrome effect was discovered for its thicknesses from 150 ± 28 nm to 820 ± 80 nm. At the same time, EL ignition begins at an oxide thickness of 390 ± 74 nm, which corresponds to an anodization time of 78 ± 15 s, and from 968 ± 185 s until the end of this process, bright EL flashes are observed. Their luminosity can reach $2.8 \cdot 10^{-3}$ lm/m^2. It is shown that the cause of the outbreaks is explosive processes in dynamically changing Ta_2O_5 pores ranging in size from tens of nanometers to several micrometers and containing gas-discharge plasma from various products of electro- and plasma-chemical reactions with a temperature of the order of 12000 K, created due to Joule heating by the flowing current. It has been established that the formation of the plasma itself occurs as a result of electrical breakdown in pores, the field strength in which can reach the order of $3 \cdot 10^{8}$ V/m or more.

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Introduction:-

Metal tantalum (Ta), as well as its oxide (Ta_2O_5), are currently used in many areas of science and technology, ranging from scientific instrumentation, electrical industry [1], biomedical applications [2, 3] and ending with nuclear energy [4, 5]. Thus, for the manufacture of electric capacitors, a Ta_2O_5 film on the surface of a metal is usually formed by its anodic-electrolysis oxidation in various water-based electrolytes [1, 6, 7], and the phenomenon of electroluminescence (EL)[8]accompanying this process is considered as one of the informative means of its control [9, 10]. Since 2019, on a large list of metals such as Mg, Al, In, Ga, Ti, Zr, Hf, Nb, Ta, W, Er, Lu, as well as Si, we have shown the possibility of their high-voltage anodization in chemically pure water (distilled, double-distilled and deionized) of different isotopic compositions and some non-aqueous electrolytes [11, 12], and the EL generated during this process is proposed to be used as a means of controlling the growth and formation of oxide-barrier nanostructures on the surface of these metals [13–15]. As a result of research, it was found that only for Zr and Ta a flash character of luminescence is observed, and for the latter metal it turns out to be the brightest compared to all the others when they are anodized in distilled water (DW) [16]. Moreover, the brightness of EL Ta is such that it allows it to illuminate not only the technical elements inside the luminescent-electrolysis cell, but also

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objects located near it at a distance of several centimeters. The described feature of this nature of the manifestation of EL in Ta served as the basis for conducting separate studies to identify its causes. The present work is devoted to the results of these studies.

Experiment, discussion and analysis of its results:-

To ensure the unity of organization of studies on EL of anodized metals in water, these studies were carried out using the method and installation previously described in [12, 16]. The anode was a Ta wire with a diameter of 0.5 mm and a metal purity of 99.99 %, and the cathode was a platinum (Pt) wire of the same diameter and the same length as the anode. The distance (H) between the centers of the electrodes was 12 mm, and the area of their working surface was determined by the height of the anodized part of the wires, 22 ± 2 mm. The chemical purity of the Pt-cathode was 99.999 %. The specific electrical conductivity of the overboiled DW used in the work was of the order of $(1.7 \pm 0.2)\cdot 10^{-4}$ S/m, determined at a temperature of 298.0 ± 0.5 K by the conductometric method at a low-voltage frequency of 1.0 kHz. When fixing the indicated temperature value and a constant voltage of 1200 ± 3 V, anodization of Ta was carried out for the following time periods(t): 30, 50, 60, 70, 100, 300, 500, 800, 1100, 1400 and 1700 s. Each time interval corresponded to three repetitions with a new portion of Ta-wire, and the final anodizing time corresponded to a specific thickness of the oxide film with its morphostructure. During anodization, the current density (J) flowing through the luminescent electrolysis cell and the luminescence kinetics (I) of the EL of the resulting Ta_2O_5 were recorded. The structure of the latter was visualized using a scanning electron microscope (SEM) with image magnification up to 10000 times. At the same time, an analysis of the chemical composition of the oxide films was made using the energy dispersive method from ten areas with an area of 2.25 μm^2, as well as optical microscopic images of Ta_2O_5. Based on the obtained SEM images, the thickness (d) of the formed oxide and the geometric dimensions of its structural elements were estimated. Based on the values d found, the dependence of the growth of the oxide film on the time of anodization of the metal was plotted $d(t)$. Similar dependencies were determined for $J(t)$ and $I(t)$. In order to establish a possible change in the chemical composition of the DW after anodization, its optical density (D) was assessed at a wavelength of 190 nm.

Table 1 presents the results of energy dispersive analysis of the chemical composition of Ta_2O_5 films, averaged over three samples and the above number of analysis areas, and in Fig. 1 – dependence $d(t)$. As can be seen from Table 1, the resulting oxide consists only of chemical elements – tantalum and oxygen, and their weight and atomic content completely satisfies the well-known chemical formula Ta_2O_5. In this case, a linear increase in the oxide thickness is observed until approximately the sixtieth second of Ta anodization. Further, the linearity is violated and, on average from 300 s, the growth of Ta_2O_5 slows down significantly, as can be seen from Fig. 1. The range from 0 to 30 s highlighted on it with a dash-dot line refers to the expected dependence (for which there are no experimental data yet). In the same figure, a red diamond marks the moment of metal anodization, at which the ignition of the EL is reliably recorded, corresponding to a time of the order of 78 ± 15 s. The noted time instant corresponds to an oxide thickness of the order of 390 ± 74 nm.

Table 1:- Results of energy dispersive analysis of Ta_2O_5 films formed in DW(based on the example of Ta anodized for 800 s).

Chemical element	**Content, %**	
	Weight	**Atomic**
Ta	81.59 ± 8.16	32.44 ± 3.24
O	18.41 ± 1.84	67.56 ± 6.76

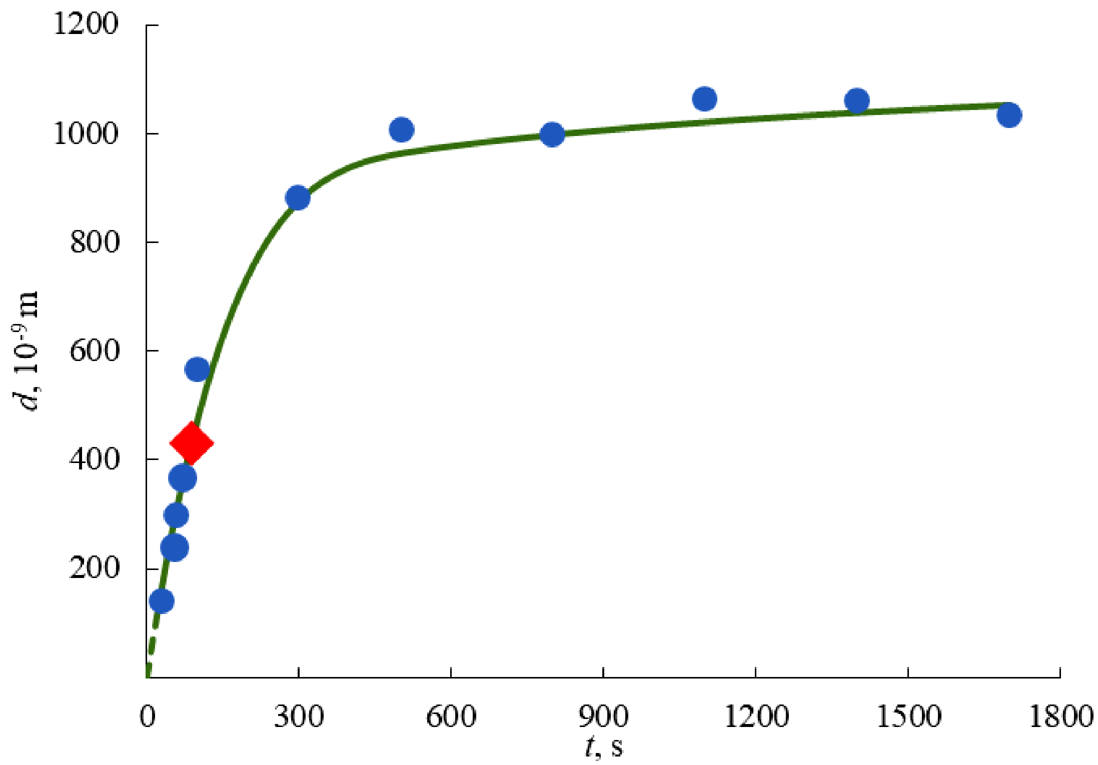

Fig. 1:- Kinetics of growth of Ta_2O_5 thickness over a time of 1700 shigh-voltage anodizing (description in text).

Note that starting from its initial thickness of 150 ± 28 nm (initial anodization interval 30 s) and up to 820 ± 80 nm (anodization time 250 s), a polychrome effect is observed in Ta_2O_5 films. It completely disappears when their thickness is more than 900 nm (anodizing time is about 300 s or more). Fig. 2 confirms this fact, which shows optical microscopic images of Ta_2O_5 films obtained at anodizing times of 30, 50 and 300 s, and in Fig. 3 – SEM images of transverse cleavages of the same films with an additional image for the film obtained during anodization time of 70 s, at which EL is detected. In addition, thanks to the graphically constructed kinetics of oxide growth over the entire anodization period up to 1700 s (Fig. 1), it was possible to approximate the dependence $d(t)$ with an error of up to 60 %, obeying a polynomial equation of the form:

$$d(t) = a_1t^6 + a_2t^5 + a_3t^4 + a_4t^3 + a_5t^2 + a_6t\,, \tag{1}$$

where $a_1 - a_6$ – are the corresponding coefficients of the polynomial, the order of magnitude of which varies from minus twenty-fifth to minus ninth power. The values of the listed coefficients with their dimensions are given in Table 2.

Table 2:- Values and dimensions of the coefficients included in equation (1).

Coefficient	Meaning and dimension
a_1	$-9.9309193839605\cdot10^{-25}$ m/s^6
a_2	$6.39312385114888\cdot10^{-21}$ m/s^5
a_3	$-1.66072819319705\cdot10^{-17}$ m/s^4
a_4	$2.22291796063145\cdot10^{-14}$ m/s^3
a_5	$-1.61749208224649\cdot10^{-11}$ m/s^2
a_6	$6.16811568600315\cdot10^{-9}$ m/s

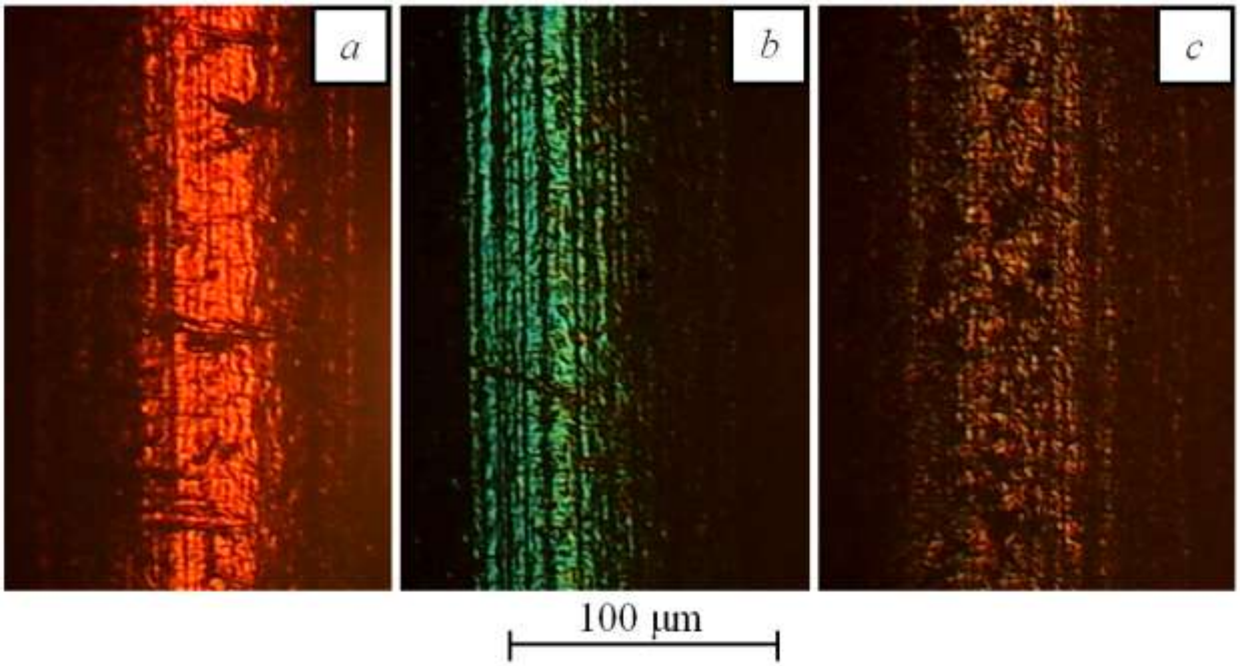

Fig. 2:- Optical microscopic images of Ta_2O_5 films formed during anodization:30 s (*a*), 50 s (*b*) and 300 s (*c*)

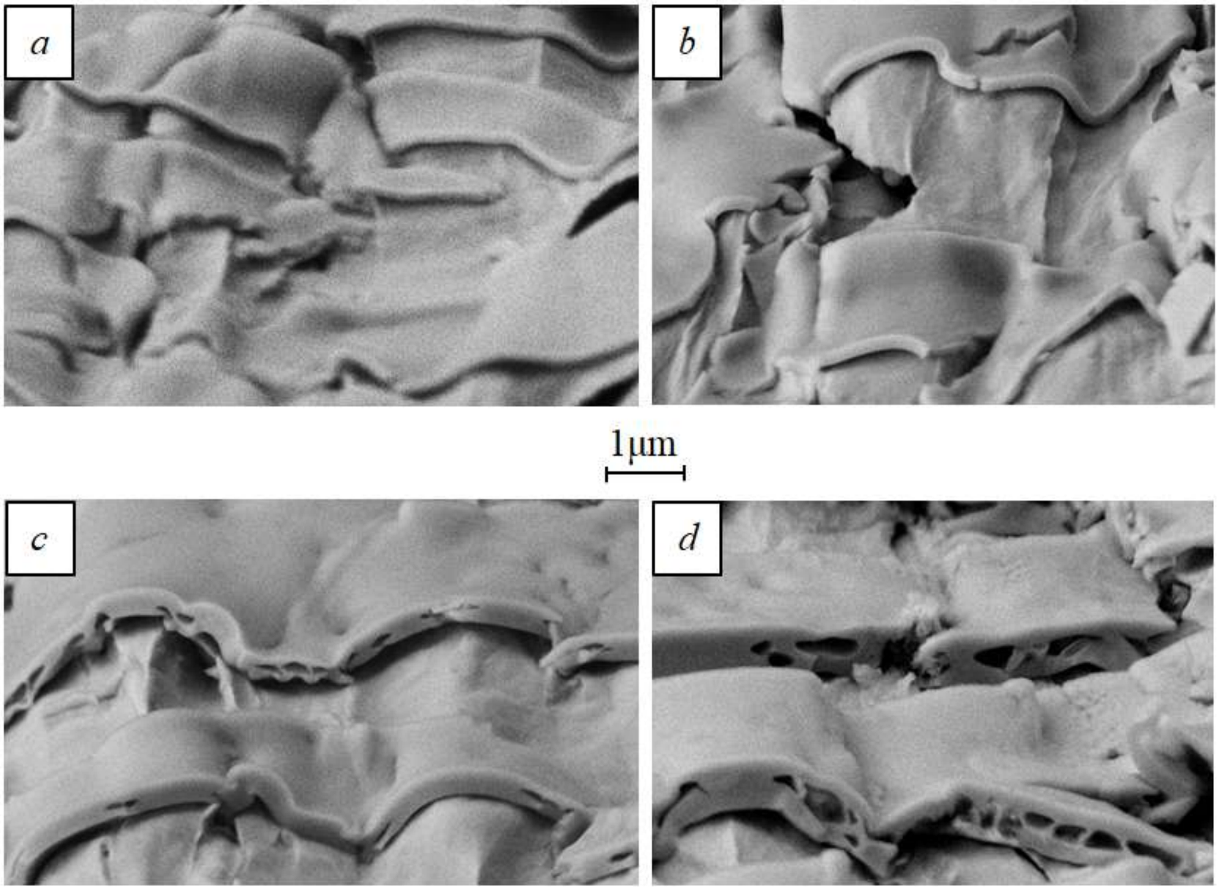

Fig. 3:- SEM images of transverse cleavages of Ta_2O_5 films, formed during anodizing time:
30 s (*a*), 50 s (*b*), 70 s (*c*) and 300 s (*d*)

As can be seen from Fig. 3, the Ta_2O_5 film formed at 30 s and 50 s does not have any pronounced morphostructural features. It is represented by a continuous formation, tightly adjacent to the metal and repeating the relief of its surface (Fig. 3*a* and 3*b*). For films formed for 70 s and 300 s, individual pores or small groups of them are already observed (Fig. 3*c* and 3*d*). Thanks to these data, it becomes clear that the appearance of luminescence corresponds to a certain thickness of Ta_2O_5, and its porous structure ensures the maintenance of EL due to the balance between the electrical charges retained and those leaving through the through pores to the anode. Thus, for the latter, the oxide film plays a unique role as a semipermeable membrane. This hypothesis is supported by the kinetic data $J(t)$ presented in Fig. 4*a*. So, at the initial moment of voltage(U)applied to the electrodes, the electric field created between them in water will ensure unhindered transfer of charges (in accordance with the electrical conductivity of the DW for these conditions), which explains the highest current density of the order of 370 A/m^2 at the named moment in time. Over a very short anodization period of 78 ± 15 s, the current quickly drops by 140 A/m^2, which indicates the formation of an obstacle in the form of Ta_2O_5, limiting current transfer. Further, upon reaching a value of 200 ± 35 A/m^2, a quasi-stationary flow regime is established J , lasting about 620 ± 118 s. During the same anodization period, similar EL combustion kinetics are observed (Fig. 4*b*). Then the current begins to gradually increase until the anodization procedure is completed, but does not reach its original value. In our opinion, this portion of the growing kinetics is due $J(t)$ to the following circumstances.

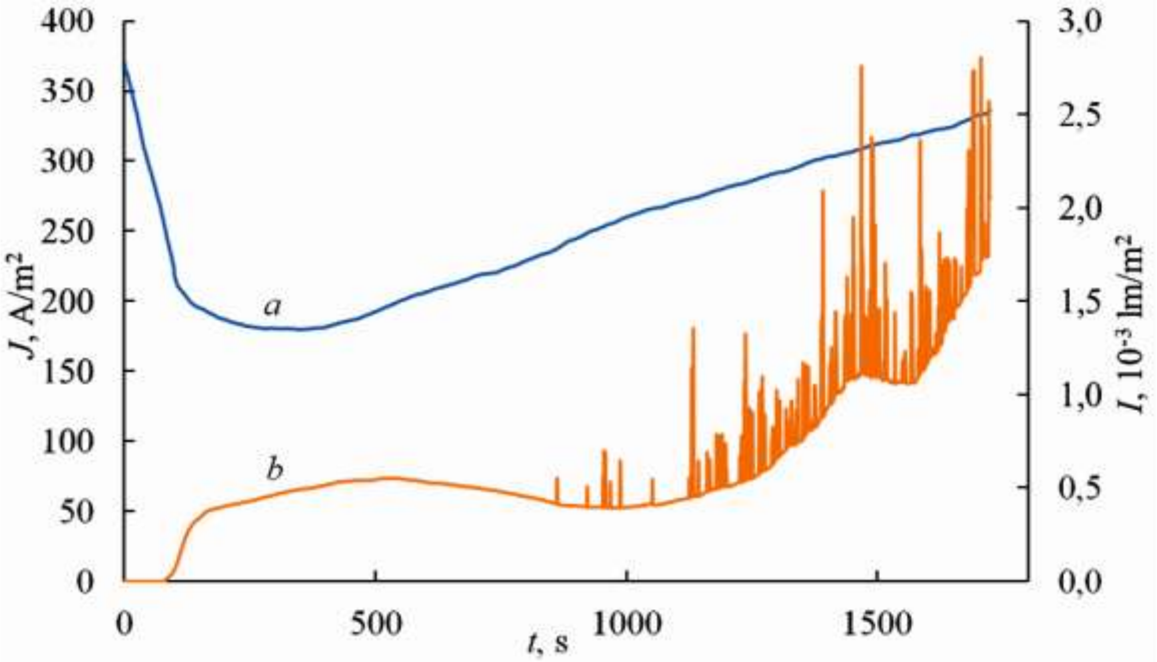

Fig. 4:- Kinetics of current density (*a*) and EL luminosity (*b*)

Intense pore formation in the growing Ta_2O_5 film leads to such conditions that the charge accumulated in the pores is capable of creating an electric field strength in them that exceeds its average value in the oxide and is sufficient for the breakdown of the DW or the ionization of gases formed during electrochemical reactions. Thus, electrical breakdown in the pores creates a qualitatively new state of matter in them – gas-discharge plasma. In turn, its appearance will lead to new physical processes, in particular, rapid local heating of the medium surrounding the electrode, which is both the oxide itself and the water in contact with it. In addition, plasma formation is accompanied by intense light emission due to energy transitions of the excited atoms and/or ions contained in it. Apparently, this process has a decisive influence on the kinetics of EL luminosity with the appearance of bright flashes in it at 968 ± 185 s of anodization, the periodicity and luminosity of which increases towards the end of this process, reaching $2.8 \cdot 10^{-3}$ lm/m^2 at the current density about 320 A/m^2 (Fig. 4*b*). Finally, the combination of the described processes involving gas-discharge plasma leads to the formation of new chemical reaction products that accumulate in water. This follows from Fig. 5, in which the change D in the DW hasatime dependence, correlating with the growth of the oxide film. The accumulation of plasma-chemical reaction products also contributes to an increase in the electrical conductivity of water [16], actually making it an aqueous solution. It should be noted that such processes are not observed, for example, during the anodization of aluminum under the same conditions and modes, as well as during its anodization in some non-aqueous electrolytes [12].

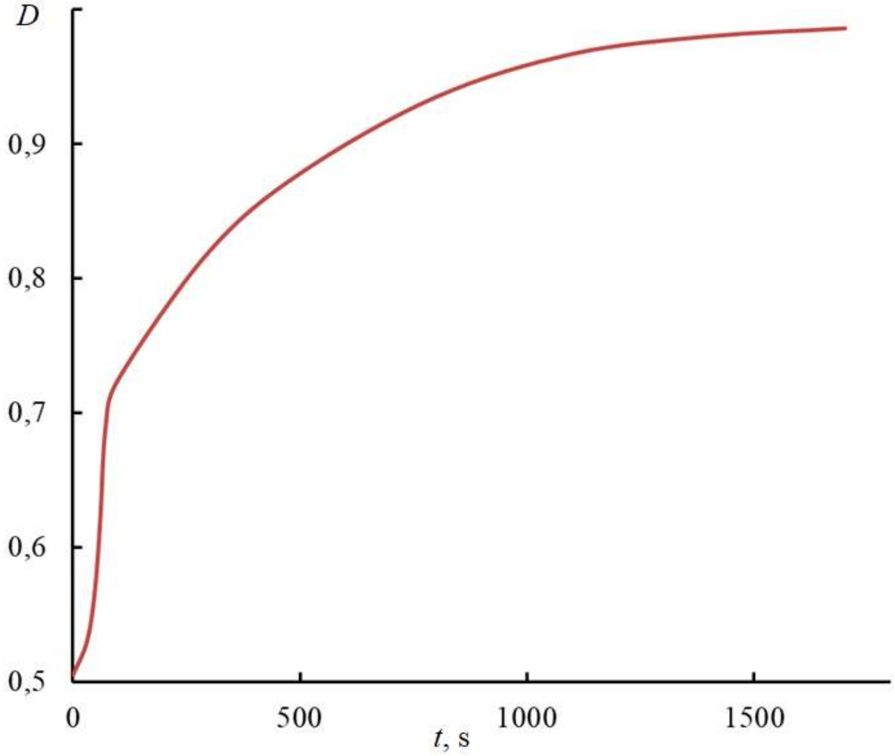

Fig. 5:- Change in optical density of DW during anodization Ta for 1700 s.

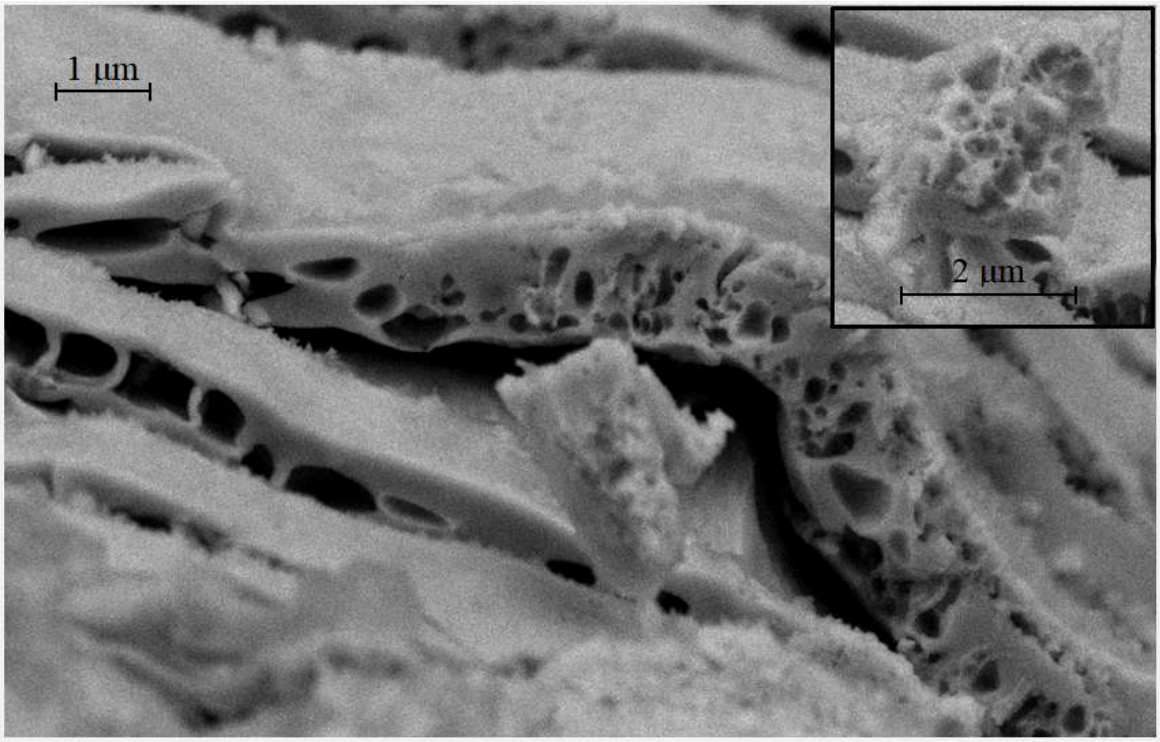

Fig. 6:- SEM image of a transverse cleavage of a Ta_2O_5 film, formed in the DW during anodizing time of 1700 s (description in the text).

Intense pore formation in the growing Ta_2O_5 film is clearly demonstrated in Fig. 6, which shows a SEM image of a transverse oxide chip (with an enlarged fragment of the lower side of its fragment adjacent to the anode), formed at the final stage of anodizing the metal at 1700 s. At the same time, the oxide film has morphostructural features. Two layers of different thicknesses are clearly distinguished in it: the lower layer with an average thickness of about 1.5 ± 0.9 μm, consisting of randomly distributed pores with a diameter of 40 ± 18 nm to 1.2 ± 0.6 μm, and the upper layer with a thickness of 220 ± 130 nm of fine particles without any clearly defined structural organization. At the same time, as can be seen from Fig. 6, there is some open pores overlapping the lower and upper layers of the oxide film. Thanks to the information obtained on the morphology and dimensions of the structural elements of Ta_2O_5, it is possible to estimate the magnitude of the electric field strength in the pores ($E_{\max}$) and thus justify the possibility of creating conditions for plasma generation in them.

The luminescent-electrolysis cell used in this work is a system of a two-layer capacitor with cylindrical electrodes, in which one dielectric layer is a DW, and the second is a Ta_2O_5 film in contact with water. Since we are interested in the processes developing in the last layer, the parameter can be determined using the following mathematical relationship, which takes into account not only the dielectric constant, but also the electrical conductivity of the layers [12]:

$$E_{\max} = \Psi\left(E\cdot\exp(-At)\cdot\left[\frac{\varepsilon_2\left((R+d_1)\ln\left(\frac{R}{R+d_1}\right)+(R+d_2)\ln\left(\frac{R+d_2}{R}\right)\right)}{\varepsilon_1(R+d_2)\ln\left(\frac{R+d_2}{R}\right)+\varepsilon_2(R+d_1)\ln\left(\frac{R}{R+d_1}\right)} - B\right] + E\cdot B\right), \quad (2)$$

where $E = \frac{U}{H\cdot\ln(H\cdot R^{-1})}$ – average field strength in a capacitor with electrode radii $R = 2.5\cdot10^{-4}$ m; $d_1 = d = 1.5\cdot10^{-6}$ m (at final anodizing time 1700 s); $d_2 = H - 2R - d_1$ – thickness of the DW layer enclosed between the Pt-cathode and the Ta_2O_5 film on the anode; $\Psi = \frac{4\pi\left(r_1^3 + r_2^3\right)}{3a^3}$ – structural coefficient (or electric field amplification/weakening coefficient), depending only on the geometric dimensions and shape of the pores, which, to simplify calculations, will be assumed to be spherical radii r_1 and r_2, located at the shortest distance a apart from each other;

$$A = \frac{\sigma_1(R+d_2)\ln\left(\frac{R+d_2}{R}\right)+\sigma_2(R+d_1)\ln\left(\frac{R}{R+d_1}\right)}{\varepsilon_0\left(\varepsilon_1(R+d_2)\ln\left(\frac{R+d_2}{R}\right)+\varepsilon_2(R+d_1)\ln\left(\frac{R}{R+d_1}\right)\right)};$$

$$B = \frac{\sigma_2\left((R+d_1)\ln\left(\frac{R}{R+d_1}\right)+(R+d_2)\ln\left(\frac{R+d_2}{R}\right)\right)}{\sigma_1(R+d_2)\ln\left(\frac{R+d_2}{R}\right)+\sigma_2(R+d_1)\ln\left(\frac{R}{R+d_1}\right)};$$

$\varepsilon_1, \varepsilon_2 \approx 80$ and σ_1, σ_2 – respectively, the dielectric constants and specific electrical conductivities of the oxide film in contact with the DV and the water itself; $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m– electrical constant.

As follows from Fig. 6, the Ta_2O_5 film pores formed in the DW and filled with it form a heterogeneous oxide–water system, for which it can be determined from the following relation [12]:

$$\varepsilon_1 = \frac{(3P_1 - 1) \cdot \chi + (3P_2 - 1) \cdot \varepsilon_2}{4} + \sqrt{\frac{[(3P_1 - 1) \cdot \chi + (3P_2 - 1) \cdot \varepsilon_2]^2}{16} + \frac{\chi \cdot \varepsilon_2}{2}}, \tag{3}$$

where $\chi = 25$ – dielectric constant of Ta_2O_5 in an air-dry state [17]; P_1 and $P_2 = 1 - P_1$ –volume fractions of Ta_2O_5 and pores in it, which were determined from SEM images (according to these data for Ta_2O_5 formed over a time of 1700 s, the value P_1 was about 0.76, and P_2, accordingly0.24). The value of the second parameter $\sigma_1 = \sigma_2 - \gamma$ can be assessed by the difference in the specific electrical conductivity of the DW at the initial moment of anodization $\sigma_2 = J_0 \cdot (H - 2R) \cdot U^{-1}$ and final $\gamma = J_{1700} \cdot (H - 2R - d_1) \cdot U^{-1}$ (where J_0 and J_{1700} is the current density at the moment of applied voltage and at the end of anodization, determined from the data in Fig. 4), which corresponds to the specific electrical conductivity of the water layer and the adjacent Ta_2O_5–DW layer. At the experimentally established value $J_0 = 370$ A/m^2 value $\sigma_2 = 3.54 \cdot 10^{-3}$ S/m, which is an order of magnitude greater than the same parameter for DW measured by the conductometric method at low voltage and indicates the manifestation of the M. Wien effect – an increase in the electrical conductivity of electrolytes in high-intensity electric fields [18].Accordingly, when $J_{1700} = 320$ A/m^2 value $\gamma = 3.07 \cdot 10^{-3}$ S/m. Then the specific electrical conductivity of a porous Ta_2O_5 film impregnated with DW (more precisely, with a substance in the pores in an ionized state) will be $\sigma_1 = 4.70 \cdot 10^{-4}$ S/m.

Based on the totality of the above data, the estimate $E_{\max}$ shows that even with $\Psi = 1$, the field value in the pores exceeds its average value by 7.5 times. However, as follows from Fig. 6, the combination of pore radii and their mutual distances determined from it can enhance the initial field value by more than 1000 times, ensuring its strength in the pores up to $E_{\max} \geq 3 \cdot 10^8$ V/m. If we take into account that under standard thermodynamic conditions the breakdown field value for the DW is of the order of $7 \cdot 10^7$ V/m [19], and for gaseous hydrogen and oxygen (into which DW can decay in plasma [20]) – 10^7 V/m [21, 22], then the found value $E_{\max}$ is more than sufficient not only for ionization processes, but also for the manifestation of the Richardson-Schottky and Poole-Frenkel effects [23]. In addition, an electric field of such strength can lead to strong Joule heating of the plasma as a result of the current flowing through it and, accordingly, to Ta_2O_5 in contact with it, and this in turn leads to a decrease in the breakdown strength of the field [24]. It is obvious that the heating will be most intense from the moment the flash combustion of EL appears (t_{968}) until the end of anodizing (t_{1700}).

Since we do not know the electrical conductivity of the plasma in individual pores, we will make approximate estimates of the temperatures T_1 and T_2, averaged over the growing Ta_2O_5 film with pores (at $\Psi = 1$) due to the flow of current through it at the initial and final moments of time t_{968} and t_{1700}. To do this, we use the well-known relation:

$$T = \sigma_1 E_{\max}^2 t \cdot C^{-1}, \tag{4}$$

where $C = 2.56 \cdot 10^6$ J·m^{-3}·K^{-1} – volumetric heat capacity of Ta_2O_5 (calculated according to data from [25, 26]). The remaining parameters correspond to those described above.

The results of estimates from (4) taking into account formulas (2) and (3) show that by the time flash combustion occurs, the Ta_2O_5 film with pores containing ionized matter can heat up to $T_1 = 2289$ K, and by the end of anodizing to $T_2 = 11833$ K. Thus, over the anodizing period $t_{1700} - t_{968} = 732$ s, the temperature difference will be $\Delta T = T_2 - T_1 = 9544$ K. Plasma existing at this temperature is classified as «cold» or low-temperature[27]. However, it exceeds the melting temperature of the oxide, which is 2145 K. Let us recall that the obtained temperature values are averaged between Ta_2O_5 itself and the pores in it with the ionized substance. Therefore, it is obvious that due to the very large difference in thermal conductivity of the oxide film(0.12 W·m^{-1}·K^{-1} [28]) and plasma (2.57 W·m^{-1}·K^{-1} at 12000 K [29]), differing by a factor of 21.4, the temperature maximum will occur in the latter, that is, most of the heat will remain in the plasma. It is clear that at Ψ >>1 and U >>1200 V, local heating of the plasma in the pores and its thermal conductivity will also increase, affecting the state of aggregation of Ta_2O_5.

Heating of the plasma will inevitably lead to an increase in pressure in the pores, which will contribute to an increase in their size. Since the concentration of plasma particles directly related to electrical conductivity for individual pores is also unknown to us, we will make indirect estimates of pressure by comparing the volumes of pore space in the Ta_2O_5 film and gases formed during electro- and plasma-chemical reactions at the anode. According to [30], the electrochemical oxidation of Ta at the anode occurs according to the following equation: $2Ta + 5H_2O \rightarrow Ta_2O_5 + 10H^+ + 10e^-$. It follows from the equation that, in addition to the oxide, protons and electrons will be formed at the anode, which can only exist in this state at temperatures of 10000 K and above [31]. Therefore, under normal thermodynamic conditions (which take place at the initial stage of anodization before the appearance of EL), the electrochemical oxidation of Ta will be accompanied by the formation of five moles of molecular hydrogen: $10H^+ + 10e^- \rightarrow 5H_2\uparrow$. Thus, the first pores in the oxide can be created by this gas. On the other hand, during an electrical breakdown in them, DW will be added to this hydrogen from decomposed water molecules, as well as oxygen according to the following stoichiometric equation [32]: $6H_2O \rightarrow 2H_2O_2 + 4H_2\uparrow +$ $+ O_2\uparrow$. From the above equations it can be seen that the total amount of hydrogen produced will be nine times greater than oxygen. Therefore, for hydrogen we will carry out the above estimates of its volume. The value of this parameter for the pore space of the Ta_2O_5 film formed during 1700 s of anodizationwas $1.26 \cdot 10^{-11}$ m^3, and the total volume of hydrogen formed during the same time was $1.77 \cdot 10^{-7}$ m^3. If we take the 24 % share of the volume of the latter that is occupied by the pore space in the oxide film, then the resulting volume of hydrogen will be $4.25 \cdot 10^{-8}$ m^3, which is 3373 times greater than that for the pore space. It follows from this that the gases formed in the pores are in a compressed state to a pressure of at least thousands of Pascals. For comparison, let us estimate the magnitude of the effect of DW on a Ta-anode with an oxide film immersed in it. Estimates show that at the above-mentioned depth of 22 ± 2 mm, the pressure will be about 215 Pascal. Thus, the pressure in the pores is no less than ten times higher than that on the Ta_2O_5 film from the water side. However, if we take into account that such a gas in the pores is in an ionized state at an average temperature $(T_1 + T_2) \cdot 0.5 \approx 7000$ K, then its pressure will already be at least a million Pascals and exceed that from water by hundreds of thousands of times. Therefore, the release of ionized products of various reactions into the DW from opening pores can be explosive.

The assessments of the electrical and thermophysical processes occurring on the oxide film make it possible not only to answer the question about the nature and causes of the appearance of bright flashes in the kinetics of EL combustion, but also to explain the feature of the Ta_2O_5morphostructure observed in SEM images. Thus, at the initial stage of the formation of the oxide film, when there are few or no pores in it, and the current is the smallest, a dynamic equilibrium is established between the heat given off by the growing film and received by the water washing the anode. Once the oxide reaches a certain thickness, the freedom of release of the resulting gaseous reaction products is limited. This promotes pore formation and at the same time increases the electric field strength in the pores, as well as the gas pressure in them. Having reached the breakdown value, all the substance located in the pores turns into plasma. Its contact with Ta_2O_5 leads to local melting of the latter and heat transfer throughout the entire volume of the oxide. However, the continuous circulation of water at a constant temperature (298 K) washing the electrodes removes excess heat, thus preventing rapid melting of the oxide film. Due to the established thermal equilibrium, the Ta_2O_5 film «softens», finding itself in a viscous-fluid state (compared to water). In such a viscous «liquid», pores filled with ionized products of electro- and plasma-chemical reactions intensively form, expand, and mostly merge. It is obvious that the zone of lowest viscosity will be near the contact of the oxide to the Ta-anode, and the highest – to the DW. This explains the peculiarity of the preferential distribution of pores of larger volume in the Ta_2O_5 zone adjacent to the anode (Fig. 6). Since the processes of formation and transformation of pores are dynamic and associated with a constant influx of these products in an ionized state at temperatures of thousands of Kelvins, their pressure in closed pores will be no less than hundreds of thousands of times higher than that in the environment. Therefore, as noted above, the opening of pores on the surface of the oxide can be explosive in nature with the release of their ionized contents into the DW and rapid decay of the plasma, which is reflected in the kinetics of EL luminosity by bright flashes (Fig. 4). Then the pores collapse and the process repeats. As data from previous studies [16] and the present ones show, the process of ejection of ionized substance is accompanied by partial capture of the oxide itself (obviously in a molten state), which, upon rapid cooling with contacting water, forms the thin (220 ± 130 nm) layer of Ta_2O_5 film described above from fine particles.

Summary:-

Anodizing metals in chemically pure water is not something new and dates back to the first works of Soviet scientists in the 1960s [33]. However, the high-voltage mode of implementation of this process and the discovery of the EL phenomenon in this case made it possible to establish its similarity with that during the anodization of metals in aqueous solutions of electrolytes at lowvoltage [8, 9, 12, 34]. At the same time, the question of the physical nature of luminescence still remains controversial. A number of researchers believe that it refers to typical EL of condensed matter, arising as a result of electron-hole recombination [8, 34] or the discharge of hydroxyl radicals at the anode [35], while others consider it to be the result only of plasma phenomena (that is, light emitted by the plasma itself) [36, 37]. The results of this work clearly support the latter opinion. However, we consider this conclusion to be valid only for Ta_2O_5 and its structure and properties similar to oxides for the following reason. Since plasma is a wide-range light source (especially in the short-wavelength region of the spectrum), the situation cannot be ruled out that it will excite photoluminescence of the oxide itself, the radiation of which will already satisfy the electron-hole mechanism and be secondary in relation to the plasma one, superimposing on it. It is clear that the fractional contribution of light from one or another source depends on the conditions of occurrence of the source itself, directly determined by the properties and structure of the oxide being formed, as well as the conditions and modes of metal anodization. An example of such a situation is the EL of aluminum oxide formed on a metal under conditions identical to those described for Ta_2O_5. However, in the kinetics of its luminescence there is no flash character of combustion, and the morphostructure of aluminum oxide is expressed by an ordered system of cells [12]. Even the disordered structure of aluminum oxide formed in alcohols from pores of different sizes does not lead to flash combustion of EL, although the values $E_{\max}$ for both conditions of aluminum anodization reach those calculated in Ta_2O_5 pores [12]. This indicates a possibly different mode of plasma combustion in the «constrained» conditions of nanopores of aluminum oxide cells, in contrast to the structure and properties of Ta_2O_5 described above. Thus, based on the results obtained in this work, the following conclusions can be drawn:

1. Over a period of about 60 s of high-voltage anodization of Ta in the DW, linear growth of the Ta_2O_5 film occurs. Further, linearity is violated and at an oxide thickness of 390 ± 74 nm, EL ignition is reliably recorded, corresponding to an anodization time of the order of 78 ± 15 s. It was found that starting from an initial oxide thickness of 150 ± 28 nm (initial anodization interval 30 s) and up to 820 ± 80 nm (anodization time 250 s), Ta_2O_5 films exhibit a polychrome effect, which completely disappears when their thickness is more than 900 nm.

2. It has been shown that during the growth of the Ta_2O_5 film, intensive formation and transformation of pores with a diameter from tens of nanometers to several micrometers occurs. This process contributes to a local increase in the electric field to a value of the order of $3 \cdot 10^8$ V/m and the creation in the pores of conditions for the generation of gas-discharge plasma due to the breakdown and ionization of both the DW itself and the gaseous products of various chemical reactions – oxygen and hydrogen. In this case, the plasma temperature by the end of anodization (at 1700 s) can reach almost 12000 K. Contact of plasma with Ta_2O_5 leads to local melting of the latter and «softening» of the entire oxide film due to heat exchange (in fact, between the plasma and the DW through the Ta_2O_5 film), acquiring the property of very viscous «liquid» (compared to water). In such a «liquid», conditions are created for an increased pressure of the ionized substance in the pores in relation to the surrounding oxide environment by at least hundreds of thousands of times. As a result, the release of ionized products of electro- and plasma-chemical reactions from pores that are constantly changing in size and shape can be explosive, which is reflected in the

kinetics of EL luminosity with bright flashes starting from 968 ± 185 s of anodization and accompanying luminescence until the end of this process. In this case, the luminosity of individual flares can reach $2.8\cdot10^{-3}$ lm/m^2.

3. The result of the release of pore contents into the DW surrounding the Ta-anode is contamination of the latter with products of plasma-chemical reactions, the degree of accumulation of which correlates with the kinetics of growth of the oxide film.

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