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## Anodic aluminum oxide formed in aqueous solutions of chelated complex zinc and cobalt compounds

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The galvanostatic anodizing results of specially prepared high-purity aluminum in aqueous solutions of complex compounds  $K_3[Co(C_2O_4)_3]$  and  $K_2[Zn(edta)]$  of various concentrations in the current density ranges  $1.5-1.10 \cdot 10^2$  and  $1.5-30 \text{ mA} \cdot \text{cm}^{-2}$ , respectively. The kinetic features of anodizing have been established, indicating the occurrence of an oscillatory electrochemical process. Morphological features of a flaky and loose nature for  $K_2[Zn(edta)]$  and monolithic for  $K_3[Co(C_2O_4)_3]$ , uncharacteristic for anodic aluminum oxide, were revealed. The elemental composition, IR spectroscopic and photoluminescent characteristics of the formed oxides are shown.

**Keywords:** anodic aluminum oxide, chelated complex compounds, anodizing.

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### Introduction

Creation of nanosized structures and composite materials using porous anodic aluminum oxide (AAO) as a high-ordered nanostructured matrix is a popular and rapidly developing direction of nanotechnologies [1–3]. Cellular and porous structure of AAO provides wide possibilities for controlled variation of its morphological parameters, allowing to create a wide range of functional materials [4–10].

Electrolyte composition plays an important role in the process of structure formation of oxides of valve metals: titanium, hafnium, niobium, tantalum, tungsten, vanadium and zirconium [11–14]. It should be noted that formation of porous and tubular oxides of these metals has become possible due to adding of small quantities of fluoride ions, that are ligands, creating strong complex compounds with many metal ions, to anodizing electrolytes [15]. Aluminum anodizing electrolyte composition [16–18] and experimentation modes [18–20] also significantly influence the properties and composition of its anodic oxide. In terms of additional opportunities for AAO composition control, the biggest interest is generated in processes of AAO formation in electrolytes, which composition includes complex compounds and/or ligands, capable to create stable complex compounds [15].

The idea of complexing additives adding to electrolytes for cathodic deposition of coatings is not new, it is a long-established practice [22,23]. Processes related to alternating current or cathodic coloring of pre-formed layers of AAO also usually assume presence of complexing organic reagents [24]. AAO modification process, consisting in cathodic deposition of indium antimonide to AAO pores, also includes significant concentration of citrate-anions [3].

It should be noted that some acids, used during anodizing electrolyte preparation [25–28], are prone to creation of soluble complex compounds with aluminum ion [15]. As was demonstrated before [18], special addition of substances, containing ligands, creating stable soluble complex compounds with aluminum [15], is possible, resulting in significant change of both anodic oxidation process nature and its anodic oxide morphology. Similar studies were performed using organic reagent Arsenazo I (disodium salt of 3-[(2-arsonophenyl)azo]-4,5-dihydroxy-2,7-naphthalenedisulfonic acid), creating very stable chelated complexes with  $Al^{3+}$  ion and some others [15]. The first brief message on this topic is dated back in 2003 [29], and after that the studies followed and were presented in some brief messages [30–35]. In the mentioned studies it was shown that with increase of Arsenazo I concentration the abrupt growth of dissolution rate and drop of maximum and stationary voltage values of anodizing kinetics are happened; there is a tendency towards increase of additive threshold concentration with increase of anodic current density, while the „burning point“ phenomenon, described, for instance, in [36–38] disappears; and in [31,32,39] the authors claim that they observed the anomalously high content of electrolyte components, integrated into AAO structure directly during its formation, for the first time.

Addition of new additives, creating stable complex compounds insoluble in electrolyte, for instance, o-hydroxyquinoline and/or its derivatives, is possible [15]. Anodizing in electrolytes with similar additives results in improvement of electrophysical characteristics of the formed AAO [40] and change of its spectral-luminescent properties [39].

Besides adding of substances additives, containing ligands, capable to create soluble or insoluble complex compounds with ions of anodized valve metal, to the anodizing electrolyte, the approach, when additive is a pre-synthesized stable complex compound, containing ion of a complexing agent of a nature, other than anodized metal ion, is also possible. Only small number of studies dedicated to this topic is known [39,41,42].

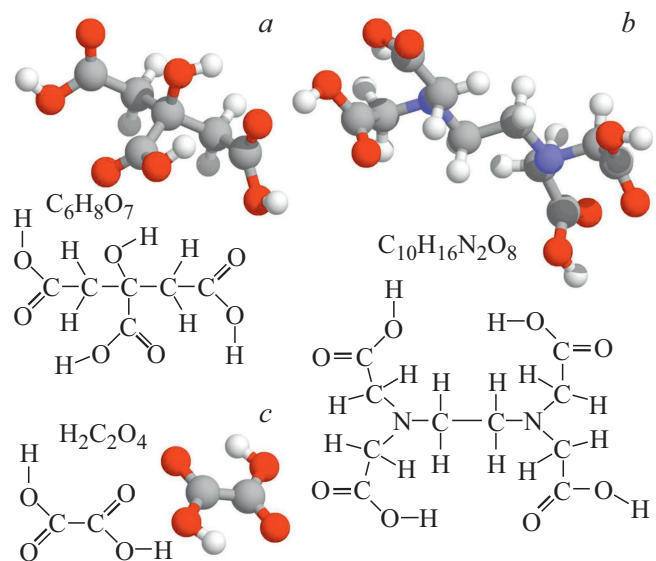
In studies on anodizing in solutions of complex zinc and cobalt compounds [39,41] the phenomenon of periodic voltage oscillation was mentioned and unusual morphology of AAO surface was observed. In study, dedicated to anodizing in presence of chelated complex copper compounds, it was shown, that the higher oxide growth rate (higher voltage and temperature), the more copper is included in aluminum oxide walls, resulting in degradation of nanopores arrangement regularity. Photoluminescence (PL) study confirmed the inclusion of chelated copper complexes [42].

Reproducible and intentional control of not only morphology, but composition of AAO is the crucial task of the applied physics and materials science, solving of which would allow to create AAO with specified electrophysical characteristics and morphology during formation, to alloy walls of oxide cells, giving them conductive, semiconductive and special optical properties, thus expanding the scope of AAO application. Anodizing in complexing solutions or solutions, containing complex compounds of various metals, is one of the ways to change such electrophysical and/or optical characteristics of AAO. Despite the experience of practical approbation [40], this topic is not sufficiently studied. There is only a small number of publications, mainly the conference abstracts of various degree, and even smaller number of articles. Studies, described above, do not make the full and specific picture of the process of AAO formation in electrolytes with additives or based on complex compounds and require supplementation and clarification of results. This study is intended both to supplement the results of the previous studies and to deeper research the process of anodizing in aqueous solutions of chelated complex zinc and cobalt compounds, to characterize the formed AAO and provide additional information for making the general picture of anodizing process under specified conditions.

## 1. Experimental technique

### 1.1. Aluminum preparation for anodizing

In this study we used Al (99.999%) and chemical reagents made by Aldrich Chemical Company. Aluminum thickness was 1 mm. For the following anodizing the aluminum sheets were cut into samples of required size in such a way for the anodized area to be about 1 cm<sup>2</sup>. After cutting the samples were heat treated for stress relieving and dislocation number reduction [43,44]. At first the samples were annealed at temperature of 753 K for 1 h, and then they were cooled at room temperature.



**Figure 1.** Structural formulas and 3D models of molecules of organic acids: *a* — citric, *b* — ethylenediamine tetraacetic and *c* — ethanedioic.

After heat treatment the mechanical treatment of samples was performed, consisting of consecutive sanding and polishing of metal surface from both sides. Samples were sanded using special sandpaper MicroCut for wet sanding with SiC-based abrasive and abrasive grain size of 1200 in accordance with ANSI standard, and after that the consecutive polishing, using polishing discs and diamond pastes with grain size of 3 μm, and finished machining of abrasive OPS suspension based on aluminum oxide were performed. Surface quality after treatment corresponded to cleanness grade of 14.

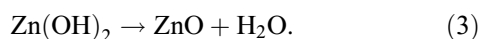
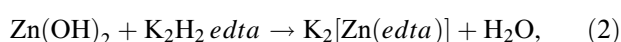
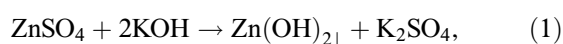
Due to relatively high cost of materials, for costs reasons many samples were used 2–3 times, while at first the heat treatment was performed again, and then the sanding and polishing were performed as per above mentioned technique. Logically enough, such samples thickness reduced to 0.7–0.3 mm depending on number of cycles. It is assumed that samples composition and properties were the same.

Meniscus area before anodizing was protected with barrier oxide, formed in 1% citric acid (structural formula is showed in Fig. 1, *a*) in the combined mode. At first, the voltage was expanded in potentiodynamic mode with a rate of 2.0 V · s<sup>-1</sup>, then, upon reaching 290 V, it was transitioned to potentiostatic mode, ceasing the anodizing upon reaching the current value, differ from initial by 1%. Anodizing was performed in galvanostatic (GSt) mode ( $j_a = \text{const}$ ) in a glass electrochemical cell with a flat platinum cathode, comparable with anode in terms of area; anode and cathode were located vertically and parallel to each other, while one side of anodized sample was oriented towards cathode and another — in opposite direction.

## 1.2. Anodizing electrolytes

Anodizing electrolytes were represented by aqueous solutions of complex compounds of Co (III) and Zn (II), synthesized as per below described techniques. Complex cobalt and zinc compounds preparation techniques are the same in principle. At first, the deposition of the corresponding metal hydroxide was performed from aqueous solution of its sulfate by means of pouring the potassium hydroxide solution, added to sulfate solution in equivalent amount (equation (1)). Sulfates were preferred, opposite to chlorides for example, mainly because small impurities of chloride-ions, that could present in synthesized compounds even after their thorough cleaning, could make impossible the following process of aluminum and/or its alloys anodizing due to pitting [45]. As for precipitating agent, the potassium hydroxide was preferred, opposite to sodium hydroxide for example, since it is known that sodium ion exhibits rather high mobility, making its presence highly undesired in the processes of the microelectronic devices hardware components manufacturing.

Sediment was pumped out on fine-mesh paper filter using waterjet pump and repeatedly washed with distilled water. Then, to obtain the ethylenediamine tetraacetic complex (equation (2)), the sediment along with filter paper was transferred to pre-prepared solution of dipotassium salt of ethylenediamine tetraacetic acid (structural formula is presented in Fig. 1, *b*). Metal hydroxide dissolution was performed with thorough mixing. All reactions were performed as quick as possible and at room temperature, without heating, to prevent from decomposition of unstable hydroxides due to dehydration (equation (3)), that, in its turn, could complicate the complex formation process.



Then the solutions were filtered and after the corresponding dilution they were used for anodizing. Complex cobalt compound of  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$  composition (cobalt coordination number in oxidation degree +2 and +3 is usually six) was synthesized the similar way, but ethanedioic acid was used instead of  $\text{K}_2\text{H}_2\text{edta}$  (Fig. 1, *c*).

## 1.3. Devices and equipment

Composition of observed experimental samples was studied using X-ray photoelectron spectroscopy (XPS) method (Physical Electronics PHI 5600XP-spectrometer), IR spectroscopy with spectral resolution of  $1\text{ cm}^{-1}$  (Perkin-Elmer-180) and Auger electron spectroscopy (Physical Electronics PHI 670). Electron microscopical studies were performed using scanning electronic microscopes JEOL JSM 6400 and Hitachi S4800 with electron probe device Genesis 4000. Optical images were observed at microscope Micro 200-01. Photoluminescence spectra were observed

using spectrofluorometer SFL-1211 A with spectral width of a slit of 1 nm. X-ray diffraction spectra were observed at modified unit DRON-3 using  $\text{CuK}\alpha$ -radiation and graphite filter with scan step of  $0.04^\circ$  and exposure in each point for 3 s in a range of  $2\theta$  15–100°.

## 2. Results and discussion

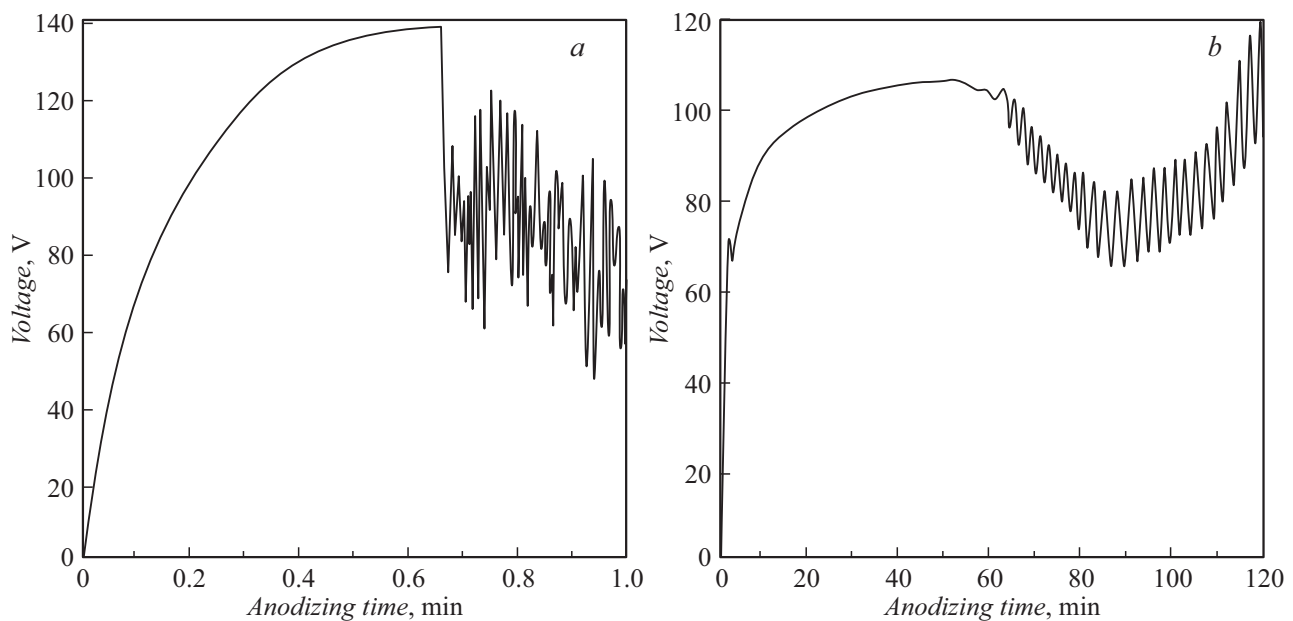
In case of aluminum anodizing in electrolyte, that is a aqueous solution of complex compound of  $\text{K}_2[\text{Co(edta)}]$  composition (0.75 M,  $1.5\text{ mA} \cdot \text{cm}^{-2}$ ), there was a strongly pronounced occurrence of „burning“, characterized by oscillations of anodic voltage at kinetics, despite the intensive mixing and low values of anodic current density; such occurrence is described in [46]. Typical kinetics of anodic process in this electrolyte are presented in Fig. 2, *a*. Absolutely different picture was observed at high quality aluminum samples anodizing in  $\text{K}_2[\text{Zn(edta)}]$  solution [41]. Complex salt concentration in all cases was 0.5 M, anodic current density  $j_a$  varied within  $1.5\text{--}30\text{ mA} \cdot \text{cm}^{-2}$ . Kinetics of one of the samples anodizing (time dependence of anodic voltage  $U_a$ ) are presented in Fig. 2, *b*.

Anodic process, performed in  $\text{K}_2[\text{Zn(edta)}]$  solution, has some significant kinetic features. At first, like in acid electrolytes, there is an almost linear growth of anodic voltage with time up to the maximum value, and then the voltage decreases, after which, instead of transition to stationary mode, the rather significant, gradually slowing growth of anodic voltage is observed. After several dozens of minutes, when  $U_a$  growth is almost over, the periodical voltage oscillations start.  $U_a$  value reaches maximum of about  $\sim 100\text{ V}$ , while oscillation amplitude is up to 20 V. With anodizing duration of up to 120 min the oscillations do not stop. This should be discussed in detail. Currently a large number of oscillating chemical reactions is known [47], while the first cases related to oscillating behavior of electrochemical systems were observed in the beginning of XIX century [48]. Since then the large amount of experimental results of self-organization cases, happened during electrode processes, has been accumulated. Up until recently four groups of oscillatory electrochemical reactions were known [48]. These are oscillations happened at:

- anodic dissolution of metals;
- anodic oxidation of nonmetals (mainly organic compounds and hydrogen);
- cathodic deposition of metals;
- anions electroreduction.

It can be observed that periodical reactions, happened during anodic passivation, were not registered until now. Therefore the comprehensive study of obtained films is of special interest.

Fig. 3, *a–c* shows electron microscope images of surfaces of samples, anodized in 0.5 M solution of  $\text{K}_2[\text{Zn(edta)}]$  at various values of  $j_a$ . It can be observed that already at small current density of ( $1.5\text{ mA} \cdot \text{cm}^{-2}$ ) and 30 min duration of anodizing there are bulges formed on surface,



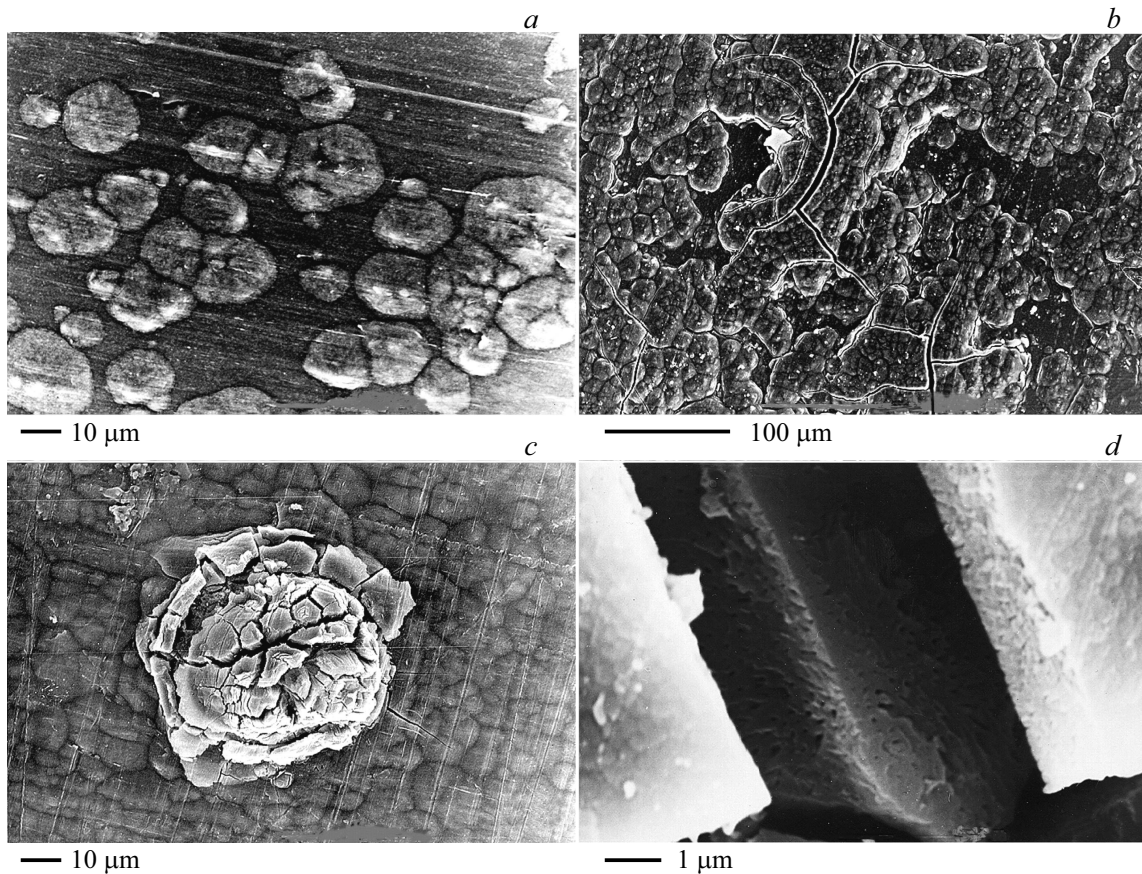
**Figure 2.** Kinetics of Al anodizing in 0.75 M aqueous solution of *edta* complex of Co at current density of  $j_a$   $1.5 \text{ mA} \cdot \text{cm}^{-2}$  (a) and in 0.5 M aqueous solution of  $\text{K}_2[\text{Zn}(\text{edta})]$  at current density of  $j_a$   $5 \text{ mA} \cdot \text{cm}^{-2}$  (b).

that at increase of current density of ( $4.0 \text{ mA} \cdot \text{cm}^{-2}$ ) and process duration of 2 hours merge into continuous cracking fields. With further increase of  $j_a$  ( $10.0 \text{ mA} \cdot \text{cm}^{-2}$ ) and anodizing during 20 min the „flaky“ (or „loose“) bulges appear, sizes and surface density of which increase with the further increase of anodizing duration and current density up to  $25 \text{ mA} \cdot \text{cm}^{-2}$ . Electron microscope image of a crack under high magnification is presented in Fig. 3, *d*. It can be observed that AAO at crack rupture has cellular and porous structure. Buildups, visually presented in Fig. 3, resemble the objects, presented on SEM images in previous studies, dedicated to aluminum anodizing in various acids [49–51], in recent study [20], as well as micro-cones, growing at titanium anodizing [52,53]. This observation can suggest the general reasons, resulting in such buildups formation. Presumably, the local redistribution of current density and concentration of ions of various type, consistent in a sense, is happened, that can result in both growth of more or less regularly interspaced micro-bulges [20,52,53] and creation of randomly located breakdowns [49–51].

Appearance of „smooth“ bulges at small values of  $j_a$  and „flaky“ bulges at further increase of anodic current density can be explained by the fact that small-sized impurity anions, presenting in the solution in traces, as a result of redistribution of current density, are concentrated near certain surface areas and cause local non-uniform conductivity of electrolyte. Also, impurities can integrate into AAO uniformly over the whole area or non-uniformly [16]. In the latter the oxide section with the most anions has the higher conductivity, resulting in its growth rate. Thus, presumably, the relief irregularities occur during anodizing in the examined solutions of complex compounds in our case.

In this study the analysis of AAO films, made by electrochemical GSt anodizing of aluminum in solution of  $\text{K}_2[\text{Zn}(\text{edta})]$  using electronic probe, Auger spectroscopy and XPS, was also performed. In case of dielectric materials, to which  $\text{Al}_2\text{O}_3$  belongs, XPS analysis is related with certain difficulties in interpretation of the observed spectra [54]. During analysis using this method the charge is accumulated on samples, therefore it was necessary to perform correction of peak positions in relation to Auger peak of oxygen, and that allowed to define electrons binding energies and elements valence state. Auger electron and XPS analyses showed the presence of carbon, nitrogen and sulfur impurities in AAO composition. Fig. 4 shows the analysis results of the „loose“ bulge of the sample, made by anodizing within 55 min at anodic current density of  $25 \text{ mA} \cdot \text{cm}^{-2}$  after regular (Fig. 4, *a*) and extensive washing (Fig. 4, *b*), while Fig. 4, *c–e* — analysis results of a state of some elements, included in this object.

The samples were washed in distilled water of room temperature with thorough mixing in amount of  $\sim 100 \text{ mL}$ , while washing water was changed three times; overall duration of washing was  $\sim 15 \text{ min}$ . Repeated analysis was performed after fifth washing under the same conditions, but with overall duration of 5 h. As the analysis results show, sulfur, presenting presumably as sulfate-anion, is included in oxide composition, and not occluded by the loose structure of extended bulge on a surface, since it was not washed away after such a long washing. As a result of analysis of the elements valence state, it was observed that aluminum oxide is in the form of  $\alpha$  or  $\gamma$  modification (more accurate identification is not possible with this method); carbon is connected by non-polar or low-polar bond (C-C, C-H or C-S type); while sulfur presents in oxidized condition (i.e.



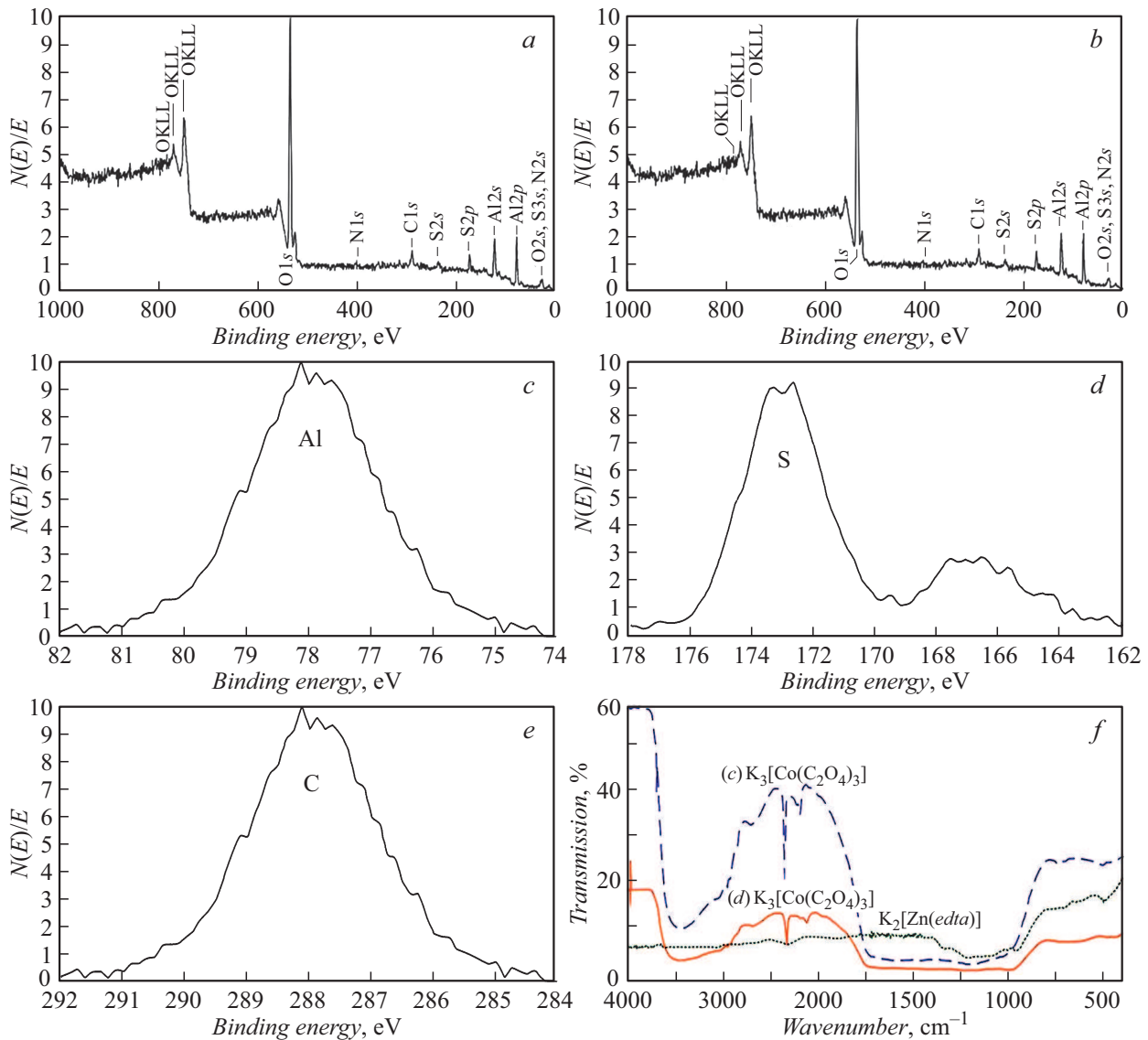
**Figure 3.** Microphotographs of a surface of AAO, formed in 0.5 M solution of  $K_2[Zn(edta)]$  at  $j_a$  1.5 (a), 4.0 (b) and  $10.0 \text{ mA} \cdot \text{cm}^{-2}$  (c) within 30 min, 2 h and 20 min, respectively, and cracks on a surface of AAO, formed within 2.5 h at current density of  $14.0 \text{ mA} \cdot \text{cm}^{-2}$  (d).

actually is in the form of sulfate-anion). Presence of sulfur is explained, presumably, by contamination of synthesized complex compound with potassium sulfate; while sulfate-anion, despite its trace level in electrolyte, due to small ionic radius and higher mobility is integrated into appearing oxide more efficiently. Carbon could enter AAO film with *edta* acid residue only. In support of the latter the nitrogen impurity, also included in ethylenediamine tetraacetic acid, is presented in the oxide. Analysis did not show signal from high-polar bonds of C=O, C-O, since, first of all, share of such atoms in  $edta^{4-}$  anion is small comparing with number of atoms, connected with low-polar or non-polar bond, and secondly, the overall carbon amount in the film is insignificant. However the presented analysis results indirectly suggest the presence of zinc in the composition of formed AAO, that could not enter the film as part of highly strong complex chelated ethylenediamine tetraacetic double charged anion  $[Zn(edta)]^{2-}$  [15]. Indeed, zinc impurities were observed in the oxide using electron probe studies. Quantity of each of the impurity elements does not exceed  $\sim 1 \text{ at.}\%$ . Impurities are caused by electrolyte components entering the AAO structure.

Fig. 5, a shows PL spectra of AAO, made by anodizing in solution of  $K_2[Zn(edta)]$  within 55 min at anodic current

density of  $25 \text{ mA} \cdot \text{cm}^{-2}$  with excitation wavelengths of 260 and 340 nm. As the figure shows, at the specified values of  $\lambda_{in}$  the PL spectra of this sample are almost the same as spectra of samples made in conventional acid electrolytes. At the same time the sample tremendously absorbs not only in visible range, but in IR range also. Fig. 4, f shows the spectrum of IR radiation transmission by the same sample in a wide range of wave numbers. Even in the longest-wave region of  $(800-400 \text{ cm}^{-1})$  — region of the biggest transparency of this sample, the relative transmission barely reaches 20%. Due to extremely high absorption and non-expressiveness of transmission minimums even at high sensitivity of IR spectrometer the analysis and interpretation of spectrum is complicated.

Series of experiments on high-purity aluminum samples anodizing in GST mode in a solution of oxalic chelated complex of cobalt of  $K_3[Co(C_2O_4)_3]$  composition was performed. Electrolyte concentration in experiments was 1.1 and 1.9 M, current density varied within  $1.5-1.10 \cdot 10^2 \text{ mA} \cdot \text{cm}^{-2}$ . Anodizing kinetics is generally similar to the one described for ethylenediamine tetraacetic complex of zinc, but, first of all, anodic voltage values in maximum barely reached 100 V, and secondly, the



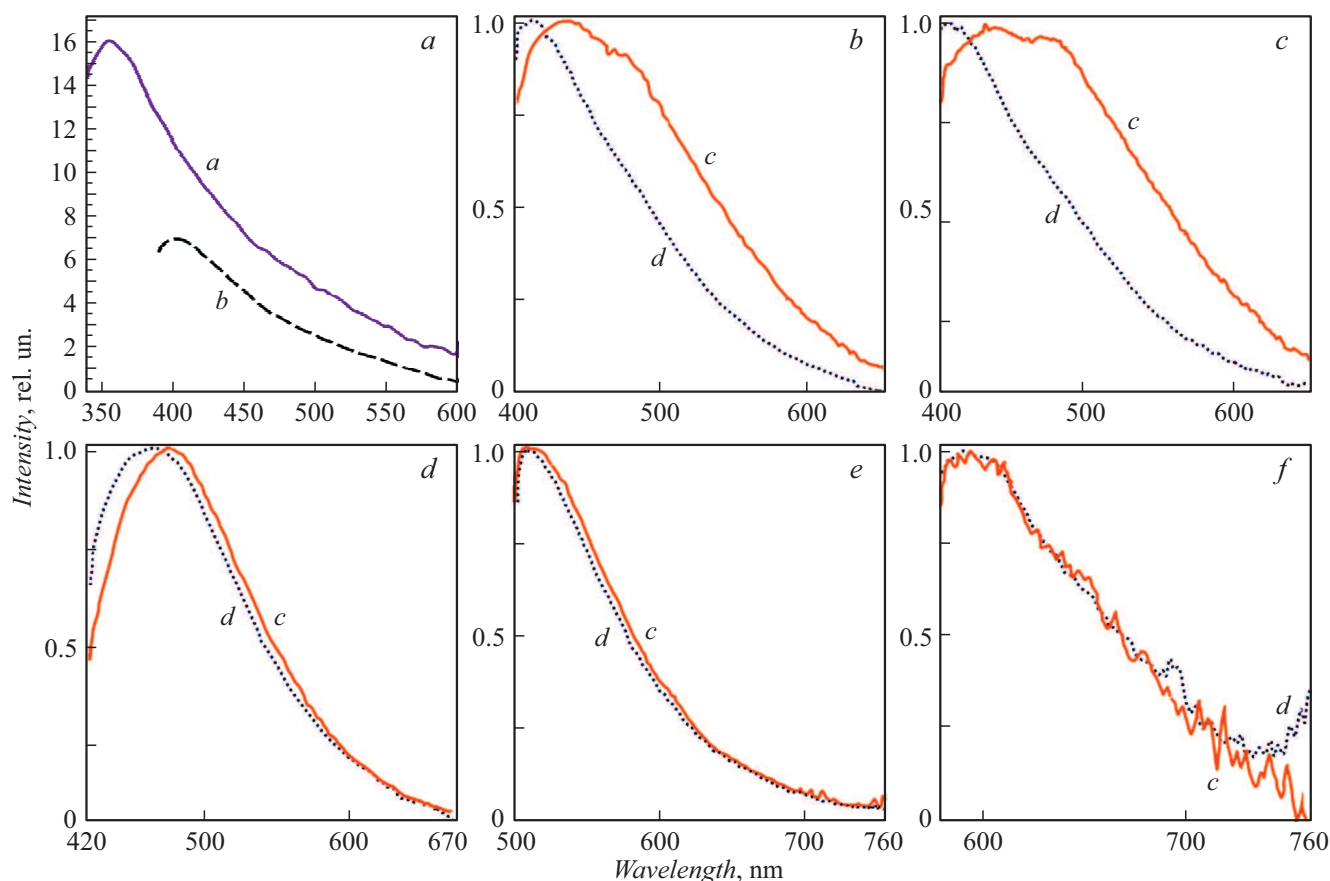
**Figure 4.** XPS review of „loose“ bulge of sample, made by anodizing within 55 min at anodic current density of  $25 \text{ mA} \cdot \text{cm}^{-2}$  after regular (a) and extensive washing (b). XPS identification of valence state of elements (aluminum (c), sulfur (d) and carbon (e)) as part of „loose“ bulge; IR transmission spectra of sample (f), made in 0.5 M solution of  $\text{K}_2[\text{Zn}(\text{edta})]$  within 55 min at anodic current density of  $25 \text{ mA} \cdot \text{cm}^{-2}$ , and samples presented in Fig. 6, c, d.

oscillation frequency was higher, while amplitude was  $\sim 1 \text{ V}$ .

Surface images of AAO, formed by Al anodizing within 74 min in 1.9 M solution of  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$  at current density of  $50.0 \text{ mA} \cdot \text{cm}^{-2}$ , observed using electronic and optical microscopes, are presented in Fig. 6, a, b. Due to higher resolution and focusing depth of electronic microscope [55], we can observe the sample surface in detail, while optical image allows to show color of the formed AAO. It can be observed that on relatively even surface of AAO the extended bulges of conical shape or similar to four-cornered pyramid are located; under certain conditions they merge into continuous fields. Nature and overall area of these bulges depend on anodizing electrical mode and orientation of anodized sample with respect to

cathode. Fig. 6 shows optical photo images of AAO, made by anodizing in 1.9 M solution of  $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_3]$  within 29 min at

It was established that presence of the mentioned bulges causes significant differences of PL properties compared to other films formed under the similar conditions. Fig. 5, b–f shows PL spectra of different sides of the same sample, presented in Fig. 6, c, d, and recorded at different excitation wavelengths ( $\lambda_{\text{in}}$  270, 308, 370, 415 and 520 nm). Curve c on diagrams corresponds to AAO spectrum at the sample side oriented towards cathode, while curve d — to the side faced away from cathode during anodizing. All luminescence spectra in Fig. 5, b–f are normalized to unity. Differences in these spectra nature are obvious. First of all, spectrum of surface with high quantity of the extended



**Figure 5.** PL spectra of AAO sample, made (a) in 0.5 M solution of  $K_2[Zn(edta)]$  within 55 min at anodic current density of  $25 \text{ mA} \cdot \text{cm}^{-2}$  (solid line *a* and dashed line *b* correspond to excitation wavelengths of 260 and 340 nm), and in 1.9 M solution of  $K_3[Co(C_2O_4)_3]$  within 29 min at  $j_a = 1.10 \cdot 10^2 \text{ mA} \cdot \text{cm}^{-2}$  with excitation wavelengths of 270 (*b*), 308 (*c*), 370 (*d*), 415 (*e*) and 520 nm (*f*) (solid lines correspond to PL surface faced to cathode and presented in Fig. 6, *c*, dashed lines *d* correspond to PL surface faced away from cathode and presented in Fig. 6, *d*).

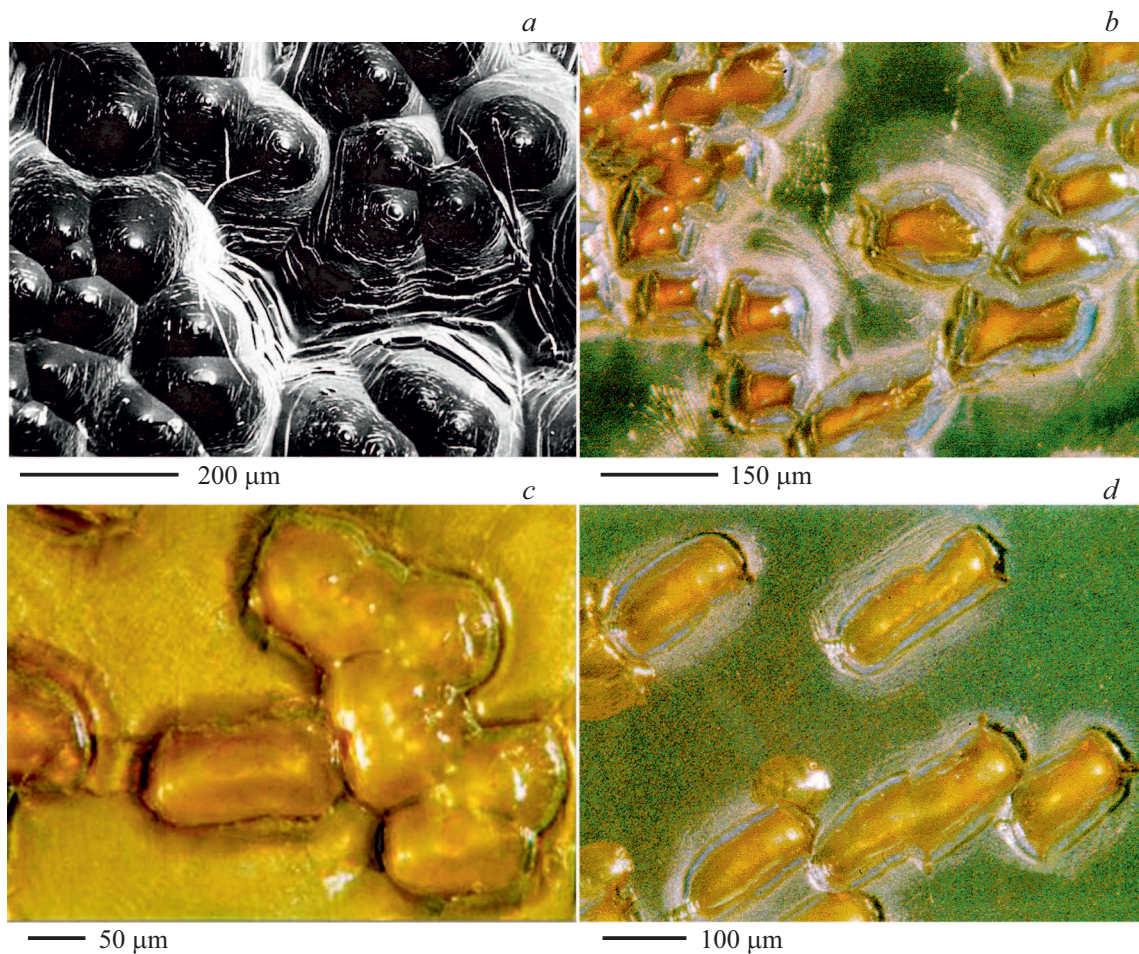
bulges is strongly shifted towards long-wave range, and, secondly, with bulges appearing on the sample surface the strongly pronounced second maximum appears, also located in longer-wave range than the main one, which disappears at increase of excitation wavelength. Both features appear stronger with decrease of excitation light wavelength. This fact indicates the presence of luminescence centers, excited with shorter waves, as part of the bulges. Determination of these centers nature and observance of differences of structure and composition of AAO layers with bulges and without them require further study.

Fig. 4,*f* shows IR spectra of sample made by aluminum anodizing in solution of  $K_3[Co(C_2O_4)_3]$  and presented in Fig. 6, *c, d*. Curve *c* on diagrams corresponds to AAO spectrum of the sample side oriented towards cathode, while curve *d* — side faced away from cathode during anodizing (both surfaces are presented in Fig. 6, images *c* and *d*, respectively). Compared to similar spectra, characteristic for electrolytes without addition of complex cobalt compounds, the new absorption bands appeared. Bands in the ranges of  $3750\text{--}2800$  and  $2100\text{--}800 \text{ cm}^{-1}$  are extremely wide and intensive even at small sensitivity of

spectrometer. Not so intensive, but very narrow absorption bands with sharp minimums in the range of wave numbers near  $2350$  and  $2150 \text{ cm}^{-1}$  (the last band is double) also appeared. In attempt to examine the mentioned bands the device sensitivity was lowered so much that usually well-defined wide intensive absorption band in a range of  $1000\text{--}400 \text{ cm}^{-1}$ , actually consisting of several bands and belonging to valence vibrations of Al-O, is almost undistinguished.

In study [57] issues of IR spectroscopic analysis of AAO, made in aqueous solutions of sulfuric, orthophosphoric, ethanedioic and malonic acids, are discussed in detail and it is shown that AAO, made in the mentioned electrolytes, exhibits low (at the limit of spectrophotometer sensitivity) degree of hydration and low boehmite concentration in it. Presence of intensive absorption bands in interval of  $3700\text{--}3000$  and near frequency of  $1060 \text{ cm}^{-1}$  is interesting, indicating in our case of the appearance of the new phase in the form of inclusions of tri- and monohydrates of Al, which usually appear only as a result of treatment in hot ( $340\text{--}373 \text{ K}$ ) water. In case of AAO, made in the solution of complex cobalt salt, we observe quite intensive





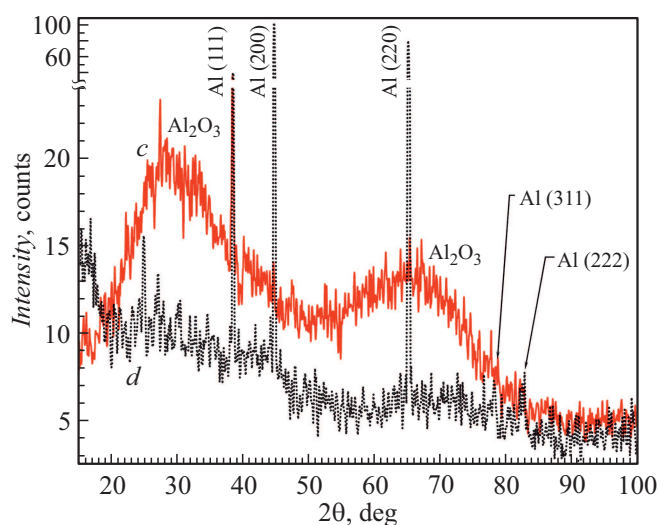
**Figure 6.** Surface images of anodic aluminum oxide, made by anodizing within 74 min in 1.9 M solution of  $K_3[Co(C_2O_4)_3]$  at current density of  $50.0 \text{ mA} \cdot \text{cm}^{-2}$ , recorded using electronic (*a*) and optical (*b*) microscopes; optical photo images of AAO, made by anodizing in 1.9 M solution of  $K_3[Co(C_2O_4)_3]$  within 29 min at  $j_a = 1.10 \cdot 10^2 \text{ mA} \cdot \text{cm}^{-2}$ , on the side faced to cathode (*c*), and to opposite side (*d*).

absorption both in the mentioned ranges and in short-wave IR range near  $3800\text{--}3300 \text{ cm}^{-1}$ , corresponding to valence vibrations of coordinated and adsorbed OH-groups, as well as absorption in mid-frequency range near  $1620 \text{ cm}^{-1}$ , related to deformation vibrations of bonds of Al-OH tri- and monohydroxides of Al and at frequency of  $1080 \text{ cm}^{-1}$ , characterizing valence vibrations in initial boehmite.

Thus, phase composition and degree of hydration of aluminum anodic oxide film, made in „conventional“ acid electrolytes and electrolyte under study, that is a solution of  $K_3[Co(C_2O_4)_3]$ , are significantly different. In the latter case AAO differs by significant amount of hygroscopic and chemically-bound moisture and presence of phases of hydrargillite and boehmite on the back of almost complete lack of unhydrated aluminum oxide.

Fig. 7 shows X-ray diffraction spectrum of AAO, presented in Fig. 6, *c, d*. Diffractograms of both sample sides include five peaks with maximums, corresponding to the values of  $2\theta$   $38.47$ ,  $44.72$ ,  $65.10$ ,  $78.20$  and  $82.31^\circ$ . These results are in a good agreement with data from the International Centre for Diffraction Data (ICDD) database [58], files 85-1327, 89-2769 and results of this

study [59]. Intensities of specified peaks are significantly different for both sides. Intensities of X-ray diffraction maximums, corresponding to metallic aluminum phase, are high for the side faced away from cathode during anodizing (presented in Fig. 6, *d*), all four specified peaks are well visible. At the same time X-ray diffraction image of the side oriented towards cathode during anodizing (Fig. 6, *c*) is significantly different. First of all, intensity of X-ray diffraction responses, corresponding to metallic aluminum, was significantly less. Secondly, there are 2 wide peaks with maximums, almost corresponding to values of  $2\theta$   $29$  and  $68^\circ$ . These peaks are caused by the presence of AAO layer. Its presence due to X-ray radiation absorption significantly obstructs the appearing of maximums, characteristic for metallic aluminum phase, that is located under rather heavy oxide layer. At the same time diffraction of X-ray beam on AAO layer is almost non-existent on a curve, built for the side faced away from cathode. This indicates the significant difference in thickness of AAO films, formed on different sides of anode, that is in good agreement with the optical images (Fig. 6, *c, d*) and the results of studying the IR spectroscopic



**Figure 7.** X-ray diffraction spectra of sample, made in 1.9 M solution of  $K_3[Co(C_2O_4)_3]$  within 29 min at  $j_a = 1.10 \cdot 10^2 \text{ mA} \cdot \text{cm}^{-2}$  (solid line *c* corresponds to a surface faced to cathode and presented in Fig. 6, *c*, dashed line *d* corresponds to a surface faced away from cathode and presented in Fig. 6, *d*).

(Fig. 4, *f*) and PL (Fig. 5, *b-f*) properties. The assumption that wide peaks in ranges of  $2\theta$  20–40° and 55–80° correspond to AAO is confirmed by the analysis of the corresponding data from ICDD database. Intensive peaks in the specified ranges (for instance, database files PDF2 31-0026, 46-1215, 04-0876, 08-0013, 09-0440, 52-0803, 71-1125, 79-1559, etc.), that in material with significant structure disorder will inevitably be „blurred“, present on the X-ray diffraction spectra of almost any modification of aluminum oxide. At the same time, the studies are known, examining structure of porous AAO, made in solutions of ethanedioic acid (the closest conditions) [60–65], as well as in other electrolytes [20,63,64], in which AAO has the similar X-ray diffraction picture, characteristic for X-ray amorphous material.

Examination of X-ray diffraction spectra, presented in Fig. 7, did not reveal significant differences compared to the results published earlier, but confirmed the conclusion again that the anodizing electrolyte under study has small dissipating ability, and AAO making depends on orientation of anode surface in relation to cathode on a side faced to cathode, while thickness of formed AAO is bigger than on the side faced away from cathode.

## Conclusion

High-purity aluminum was prepared by heat and mechanical treatment and galvanostatically anodized with various current density of  $1.5\text{--}1.10 \cdot 10^2 \text{ mA} \cdot \text{cm}^{-2}$  and  $11.5\text{--}30 \text{ mA} \cdot \text{cm}^{-2}$  in aqueous solutions of complex compounds of  $K_2[Co(edta)]$  and  $K_2[Zn(edta)]$  of various concentration, respectively. As a result of the studying

the anodizing processes, morphology, composition and photoluminescence the following was observed:

1. Process of anodizing in  $K_2[Co(edta)]$ , despite intensive mixing and low values of anodic current density, is accompanied by the strongly pronounced occurrence of „burning“, characterizing with chaotic oscillations of anodic voltage on kinetics.

2. Kinetics of anodizing in  $K_2[Zn(edta)]$  has the characteristic oscillations of periodic type, notable for significant amplitude and regularity, indicating the oscillating chemical reactions.

3. Kinetics of anodizing in  $K_3[Co(C_2O_4)_3]$  has the periodical oscillations, involving higher frequency and lower amplitude compared with anodizing in  $K_2[Zn(edta)]$ .

4. On a surface of anodic oxide, made in  $K_2[Zn(edta)]$  at small current density of  $(1.5 \text{ mA} \cdot \text{cm}^{-2})$ , the bulges form, which at increase of current density of  $(4.0 \text{ mA} \cdot \text{cm}^{-2})$  merge into continuous cracking fields. With further increase of  $j_a$  ( $10.0 \text{ mA} \cdot \text{cm}^{-2}$ ) the „flaky“ (or „loose“) bulges appear, sizes and surface density of which increase with the further increase of current density and anodizing duration.

5. On a surface of oxide, formed in  $K_3[Co(C_2O_4)_3]$ , the bulges are also formed, with conical shape or shape of four-cornered pyramid. With current density increase these bulges merge into continuous fields. Surface density of these bulges depends on orientation of anode surface and is always higher on the side oriented towards cathode. Bulges, formed at aluminum anodizing in  $K_3[Co(C_2O_4)_3]$ , do not crack and do not „flake“.

6. Auger electron, electron probe and XPS analyses of AAO, formed in  $K_2[Zn(edta)]$ , showed the presence of carbon, nitrogen and sulfur impurities in its composition, while the latter was in the electrolyte in traces.

7. As a result of analysis of the elements valence state, it was observed that aluminum oxide is in the form of  $\alpha$  or  $\gamma$  modification; carbon is connected by non-polar or low-polar bond, C-C, C-H or C-S type; while sulfur presents in oxidized condition (i.e. actually is in the form of sulfate-anion).

8. Analysis of photoluminescence spectra of AAO, made in solution of  $K_2[Zn(edta)]$ , showed that at excitation wavelength values of 260 and 340 nm the spectra are not so different compared with spectra of samples, made in „conventional“ acid electrolytes.

9. It was established that photoluminescence spectra of AAO, formed in solutions of  $K_3[Co(C_2O_4)_3]$ , are characterized with more sophisticated shape of a bell and presence of the second maximum, that quickly decreases with increase of excitation wavelength. It turned out that such features are characteristic for AAO, formed on the side oriented towards cathode and notable for large number of bulges.

10. It was established that oxides, formed in solution of  $K_2[Zn(edta)]$ , have high absorption not only in visible range, but also in IR range under study. In the longest-wave region of  $(800\text{--}400 \text{ cm}^{-1})$  — region of the biggest transparency of this sample, the relative transmission barely reaches 20%.

11. X-ray diffraction studies showed that the sample of anodic aluminum oxide, formed in solution of  $K_3[Co(C_2O_4)_3]$ , is a X-ray amorphous material, and thickness of oxide, formed on the anode side, faced to cathode, is higher than on the side, faced in opposite direction.

The performed study illustrates some features of aluminum anodizing process in solutions of chelated complex compounds, compound, structure, composition, IR spectroscopic and photoluminescent properties, formed in the mentioned electrolytes of anodic oxide films on aluminum, and is the important stage at development of approaches for anodic aluminum oxide forming with the specified composition, electrical and optical characteristics.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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