

**AN X-RAY PHOTOELECTRON SPECTROSCOPY
STUDY OF Ni, Cu-CONTAINING COATINGS
FORMED BY PLASMA ELECTROLYTIC
OXIDATION ON ALUMINUM AND TITANIUM**

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A series of Ni- and/or Cu-containing coatings formed by plasma electrolytic oxidation on aluminum and titanium are examined by X-ray photoelectron spectroscopy. Binding energies of core electrons, elemental composition, chemical state of elements, and features of the structural organization of the surface and near-surface layers of the coatings are determined. A combination of the data collected indicates similar regularities of the composition and significant distinctions in the structure of the coatings formed. It is shown that the coatings formed on titanium are characterized by a considerably higher phosphorus concentration, and correspondingly, phosphates, unlike the coatings formed on aluminum, in which base metal and 3d element (Ni or Cu) oxides are dominant. In both cases, Cu is mainly concentrated in the surface layers of the coatings whereas Ni is mainly concentrated in the near-surface layers.

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INTRODUCTION

At present, the design and investigation of various novel functional materials becomes more and more relevant problem. One of the methods enabling the formation of diverse functional materials (protective, corrosion resistant, decorative, etc.) is plasma electrolytic oxidation (PEO) [1-8]. As a result of electric discharges during PEO on the metal surface (alloy) an oxide layer forms. Its composition, structure, and consequently, properties can be regulated by varying formation conditions and modes.

In recent years, PEO has been applied to form coatings with a complex chemical composition with the prospect of their use in catalysis [9, 10], medicine [8, 11], as materials with certain magnetic characteristics [12, 13]. In [9, 10, 14, 15] the formation processes, bulk composition, morphology, and the ability to catalyze the CO oxidation reaction into CO₂ of Ni- and/or Cu-containing PEO-coatings on aluminum and titanium were analyzed.

The PEO-coatings have a complex composition and structure and to establish their regularities they need a thorough investigation by current complementary research techniques.

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To determine the composition and structure of PEO-coatings, in this work the systematic studies of Ni- and/or Cu-containing coatings formed on aluminum and titanium (with a metal content no less than 99 wt.%) were carried out by means of X-ray photoelectron spectroscopy (XPS). The binding energies of core electrons, elemental composition, chemical state of elements, and the features of the structural organization of the surface and near-surface layers of the coatings were found.

EXPERIMENTAL

For XPS studies 5×25×1 mm samples were prepared from technically pure aluminum and titanium of A7 and VT1-0 grades respectively, on which oxide layers were later formed. Before PEO the pretreatment of the samples consisted of chemical polishing in a mixture of H₃PO₄:H₂SO₄:HNO₃ concentrated acids in the 4:2:1 volume ratio at temperature of 110-120 °C until the formation of a mirror surface with subsequent washing with tap water, then distilled water. The samples were oxidized in one-polar mode with anode polarization at an efficient current density of 0.1 A/cm² for 5 min or 10 min in an aqueous electrolyte containing basic components Na₃PO₄, Na₂B₄O₇, and Na₂WO₄ (further PBW [16]) and electrolytes containing, apart from the mentioned components, different amounts of nickel and/or copper acetate. A computer-controlled TER4-4/460N-2-2UHL4 (Russia) thyristor unit was used as a current source. An anoding electrochemical cell consisted of a 1 l glass beaker, a cathode in the form of hollow tube coil made of nickel alloy, and a magnetic stirrer. The solution temperature did not exceed 30 °C. Below in the text the samples are designated as Al, Ti, Al-PBW, Ti-PBW, Al-Ni_x, Ti-Ni_x, Al-Cu_y, Ti-Cu_y, Al-Ni_x-Cu_y, Ti-Ni_x-Cu_y, where Al and Ti are the bases of the coatings, *x* and *y* indicate the concentration (mol/l) of Ni(CH₃COO)₂ and/or Cu(CH₃COO)₂ acetates introduced into the PBW electrolyte respectively. For the basic coatings (Al-PBW, Ti-PBW), Ni-containing coatings on aluminum and titanium (Al-Ni_x, Ti-Ni_x), and Cu-containing coatings on titanium (Ti-Cu_y) the formation time of PEO layers was 10 min, for the Cu-containing coatings on aluminum and also mixed Ni, Cu-containing coatings on aluminum and titanium (Al-Cu_y, Al-Ni_x-Cu_y, Ti-Ni_x-Cu_y) was 5 min.

The XPS spectra were measured on an ultra-high vacuum spectrometer (Specs, Germany) equipped with a 150 mm electrostatic hemispherical Phoibos-150 analyzer. The measurements were performed in the constant analyzer pass energy mode at $E_{\text{pas}} = 50$ eV. The energy resolution of the spectrometer was ~1.8 eV for the hydrocarbon C1s line. For ionization MgK_α radiation with a photon energy of 1253.6 eV was applied. The working vacuum was 1-5×10⁻⁷ Pa. The spectra were calibrated also using the hydrocarbon C1s lines whose energy was taken to be 285.0 eV. To remove the upper layer (~3 nm thick) ion etching was used by scanning the sample surface for 5 min at an Ar⁺ energy of 5000 eV and current $I_{\text{total}} = 20$ μA. According to our estimation, the etching rate of the studied materials was about 0.1 Å/s. Before the XPS experiments no special treatment of the samples was made.

The coating thickness (*h*) was determined by a VT-201 (Russia) eddy current thickness meter. For the measurements the samples with dimensions 22×22×1 mm were used. As follows from the data obtained, the samples on titanium are characterized by the formation of much thicker coatings ($h = 25 - 35$ μm) than those on aluminum (2-12 μm), which is consistent with the data previously obtained for similar coatings [17].

RESULTS AND DISCUSSION

Initial supports. According to our data, the upper layer (~3 nm thick) of the initial aluminum and titanium samples (see Al and Ti in Tables 1, 2) used for further oxidation consists of Al₂O₃ or TiO₂ respectively, with an appreciable fraction of carbon-containing structures with carbon in different oxidation states: -COO-, -CO-, and -CC-. The occurrence of Al₂O₃ and TiO₂ is evidenced by the characteristic Al2*p* and Ti2*p* electron binding energies (E_b) of 74.2 eV and 458.2 eV respectively (Tables 1, 2). The presence of carbon in the samples under study is due to both technological features of the sample preparation and adsorption of carbon-containing compounds from the atmosphere.

In the near-surface layer (at a depth of ~3-6 nm) stripped after the Ar⁺ bombardment, along with the initial metal base oxides (Al₂O₃ and TiO₂), other oxides are observed in which metal (Al or Ti) has a lower oxidation state (Ti₂O₃ and

TABLE 1. Elemental Composition and Binding Energies of Elements in the PEO Coatings on Aluminum (at.%/eV)

| Sample | Na | Cu | Ni | O | C | P | Al | W |
|--|-----------|-----------|------------|------------|------------|------------|-----------|----------|
| Al | – | – | – | 28.6/532.1 | 59.9/285.0 | – | 11.5/74.2 | – |
| | | | | 29.7/532.3 | 1.8/285.0 | | 68.5/74.8 | |
| Al–PBW | 1.4/264.6 | – | – | 54.0/531.9 | 12.8/285.0 | 3.9/134.2 | 27.7/74.7 | 0.2/35.8 |
| | 0.5/264.1 | | | 58.5/531.2 | 1.3/285.0 | 1.5/133.6 | 38.1/74.4 | 0.1/35.2 |
| Al–Ni _{0.020} | 2.2/264.0 | – | 6.8/856.9 | 51.6/531.8 | 18.9/285.0 | 6.0/133.5 | 14.4/74.0 | 0.1/35.2 |
| | 2.0/263.7 | | 8.8/852.8 | 55.3/531.2 | 5.0/285.0 | 4.6/133.0 | 24.2/73.6 | 0.1/35.3 |
| Al–Ni _{0.080} | 0.8/263.8 | – | 9.8/857.1 | 53.5/531.6 | 13.9/285.0 | 6.6/133.6 | 15.0/74.0 | 0.4/35.2 |
| | 7.5/264.6 | | 11.4/853.7 | 53.9/532.1 | 1.6/285.0 | 4.2/134.1 | 21.3/74.7 | 0.1/36.3 |
| Al–Cu _{0.0125} | 0.4/264.3 | 2.1/934.8 | – | 38.6/532.0 | 35.7/285.0 | 4.4/134.1 | 18.6/74.7 | 0.2/36.0 |
| | 0.7/264.7 | 1.1/933.5 | | 54.3/531.9 | 3.6/285.0 | 4.6/134.5 | 35.3/75.0 | 0.4/36.4 |
| Al–Cu _{0.0375} | 1.5/264.2 | 9.0/935.7 | – | 55.2/531.7 | 15.4/285.0 | 6.1/133.5 | 12.5/74.2 | 0.3/35.5 |
| | 0.8/264.3 | 4.2/934.1 | | 61.9/532.2 | 0.7/285.0 | 4.3/134.3 | 28.0/74.8 | 0.1/36.5 |
| Al–Ni _{0.020} –Cu _{0.0125} | 2.0/263.8 | 2.7/933.8 | 3.0/856.6 | 45.0/531.5 | 18.0/285.0 | 9.8/133.8 | 18.9/74.4 | 0.6/35.6 |
| | 1.7/264.5 | 1.3/933.4 | 8.6/853.2 | 45.4/531.9 | 5.8/285.0 | 15.2/134.1 | 19.6/74.8 | 2.4/36.5 |
| Al–Ni _{0.020} –Cu _{0.0375} | 1.5/263.9 | 3.7/934.9 | 2.2/856.7 | 42.9/531.5 | 26.0/285.0 | 8.4/133.6 | 14.8/74.4 | 0.5/35.6 |
| | 1.3/264.4 | 2.2/932.5 | 3.2/853.6 | 47.6/532.0 | 4.4/285.0 | 6.8/134.2 | 33.8/75.0 | 0.7/36.5 |
| Al–Ni _{0.080} –Cu _{0.0125} | 3.2/264.0 | 1.6/933.6 | 4.6/856.6 | 42.9/531.6 | 25.9/285.0 | 9.5/133.8 | 11.8/74.5 | 0.5/36.0 |
| | 1.8/264.6 | 1.0/933.1 | 6.6/853.4 | 46.2/532.0 | 5.6/285.0 | 9.1/134.4 | 28.9/75.2 | 0.8/36.8 |
| Al–Ni _{0.080} –Cu _{0.0375} | 2.5/263.8 | 2.5/934.9 | 3.2/856.5 | 45.0/531.4 | 22.0/285.0 | 11.4/133.5 | 12.9/74.3 | 0.5/35.6 |
| | 1.5/264.8 | 1.3/933.6 | 4.7/853.5 | 47.8/532.3 | 7.2/285.0 | 8.4/134.7 | 28.5/75.3 | 0.6/36.8 |

Note. Here and in Table 2 the contents of elements and after a slash the binding energies of the most characteristic peaks (Na1s, Cu2p_{3/2}, Ni2p_{3/2}, O1s, Ti2p_{3/2}, C1s, P2p, Al2p, W4f_{7/2}) are given. The binding energies are given for the maxima of the respective bands. The upper row corresponds to the initial sample and the lower one corresponds to the sample after Ar⁺ etching.

TABLE 2. Elemental Composition and Binding Energies of Elements in the PEO Coatings on Titanium (at.%/eV)

| Sample | Na | Cu | Ni | O | Ti | C | P | W |
|--|------------|------------|------------|------------|------------|------------|------------|----------|
| Ti | – | – | – | 43.5/530.9 | 11.5/458.2 | 45.0/285.0 | – | – |
| | | | | 51.2/531.1 | 47.3/458.3 | 1.5/285.0 | | |
| Ti–PBW | 1.1/1071.6 | – | – | 61.0/530.8 | 16.4/458.8 | 9.5/285.0 | 10.7/133.1 | 1.3/35.3 |
| | 0.8/1072.3 | | | 66.1/530.8 | 23.1/458.7 | – | 9.6/133.3 | 0.4/36.0 |
| Ti–Ni _{0.020} | 2.9/1071.7 | – | 4.7/856.7 | 49.1/531.3 | 3.2/458.7 | 26.8/285.0 | 12.8/133.1 | 0.5/35.4 |
| | 6.3/1072.1 | | 8.5/853.0 | 55.5/531.2 | 8.1/458.7 | 8.6/285.0 | 12.5/133.3 | 0.5/35.6 |
| Ti–Ni _{0.080} | 0.9/1072.0 | – | 12.3/857.1 | 54.0/531.7 | 1.8/459.1 | 15.9/285.0 | 14.0/133.6 | 1.1/35.7 |
| | 4.0/1072.7 | | 15.5/852.8 | 52.7/532.3 | 4.9/459.5 | 8.7/285.0 | 13.0/134.5 | 1.2/36.6 |
| Ti–Cu _{0.0125} | 0.9/1071.8 | 14.0/935.4 | – | 53.4/531.5 | 3.4/459.1 | 15.2/285.0 | 12.1/133.5 | 1.0/35.6 |
| | 3.6/1072.0 | 10.2/932.9 | | 60.5/531.0 | 8.9/458.7 | – | 16.0/133.1 | 0.8/36.2 |
| Ti–Cu _{0.0375} | 1.7/1071.5 | 1.6/934.0 | – | 59.0/531.0 | 8.8/458.8 | 13.5/285.0 | 14.7/133.3 | 0.7/35.2 |
| | 1.6/1071.7 | 0.9/932.7 | | 65.6/530.4 | 17.0/458.1 | 1.4/285.0 | 12.8/132.8 | 0.7/35.0 |
| Ti–Ni _{0.020} –Cu _{0.0125} | 0.7/1071.5 | 4.0/934.8 | 1.5/856.3 | 42.4/531.1 | 3.3/458.5 | 39.4/285.0 | 8.3/132.9 | 0.4/35.4 |
| | 4.1/1071.4 | 4.1/932.4 | 5.0/852.6 | 57.0/530.8 | 12.6/458.6 | 5.6/285.0 | 11.1/133.4 | 0.5/35.5 |
| Ti–Ni _{0.020} –Cu _{0.0375} | 1.2/1072.0 | 16.3/935.4 | 2.0/857.0 | 50.5/531.6 | 1.8/459.0 | 16.5/285.0 | 11.0/133.5 | 0.7/35.6 |
| | 3.8/1072.3 | 12.3/933.2 | 2.6/853.3 | 54.1/531.4 | 5.3/458.5 | 6.0/285.0 | 15.4/133.6 | 0.5/35.7 |
| Ti–Ni _{0.080} –Cu _{0.0125} | 1.2/1071.8 | 7.2/935.0 | 7.2/856.5 | 52.8/531.3 | 3.0/458.7 | 16.7/285.0 | 11.4/133.4 | 0.5/35.3 |
| | 3.7/1072.4 | 5.0/933.0 | 9.1/854.0 | 58.3/531.5 | 9.5/459.0 | 1.7/285.0 | 11.7/134.0 | 1.0/36.2 |
| Ti–Ni _{0.080} –Cu _{0.0375} | 1.2/1071.4 | 5.6/934.7 | 6.5/856.5 | 49.4/531.4 | 2.8/458.7 | 22.6/285.0 | 11.5/133.5 | 0.4/35.8 |
| | 3.5/1072.9 | 5.1/933.3 | 10.1/853.5 | 54.6/531.8 | 10.3/459.5 | 5.0/285.0 | 10.9/136.3 | 0.5/36.4 |

TiO) along with Al⁰ and Ti⁰. The presence of slightly oxidized forms of aluminum (in the upper layer the Al⁰ fraction is 2.6 at.%, in the lower one it is 46.0 at.%) and titanium (the Ti⁰ fraction is 4.7 at.% and 8.7 at.% respectively) is partially caused by the ion bombardment effect, however, in our opinion, it is mostly due to the strip of low-lying, underoxidized (by atmospheric oxygen) layers of the initial sample. An almost complete absence of carbon after etching testifies to its location in the upper layer.

Basic coatings. As follows from the data obtained, the oxidation of the initial samples in the PBW electrolyte leads to the oxidation of the deeper metal base (aluminum or titanium) layers, the incorporation of electrolyte element, such as Na, P, W (see Al–PBW and Ti–PBW in Tables 1, 2), and correspondingly, compounds based on them (Figs. 1, 2). The characteristic E_b values indicate the presence of metal base oxides and phosphates, sodium phosphate, carbon compounds, and an insignificant amount of tungsten oxidized forms in the surface layers of the coatings. The presence of phosphates (initial Na₃PO₄, and also AlPO₄ and TiP₂O₇) in the coatings, which seem to form during the PEO process, can be stated from the analysis of the atomic composition of the coatings and also the characteristic P2*p* electron E_b values [18] that are 134.2 eV and 133.1 eV respectively for the coatings being studied (Tables 1, 2). In the coatings on titanium, as compared to the similar coatings on aluminum, a much less content of metal base, and correspondingly, its oxides (35-40 at.% TiO₂) is observed. A much larger amount of phosphorus, and correspondingly, phosphates (e.g., Ti(PO₃)₃ ~45 at.% or TiP₂O₇ up to 50 at.%) is incorporated into them. The occurrence of a large amount of phosphates, including titanium pyrophosphate

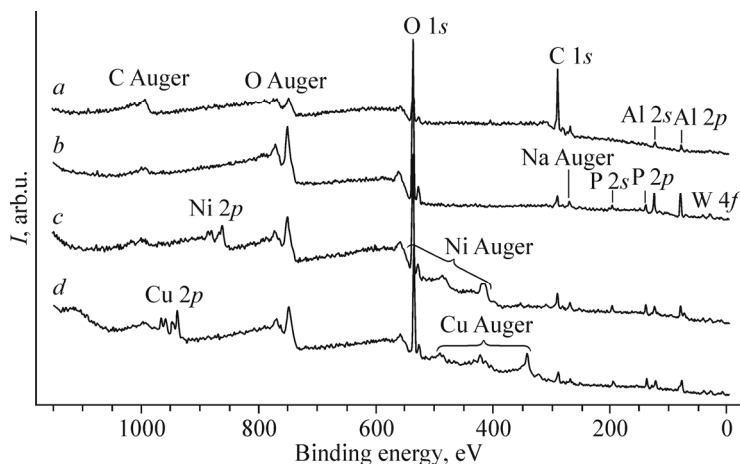


Fig. 1. Survey XPS spectra of the coatings formed on aluminum: Al (a), Al–PBW (b), Al–Ni_{0.080} (c), Al–Cu_{0.0375} (d).

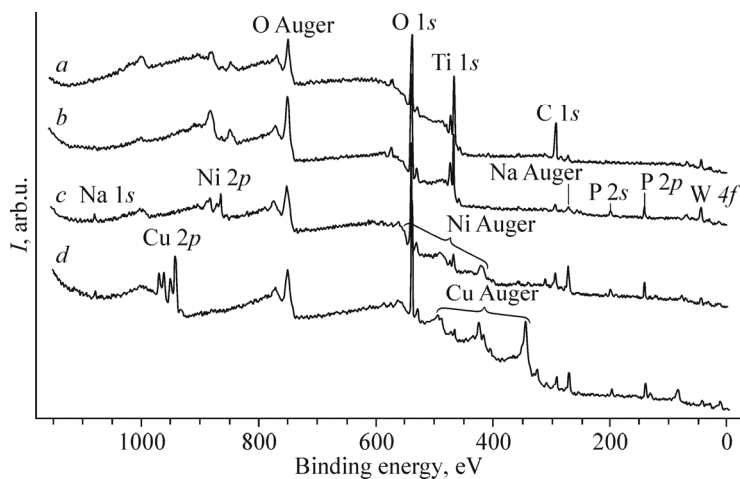


Fig. 2. Survey XPS spectra of the coatings formed on titanium: Ti (a), Ti–PBW (b), Ti–Ni_{0.020} (c), Ti–Cu_{0.0125} (d).

TiP₂O₇, in the coatings on titanium during PEO was previously established in [19]. Based on the analysis of the elemental composition of the coatings and stoichiometric arguments, the occurrence of Ti(PO₃)₃ cannot be excluded in the coatings that, as shown in [20], can be synthesized at high temperatures, which is just observed during PEO. In the coatings formed on aluminum, the Al₂O₃ alumina fraction reaches 60 at.%, and that of aluminum phosphate AlPO₄ reaches ~20 at.%. A complex contour of the C1s band evidences the presence of different carbon forms: aliphatic (about 9 at.%), oxidized (other). Finally, the W4f electron band with a maximum at 35.8 eV testifies to the occurrence of tungsten in oxidation state 6+. It is also not excluded that the base coatings contain a certain amount of boron compounds. The overlap of B1s and P2s bonds does not allow us to judge this unambiguously, however, the analysis of intensities of phosphorus 2s and 2p bands indicate this possibility. The same is supported by boron incorporation (up to 10 at.%) in the PEO coatings on aluminum from borate electrolytes, which was previously established by laser mass spectrometry in [21].

From the comparison of the surface and near-surface layers of the coatings (Tables 1, 2) it follows that the near-surface layers are characterized by a higher relative concentration of base elements and a smaller, especially for aluminum, phosphorus concentration (phosphates). The carbon concentration is also smaller in the near-surface layers, which indicates its main location on the surface. The similar oxidation states of metal base in the surface and near-surface layers (the absence of a noticeable amount of the forms reduced during etching) should also be noted. This testifies to the insignificant effect of performed ion etching, which is essential in the analysis of a number of properties of the coatings.

In general, based on the data obtained, we may assume that the coatings formed in the PBW electrolyte, in both upper part and adjacent layer, consist of the metal base oxide (Al₂O₃ or TiO₂) with incorporated additions such as metal base phosphate (-s), sodium phosphate, tungsten oxidized forms, and carbon-containing compounds (Fig. 3).

Ni-containing coatings. When nickel acetate is introduced into the composition of the PBW electrolyte, apart from the structural components typical of Al–PBW and Ti–PBW, a large amount of nickel-containing compounds formed in the surface layer of the coatings obtained. The observed Ni 2p_{3/2} E_b values near 857 eV (Tables 1, 2) reveal the presence of nickel in the strongly oxidized state, probably in the Ni₂O₃ form, and the elemental composition of the coatings allow us also to suppose the occurrence of nickel phosphates. Moreover, the experimental facts do not exclude the occurrence of more complex compounds in these coatings, e.g. spinel type NiAl₂O₄, whose fraction, according to the stoichiometric analysis, can reach 10 at.%. According to the data obtained (Tables 1, 2), the concentration of nickel compounds increases in the coatings as the nickel acetate concentration increases in the electrolyte.

In general, the coatings formed in Ni-containing electrolytes (see Al–Ni_x and Ti–Ni_x in Tables 1 and 2) are characterized by a more uniform combination of components in comparison with the coatings formed in the PBW electrolyte (Fig. 4). A significant distinction of the coatings formed on titanium from the similar coatings on aluminum is a greater incorporation of phosphorus, and correspondingly, 3d element phosphates into them (Tables 1, 2 and Fig. 4) whose fraction can reach 60 at.%.

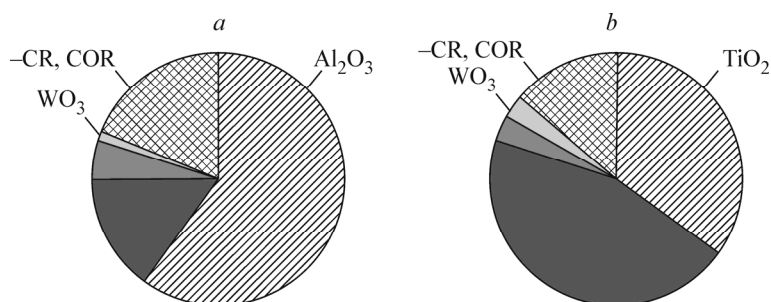


Fig. 3. Assumed composition of the surface of the base coating on aluminum Al–PBW (a) and titanium Ti–PBW (b). R = H, C, or O. Here and in Fig. 4 the combined results are presented. The sector area reflects the averaged relative content of the respective component in the coating.

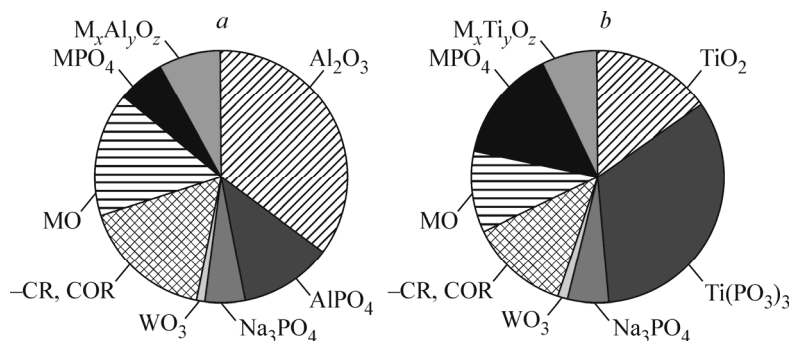


Fig. 4. Assumed composition of the surface of the Ni- or Cu-containing coating on aluminum Al–Ni_x (Al–Cu_y) (a) and titanium Ti–Ni_x (Ti–Cu_y) (b). M = Ni or Cu. MO, MPO₄, and M_xAl_yO_z and M_xTi_yO_z conventionally denote oxides of 3d elements, their phosphates, and spinel structure types.

The composition of the coatings in the near-surface area (at a depth from 3 nm to 6 nm) stripped by ion etching is characterized by higher Ni, Na, Al, Ti concentrations in them, and on the contrary, substantially lower C, P concentrations, and O, W concentrations close to the surface one (Tables 1, 2). According to the binding energies, the states of the mentioned elements, except Ni, insignificantly differ in the upper (surface) and lower layers of the coatings. In the surface layers of the coatings formed on both aluminum and titanium, nickel is in oxidation state 3+; along with it, the near-surface layers contain less oxidized forms (Fig. 5a). The relative concentration of these low oxidized forms is much higher in the coatings on aluminum than in the coatings on titanium, with strongly oxidized forms dominating over them in both cases. To a greater extent, we associate the presence of both reduced nickel forms in a low oxidation state, as well as the presence of slightly oxidized forms of aluminum and titanium in the near-surface layers of the coatings with the strip of low-lying underoxidized layers of the initial samples, into which these nickel forms incorporate during the coating formation process.

Cu-containing coatings. For the upper layers of copper-containing coatings (see Al–Cu_y and Ti–Cu_y in Tables 1 and 2) the regularities similar to those found for nickel-containing ones are observed. In the upper layers of the coatings copper is in the Cu²⁺ state, which is indicated by the shape of Cu2p spectra (the presence of shake-up satellites) (Fig. 5b) and the E_b values (Tables 1, 2). It is possible to assume that along with the above mentioned components inherent in PBW coatings, these coatings contain CuO; the presence of Cu(OH)₂ is not excluded. It is also possible that a part of analyzed copper is in the composition of spinel type structures CuAl₂O₄, Cu_xTi_yO_z, which can be supported by the characteristic binding energies of the Cu2p_{3/2} line [22-25]. Furthermore, the stoichiometric analysis indicates that a certain part of copper is in the composition of phosphates whose fraction can reach 30 at.% in the coatings on aluminum and ~60 at.% in the coatings on titanium.

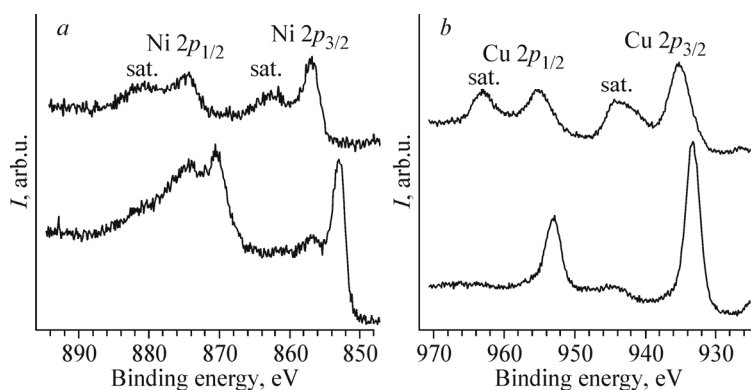


Fig. 5. Detailed Ni2p (a) (Ti–Ni_{0.020} sample) and Cu2p (b) spectra (Ti–Cu_{0.0125} sample). Upper spectra show the initial surface; lower ones show the surface after Ar⁺ etching.

In the near-surface layers stripped by Ar^+ etching of about 3 nm, a substantial growth in the metal base concentration, C burnout, and a considerable decrease in the Cu content are observed. This may evidence either the copper concentration mainly in the surface layers of the coatings or the layered structure of the coatings with the alternation of regions with a different copper content. This conclusion is valid for the upper part (about 6 nm) of micronic coatings whose formation occurs at the final stage of the PEO process. It is the uneven copper distribution over the coating thickness that is most likely to cause the non-equal content of $3d$ elements in the upper layers. The copper oxidation state in the near-surface layer is Cu^+ , as it follows from the analysis of the detailed spectra (Fig. 5b).

Ni,Cu-containing coatings. The mixed coatings formed in electrolytes containing nickel and copper acetates simultaneously contain the compounds of both $3d$ elements. The composition of their surface layers strongly depends on the ratio of components in the electrolyte and the formation time. However, the regularities of changes in the concentration and chemical state of $3d$ elements in the mixed Ni, Cu-containing coatings are similar to those observed in the coatings containing either Ni or Cu. In particular, the content of $3d$ elements increases with increasing concentration of respective acetates in the electrolyte, the nickel content decreases and the copper content increases after etching; and also less oxidized forms of $3d$ metals are observed after etching (see $\text{Al-Ni}_x\text{-Cu}_y$ and $\text{Ti-Ni}_x\text{-Cu}_y$ in Tables 1, 2).

The phosphorus content substantially differs in the coatings. In the mixed coatings on aluminum it is much higher than that in the mono-coatings (containing only one of $3d$ elements – Ni or Cu), whereas for the coatings on titanium these distinctions are insignificant at a total phosphorus concentration much higher than that in the coatings on aluminum. This seems to determine the dominance of phosphates over oxides in the coatings on titanium and the inverse situation in the coatings on aluminum. As shown in [26], the composition of phosphates can be complex and involve phosphates of both Ti and $3d$ elements. In our opinion, in the upper layers of the coatings there seem to be the situation when almost all observed titanium is contained in phosphates and $3d$ elements (Ni and Cu) are contained in the composition of both oxides and, to a large extent, phosphates.

CONCLUSIONS

The combination of the obtained data characterizes the general regularities of the composition and structure of the studied coatings. During oxidation, on the metallic support a layer forms, which consists of metal base (Al or Ti) oxides and phosphates, $3d$ metal (Ni and/or Cu) oxides and phosphates, some amount of spinel structure types, oxidized forms of tungsten and carbon-containing compounds. A remarkable distinction of the Ni- and/or Cu-containing coatings formed on titanium from the similar coatings formed on aluminum is the total insignificant concentration of metal base and a much higher content of phosphorus, and correspondingly phosphates of Ti and $3d$ elements. This determines the dominance of metal base and $3d$ metal phosphates in the coatings on titanium (up to 65 at.%), and their oxides in the coatings on aluminum (up to 60 at.%), which in turn appears to determine the distinctions in the properties of these coatings, in particular, the catalytic activity in conversion of CO to CO_2 [26, 27].

From the comparison of the XPS spectra of the initial and etched samples different attitudes of elements in the coating thickness follows. Thus, on passing from the upper to the lower layers of the coatings an increase in the aluminum (titanium) and oxygen concentrations is observed along with a decrease in the carbon and phosphorus concentrations. An increase in the nickel content and, on the contrary, a decrease in the copper content are also observed, which evidences the Cu concentration in the surface layers and Ni concentration in the near-surface layers of the coatings.

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