
NEW SUBSTANCES,
MATERIALS, AND COATINGS

Thermally Stimulated Evolution of the Surface of Ni- and Cu-Containing Plasma-Electrolytic Oxide Coatings on Titanium

V. S. Rudnev^{a, b, *}, I. V. Lukiyanichuk^a, M. S. Vasilyeva^{a, b}, and A. A. Zvereva^a

^a*Institute of Chemistry, Far East Branch, Russian Academy of Sciences, Vladivostok, 690022 Russia*

^b*Far Eastern Federal University, Vladivostok, 690091 Russia*

**e-mail: rudnevvs@ich.dvo.ru*

Received March 28, 2018; revised April 19, 2018; accepted May 25, 2019

Abstract—The effect of the temperature of annealing in air on the surface architecture and composition of oxide layers has been studied. Copper-enriched nanosized crystals of triangular shape are present on the surface at the annealing temperatures of 500–700°C. Rectangular nano- and microcrystals of a possible composition of NiWO₄ are formed on the surface after annealing at 750–850°C. Nanowhisker brushes, similar in composition to nickel titanates, cover the surface after annealing at 900–950°C. Transformation of the surface architecture and composition on the micro- and nanolevels correlates to the coatings' activity in the catalysis of the reaction of oxidation of CO to CO₂.

Keywords: plasma electrolytic oxidation, titanium, coatings, oxidation annealing, surface architecture, nano- and microformations

DOI: 10.1134/S2070205119040178

1. INTRODUCTION

“Metal/oxide coating” composites are widely used in catalysis [1–3], medicine [4, 5], and sensorics [6, 7]. To enhance their functional properties, special attention has been recently paid to the development of ways to increase the surface area of such composites, in particular, to create ensembles of nanosized particles on their surface [8–14].

Oxide nanostructures fixed on a metal surface can be produced in various ways: thermal oxidation of metal substrates [8, 9], treatment by NH₃–H₂O₂ vapors [10], anode oxidation [11], and template synthesis [12–14]. In [15], V₂O₅–TiO₂ oxide layers of nanosheet morphology were synthesized on the titanium surface by the method of plasma electrolytic oxidation (PEO).

An original method of producing Ni-containing oxide nanowhiskers on the titanium surface was first suggested in [16, 17]. The background of these studies development can be summarized as follows. As was earlier demonstrated in [18], PEO coatings formed on titanium in phosphate–borate–tungstate (PBW) electrolyte (0.052–0.079 mol/L Na₃PO₄ + 0.026–0.039 mol/L Na₂B₄O₇ + 0.003–0.009 mol/L Na₂WO₄, [19, 20]) containing Ni(II) and Cu(II) acetates catalyzed the reaction of oxidation of CO to CO₂ at temperatures above 350°C. An additional impregnation of

these composites in solutions of Ni(II) and Cu(II) nitrates with subsequent annealing in air at 500°C for 4 h led to an increase in their catalytic activity in this reaction and decrease in the temperature of the conversion initiation down to 200°C [18]. The concentrations of nickel and copper on the surface of such coatings were about 20 at %. In studies of the coatings' thermal behavior, it was shown that, starting from the annealing temperature of 750°C, individual whiskers emerged on their surface and, after annealing at temperatures >850°C, the surface was covered with a brush of whiskers with a length of 10 μm and a diameter from dozens to 200 nm [16, 17] (see Fig. 1). Note that in the course of the annealing temperature increase, copper goes from the surface into the bulk of the coating, most probably, due to thermal diffusion processes [16, 17]. The whiskers' composition was determined as Ni₅TiO₇. However, according to [21], the whiskers composition rather corresponds to Ni₅TiO₄(BO₃)₂.

With an increase in the annealing temperature and a decrease in the copper content on the surface, the activity of the samples in the oxidation of CO to CO₂ decreased [17]. Meanwhile, the samples coated with a brush of nickel–titanium oxide nanowhiskers efficiently decomposed naphthalene as a model of tar during the catalytic steam reforming process, which

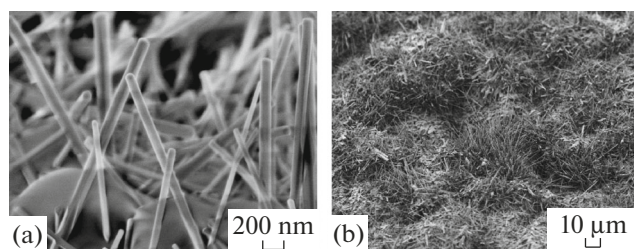


Fig. 1. SEM images of the surface of modified Ni- and Cu-containing coatings after additional annealing in air at (a) 850 and (b) 950°C [17].

makes their application promising in biomass gasification processes [16].

The development of this approach was continued in [22–24]. Excluding copper salts from the compositions of the electrolyte for PEO and impregnating solution, the authors of [22] also fabricated Ni_5TiO_7 nanowhiskers on the coating surface. They believe that Ni_5TiO_7 grains in amorphous state were already present in the initial PEO coating and served as nuclei for nanowhiskers' growth at the annealing temperature of 1050°C. Titanium oxide (rutile) in the coating and nickel sorbed in the coatings and pores are the material for their growth. Using the same strategy at the annealing temperatures of 650–850°C, Zn(II) and Ni(II) tungstates were fabricated on the surface in the form of nanorods, nanomeshes, nanoflowers, or nanobands; i.e., $\text{ZnWO}_4/\text{TiO}_2/\text{Ti}$ and $\text{NiWO}_4/\text{TiO}_2/\text{Ti}$ composites were formed [23]. The new strategy consisting in excluding the stage of impregnation in the nitrate solution was used in [24] for the synthesis of $\text{MnWO}_4/\text{TiO}_2/\text{Ti}$ composites. Essentially, the electrolyte for PEO served as an impregnating solution. Annealing at 850°C led to the growth of MnWO_4 nanowhiskers on the surface. The authors of [23, 24] believe that in the described cases ZnWO_4 , NiWO_4 , and MnWO_4 tungstates in the amorphous state were already present in the initial PEO coating and served as nuclei for corresponding nanoformations at increased temperatures. The described examples show the prospects of application of PEO layers formed in the PBW electrolyte as the basis for thermally stimulated growth of nanoobjects of specific composition fixed on their surface.

Earlier [17], we studied the thermal behavior of $\text{NiO} + \text{CuO}/\text{TiO}_2/\text{Ti}$ composites fabricated by combination of PEO and impregnation with subsequent annealing at 500°C. However, the study was conducted without controlling for changes in morphology and composition of micro- and nanostructures forming at each stage. The objective of the present work was to investigate the evolution and composition of micro- and nanostructures on the $\text{NiO} + \text{CuO}/\text{TiO}_2/\text{Ti}$ composites' surface in the whole range of annealing temperatures from 500 to 950°C.

2. MATERIALS AND METHODS

2.1. Preparation of Samples

PEO layers were formed on titanium wire of a diameter of 2 mm and a length of 16 cm made of VT1-0 titanium alloy (Ti content higher than 99.6%). Prior to oxidation, for the surface standardization, the wire was polished until a mirror-like condition was reached (8–9 grades of finishing) by the chemical method in the mixture $\text{HF} : \text{HNO}_3 = 1 : 3$ (in volume) at 70°C. Then, the samples were washed by distilled water and dried at 70°C in air.

PEO layers containing nickel and copper compounds were formed, as in [16, 17], in an aqueous electrolyte of the composition $0.066 \text{ M Na}_3\text{PO}_4 + 0.034 \text{ M Na}_2\text{B}_4\text{O}_7 + 0.006 \text{ M Na}_2\text{WO}_4 + 0.1 \text{ M Ni}(\text{CH}_3\text{COO})_2 + 0.025 \text{ M Cu}(\text{CH}_3\text{COO})_2$ in a galvanostatic mode at anode polarization at an effective current density of $i = 0.1 \text{ A/cm}^2$ for 10 min. A computer controlled TER4-100/460 thyristor device operated in a unipolar mode served as a current source. The counter electrode was a bath case made from stainless steel with a water-cooled jacket. The electrolyte was stirred by a mechanical stirrer; the solution temperature was not higher than 30°C.

The obtained samples with coatings of a thickness of $\sim 25 \mu\text{m}$ were immersed in an aqueous solution containing 1 mol/L $\text{Cu}(\text{NO}_3)_2$ and 1 mol/L $\text{Ni}(\text{NO}_3)_2$. Solutions with salt concentrations of 0.5 and 2 mol/L were used in some experiments. The compositions were held in the impregnating solution for 1 h. Thereafter, the samples were dried above the electric hot plate in air and annealed in a furnace at 500°C for 4 h. Then, the wire with a modified coating was cut into fragments of a length of 1.5 cm. The prepared samples were annealed in air at 700, 750, 800, 850, 900, and 950°C, while the samples were placed into a furnace already preheated to preset temperatures.

2.2. Methods of Study of the Samples

The surface morphology was studied using a Hitachi S5500 high-resolution scanning electron microscope (SEM) (Japan) with an UltraDry energy-dispersive spectrometer (Thermo Scientific, United States). Prior to studies, the samples were sputtered with gold. Using an energy-dispersive attachment, both average element composition of the surface sites of sizes of $60 \times 40 \mu\text{m}$ and specific formations' composition were studied focusing an analyzing beam on the sites of smaller sizes ($50 \times 50 \text{ nm}$ and larger).

The X-ray patterns of the samples with coatings were recorded using a D8 ADVANCE X-ray diffractometer (Germany) under $\text{CuK}\alpha$ -radiation. The EVA search software with the PDF-2 database was used in conducting the X-ray diffraction (XRD) analysis.

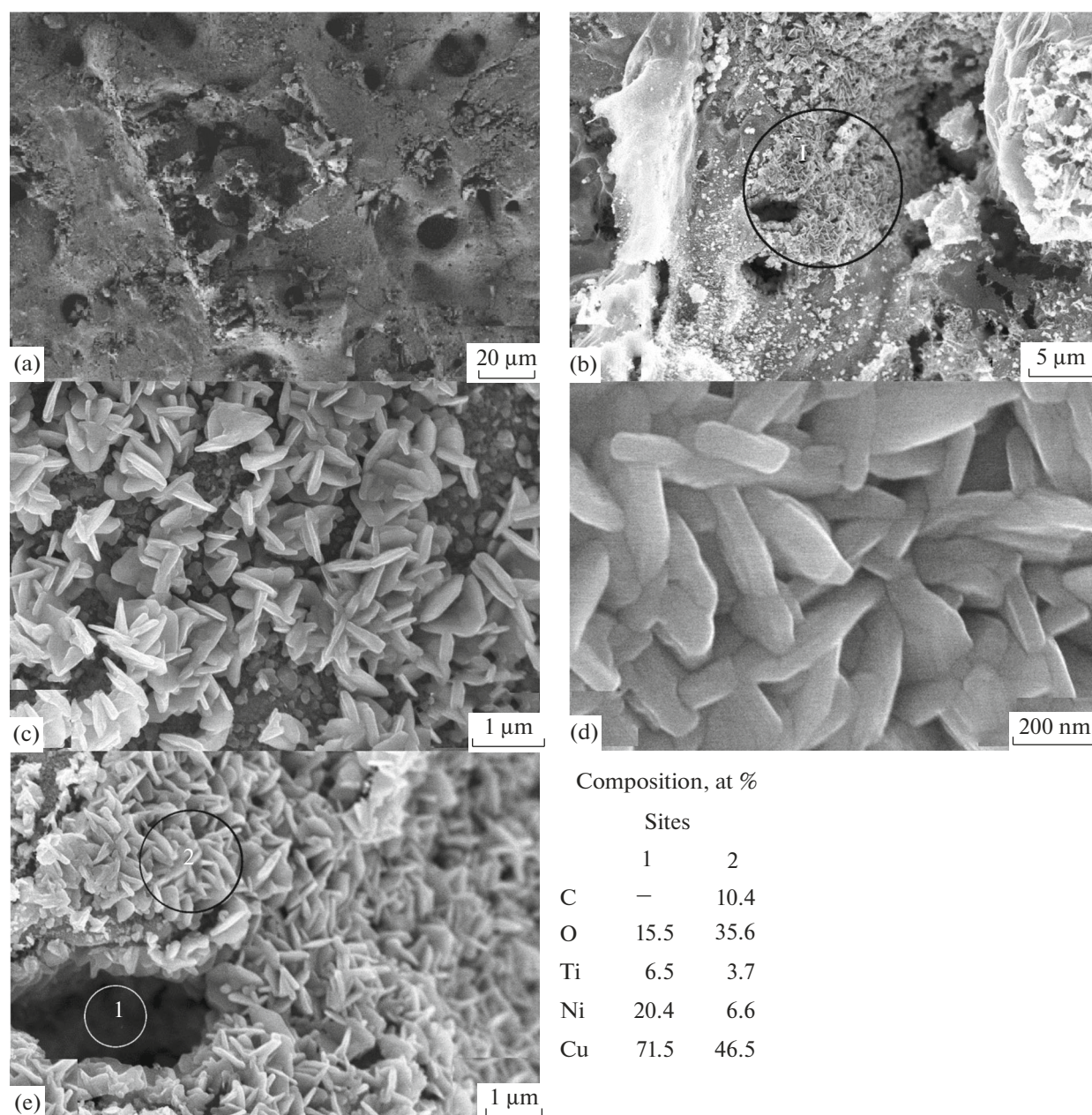


Fig. 2. The surface morphology of PEO coatings (a) formed in the PBW NiCu electrolyte and (b–e) additionally impregnated in 1 M $\text{Cu}(\text{NO}_3)_2$ + 1 M $\text{Ni}(\text{NO}_3)_2$ solution and annealed in air for 4 h at 500°C. The numbers (b) 1 and (c) 1 and 2 denote the analyzed sites. The composition of site 1 is shown in the table and the compositions of sites 1 and 2 in the figure.

3. RESULTS

3.1. The Modified PEO Coatings' Surface

The surface morphology of the initial PEO coatings is shown in Fig. 2a. As the result of impregnation and annealing at 500°C for 4 h, the ensembles of crystals of a triangular shape of a thickness of ~50 nm and a height of ~500 nm were formed on some sites of the surface (see Figs. 2b–2e). The averaged composition of the coating surface shown in the image of Fig. 2b including the systems of triangular formations, along

with the triangular crystals composition (site 1) according to the energy-dispersive analysis data, are shown in Table 1.

Analysis of the data given in Table. 1 and Fig. 2d shows that copper predominates in the composition of triangular formations. The data on the element composition of nanocrystals suggest the presence of titanium, nickel, and copper oxides with a significant predominance of the latter. Meanwhile, the nickel and copper concentrations measured for large sites (40 × 60 μm) were approximately the same (see Table 1).

Table 1. Averaged composition of the surface and triangular crystals after annealing in air at 500°C for 4 h

Element, at %	C	O	P	Ti	Ni	Cu
Surface as to XPS [17]	18.0	42.2	1.5	—	21.0	16.7
Surface, Fig. 2b	—	48.8	0.9	4.3	20.4	26.6
Composition of crystals I, Fig 2b	8.8	31.5	—	3.8	5.5	50.5

Table 2. The effect of the annealing temperature on the coatings' surface composition and on the composition and form of nano- and microcrystals

$T_{\text{ann}},\text{ }^{\circ}\text{C}$	Element composition (C, at %)							Nano- and microcrystals' form
	Surface of the coating							
	C	O	P	Ti	Ni	Cu	W	
500	—	48.8	0.9	4.3	20.4	26.6	—	Triangular
700	7.6	49.3	0.7	3.0	18.4	20.7	0.3	Triangular
750	12.4	59.9	1.9	4.7	14.5	6.0	0.6	Rectangular
800	10.5	68.5	4.9	4.9	7.5	—	3.7	Rectangular
850	28.2	54.0	3.8	5.2	7.7	—	1.1	Rectangular + individual whiskers
900								Whiskers
$T_{\text{ann}},\text{ }^{\circ}\text{C}$	Element composition (C, at %)							Nano- and microcrystals' form
	Crystals							
	C	O	P	Ti	Ni	Cu	W	
500	8.8	31.5	—	3.8	5.5	50.5	—	Triangular
700	11.1	43.6	—	1.8	8.4	35.0	0.1	Triangular
750	26.9	58.2	—	7.3	5.8	1.4	0.4	Rectangular
800	12.6	63.8	—	7.2	11.1	—	6.8	Rectangular
850	—	33.4	—	5.1	49.4	—	11.1	Rectangular + individual whiskers
900	—	57.0	—	11.0	32.0		—	Whiskers

The data on the element composition by X-ray electron spectroscopy earlier [17] are close to those obtained by energy dispersive analysis in the present work (see Table 1).

As one can see from the images in Figs. 2b and 2e, the crystals grow near pores. Apparently, components of the impregnating solution are accumulated in the pore and around it. One can observe that the crystals are located not only around the pore, but also inside it (see Fig. 2e). Analysis of the composition of crystals located inside the pore (site 1) and around the pore (site 2) confirms that the copper content in the crystals is sharply increased (Fig. 2e).

Thus, already after annealing at 500°C, one can observe a rather complex architecture of the surface: there are copper-enriched nanoformations concentrated near the pores.

3.2. The Surface after Annealing at Temperatures from 500 to 900°C

As can be seen after comparison of Figs. 3a and 3b, the samples' surfaces annealed at 500 and 700°C are

similar. The triangular nanoformations are present on a part of the surface in both cases. Accordingly, large amounts of copper are present both in average on the surface and in triangular nanocrystals (see Table 2). After annealing at 750°C, the average copper content on the surface sharply decreases, while copper in the surface layer of a thickness of $\sim 1 \mu\text{m}$ (depth of the analysis) is not found after annealing at 800 and 850°C; i.e., in compliance with the data of [16, 17], copper goes from the surface into the bulk of the oxide layer. The temperature of copper's intense thermal diffusion initiation is between 700 and 750°C (see Table 2). Note that, at an increase in annealing temperature from 500 to 800°C, the nickel content in the surface layer decreases too, but not so sharply, while the carbon, phosphorus, and tungsten concentrations increase.

Simultaneously with copper leaving the coating surface, the geometry of the nano- and microformations occupying its part is changed. After annealing at 750 and 800°C, they comprise elongated crystals of a length of about $1 \mu\text{m}$ (see Figs. 3c, 3d), while at 850°C they are crystals of a thickness of several micrometers and a length of up to $8 \mu\text{m}$. Along with the microcrystals

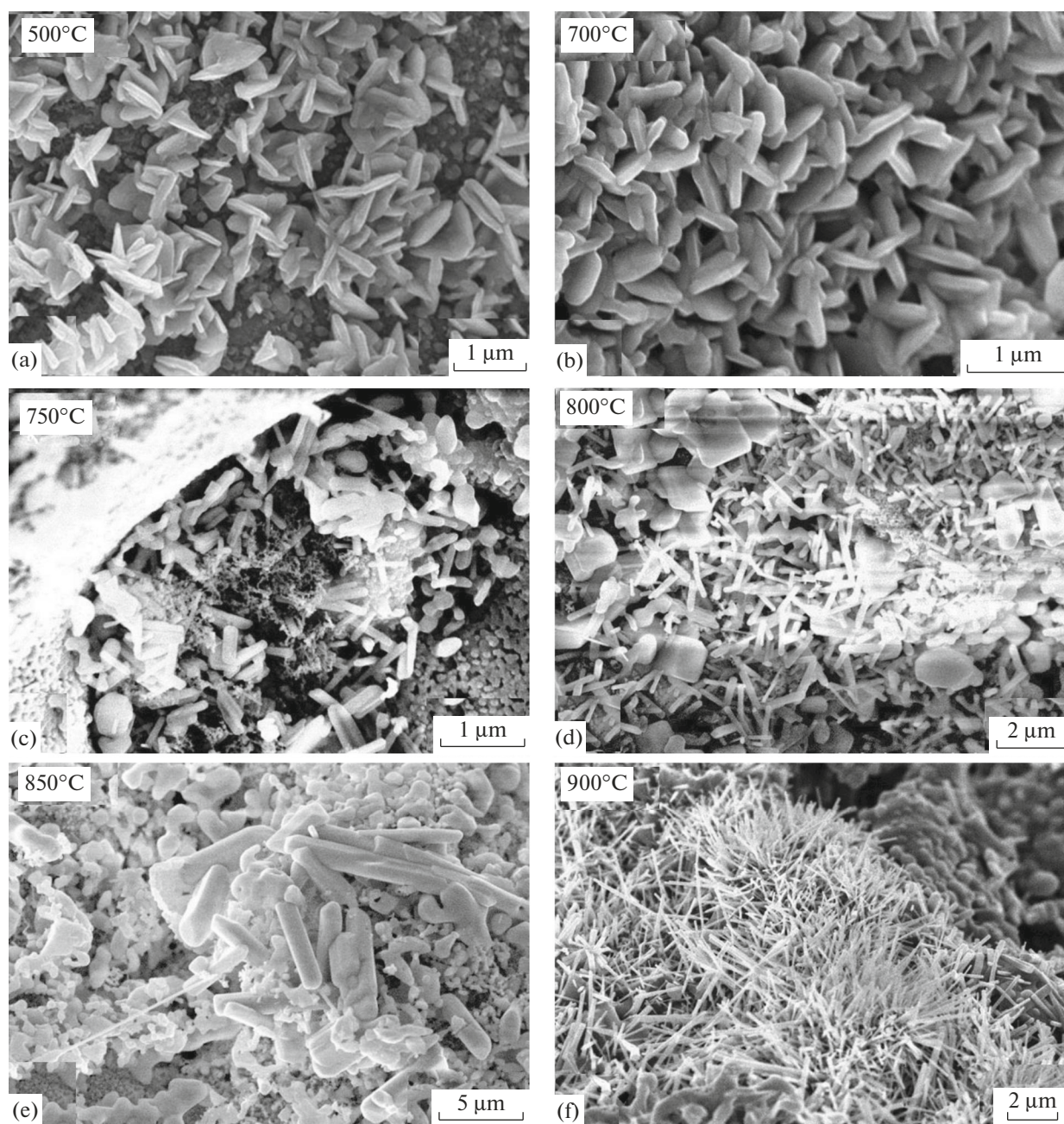


Fig. 3. Micro- and nanoformations on the surface of samples annealed for 4 h in air at the temperatures of (a) 500, (b) 700, (c) 750, (d) 800, and (e) 850°C and (f) for 1 h at 900°C.

tals presented, individual whiskers are found (see Fig. 3e). Then, in all cases at annealing temperatures of 900–950°C, the whiskers in shape and size similar to those observed in [16, 17] were predominantly formed (Fig. 3e).

In the rectangular crystals, the nickel content significantly increase along with the tungsten content until 850°C (see Table 2). It is interesting to note the absence of phosphorus in all crystals and of carbon in the rectangular crystals formed at 850°C and in whiskers at 900°C. In the first case, the measured ratio of Ni : Ti :

O : W elements in the crystals is equal 9.6 : 1.0 : 6.5 : 2.2; in the second case (in whiskers), it is 2.9 : 1.0 : 5.2 : 0.

Taking into account the data of [16, 17, 21–23], one can assume that, at the annealing temperature of 850°C, both Ni_5TiO_7 or $\text{Ni}_5\text{TiO}_4(\text{BO}_3)_2$ and NiWO_4 crystals are formed, while at that of 900°C predominantly nickel titanates or titanoborates are formed.

To determine the crystals' composition, XRD pattern of the sample with the coating annealed at 850°C was obtained (see Fig. 4a). The XRD pattern of the

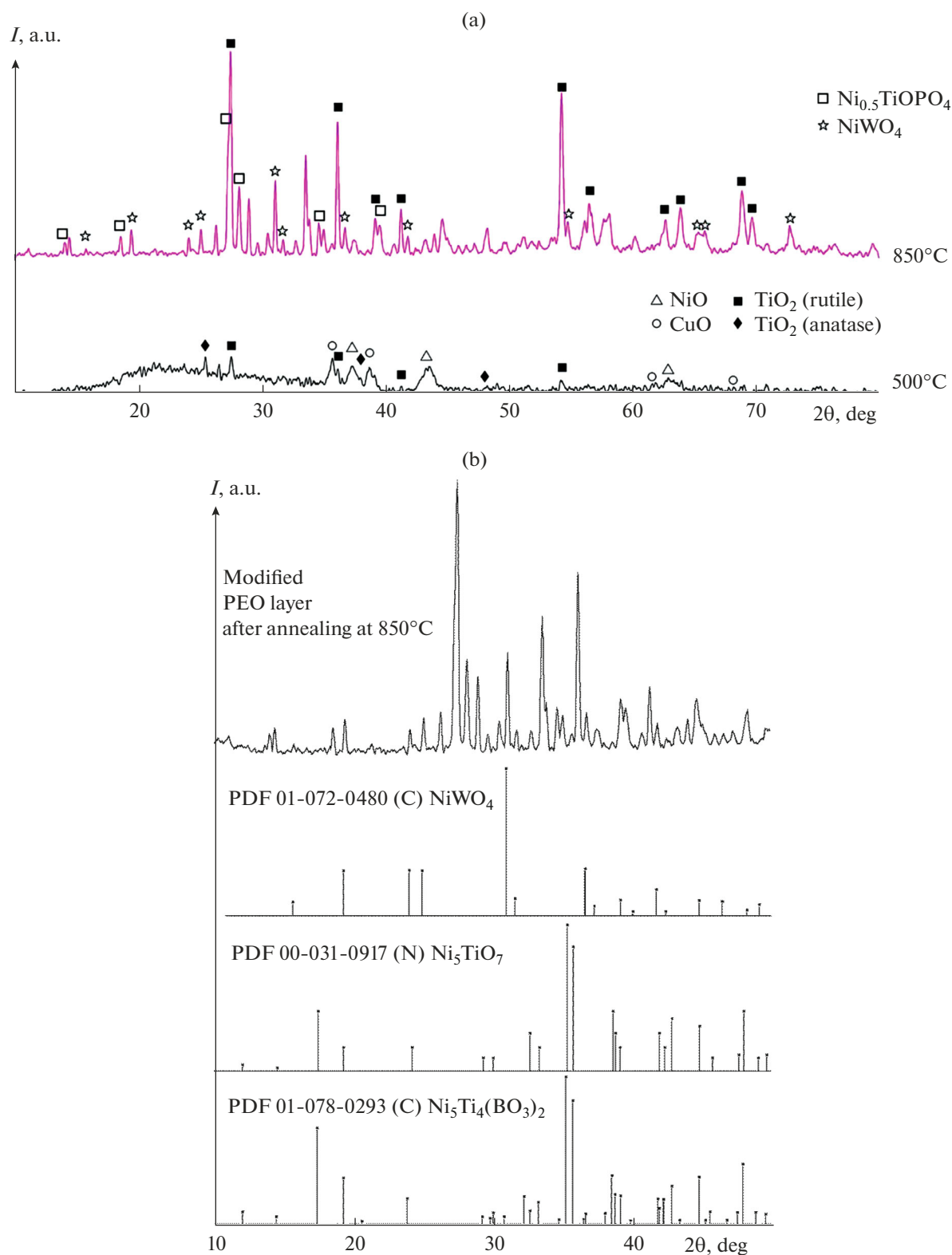


Fig. 4. (a) XRD patterns of samples with modified PEO coatings annealed for 4 h at 500 and 850°C and (b) standard XRD patterns for NiWO_4 , Ni_5TiO_7 , and $\text{Ni}_5\text{TiO}_4(\text{BO}_3)_3$.

modified coating annealed at 500°C is shown for comparison. Analysis of the XRD pattern (850°C) shows, that titanium oxide in the rutile modification, nickel

titanophosphate, and nickel tungstate are present in the coating composition, while titanate and nickel titanoborate are not revealed, see Fig. 4b.

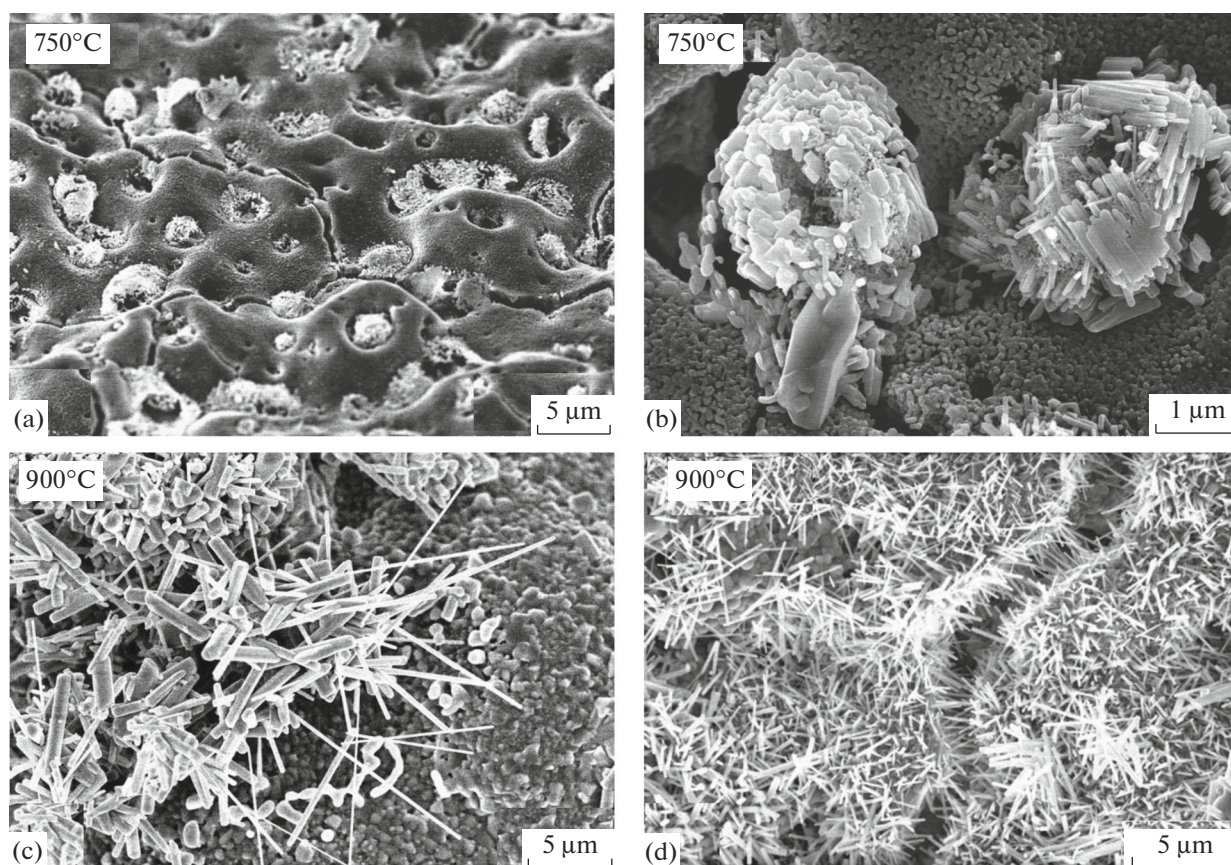


Fig. 5. SEM images of the surface of samples additionally impregnated in (a–c) 0.5 M $\text{Ni}(\text{NO}_3)_2$ + 0.5 M $\text{Cu}(\text{NO}_3)_2$ and (d) 2 M $\text{Ni}(\text{NO}_3)_2$ + 2 M $\text{Cu}(\text{NO}_3)_2$ solutions. Annealing for (a, b) 4 h at 750°C and (c, d) 1 h at 900°C.

3.3. Effect of Concentration of Impregnating Solutions

Figure 5 shows the surface of the PEO-coated samples impregnated in the 0.5 M $\text{Ni}(\text{NO}_3)_2$ + 0.5 M $\text{Cu}(\text{NO}_3)_2$ and in 2 M $\text{Ni}(\text{NO}_3)_2$ + 2 M $\text{Cu}(\text{NO}_3)_2$ solutions and annealed. One can see that air-annealing at 750°C of the samples impregnated in a solution with a reduced concentration of nitrates (Figs. 5a, 5b) results in a local growth of crystals, densely filling the pores. Apparently, at these concentrations, the volume of the impregnating solution is sufficient for the formation of crystals only in the pores. Nanowires (Figs. 5c, 5d) similar in composition to Ni_5TiO_7 or $\text{Ni}_5\text{TiO}_4(\text{BO}_3)_2$, according to the data of [16, 17, 21–23], are grown on the surface of samples annealed at 900°C for 1 h in all cases. The higher the concentration of impregnating solution, the more compact the surface filled by nanowires, but the smaller their length and diameter (compare Figs. 3f, 5c, 5d).

4. DISCUSSION

The annealing temperature used in producing initial samples was chosen according to the data of [18]. In this work, samples active in oxidation of CO to CO_2

were obtained. The samples were formed in the PBW electrolyte with additional content of 0.1 mol/L $\text{Ni}(\text{CH}_3\text{COO})_2$ and 0.025 mol/L $\text{Cu}(\text{CH}_3\text{COO})_2$ and then impregnated in the solution containing 1 M $\text{Ni}(\text{NO}_3)_2$ + 1 M $\text{Cu}(\text{NO}_3)_2$ and annealed at 500°C for complete nitrate decomposition.

The results of the present work demonstrate that, already on the particular sites of the initial coatings surface, there are triangular nano-objects of a thickness of ~50 nm and a height of ~500 nm (Fig. 2) containing copper oxides. Note that copper layers applied by the chemical or electrochemical deposition on aluminum, titanium, or fechral after the catalytic tests in 5% CO + air medium at a gradual temperature increase to 500°C [25] were transformed to triangular (“flake”) nanoformations of sizes of ~300–700 nm. Here, the data on the element analysis enable one to suggest that copper oxides, such as CuO and Cu_2O , are present in these layers. These nanoformations can be characteristic of copper oxide formed after annealing in air at 500°C on different supports.

As can be seen from Fig. 2, triangular nanoformations are predominantly placed around the pores. One can suggest that these are the sites, in which the

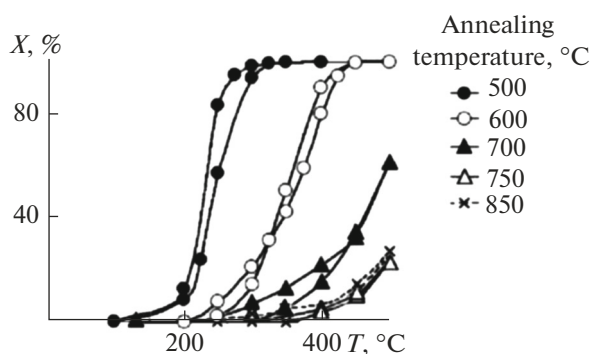
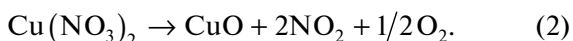


Fig. 6. Thermal dependence of the CO conversion (X) for the modified coatings annealed in air at the temperatures: 500, 600, 700, 750, and 850°C [17].

impregnating solution accumulates during the samples' annealing.

The thermal decomposition of solution components at 500°C must proceed according to the reactions [26]



Meanwhile, an increased copper content is observed in the formed crystals, despite the fact that the impregnating solution contains copper and nickel in an equimolar ratio. Besides, as can be seen from the element analysis data shown in Fig. 2e, there is an increased metal content in relation to the oxygen concentration in the crystals. This is obvious especially for the crystals in the pore. Apparently, thermal decomposition of salts according to Eqs. (1) and (2) and the removal of gaseous decomposition products from the surface occurs at the first stage. Then, the diffusion processes become predominant. Apparently, the copper diffusion coefficient is significantly higher than that of nickel in the studied composites. Under the experimental conditions, copper diffusing into the bulk and on the surface form copper-containing triangular crystals on the surface at the annealing temperatures of 500 and 700°C.

The increased metal concentrations and the decreased oxygen contents in the pores and their surroundings indicate the possible presence of both oxidized and reduced metals in these sites. The same situation is a characteristic of PEO coatings forming in the electrolytes with transition metal colloid hydroxides, such as iron and/or cobalt hydroxides [27].

With the annealing temperature increase up to 750–800°C, copper diffused predominantly into the coating depth. The triangular formations are transformed into rectangular ones of micron size with an increased nickel content and a significant one of tungsten. The data of [23], along with the XRD analysis

data (Fig. 4), enable one to suggest that micro- and nanocrystals consist of nickel tungstate in this case.

At a further annealing temperature increase to 900°C and higher, nanowires begin to fill the surface, forming nanobrushes.

Thus, the whole spectrum of nanoformations with controlled geometry and composition on the coatings surface can be obtained by setting the annealing temperature. The latter must be expressed in the formed coatings properties. Indeed, the architecture and composition of Ni- and Cu-containing nanoformations on the surface (see Table 2, Fig. 3) correlate with the coatings ability to catalyze the reaction of oxidation of CO into CO_2 (see Fig. 6). The transformation of triangular nanoformations with the increased copper content into rectangular ones with the increased nickel content leads to a drop in activity. The samples annealed at 850°C are low-activity in the oxidation of CO into CO_2 .

As was demonstrated in [23, 24], by using an electrolyte based on PBW one with additives of manganese, zinc, or nickel salts, both with or without additional impregnation in the solution of corresponding salts, after the high temperature annealing at 650–850°C, nanosized tungstates of the corresponding metals fixed on the titanium surface could be fabricated. In the latter case, the electrolyte served as an impregnating solution.

Note that the comparison of the results shown in [23] and [22] also leads to the conclusion that not only the electrolyte and impregnating solutions' composition are important, but also taking into account the used annealing temperatures' values: on the surface of composites formed under the same conditions, nanowhiskers of nickel tungstates grow at $T = 850^\circ\text{C}$, while nanowhiskers of nickel titanates at $T = 1050^\circ\text{C}$.

The formation of nanowires proceed in the same temperature range as for the output of titanium oxide in rutile modification on the surface of non-modified coatings on titanium [28, 29]. In these works, it was demonstrated that titanium diffuse through the pores to the coatings' surface at a temperature about 850°C and higher and forme regular rutile nano- and, then, microcrystals as well (see Fig. 7). Besides, it is known [27] that at the formation of PEO-coatings in the PBW alkaline electrolyte with additives of nickel, iron, and cobalt acetates, crystallite agglomerates with the increased content of these metals are formed in the pores of coatings, see Fig. 8. In this case, the walls and bottoms of the pores also contain the increased concentrations of the electrolyte's metals. At temperatures $\geq 850^\circ\text{C}$, the thermally stimulated titanium flow to the surface through the pores can lead to its interaction with nickel concentrated in the pores, with subsequent formation of nickel titanates on the surface.

In the present work, as in [16, 17, 22–24], a PBW electrolyte was used as a base one. The obvious ques-

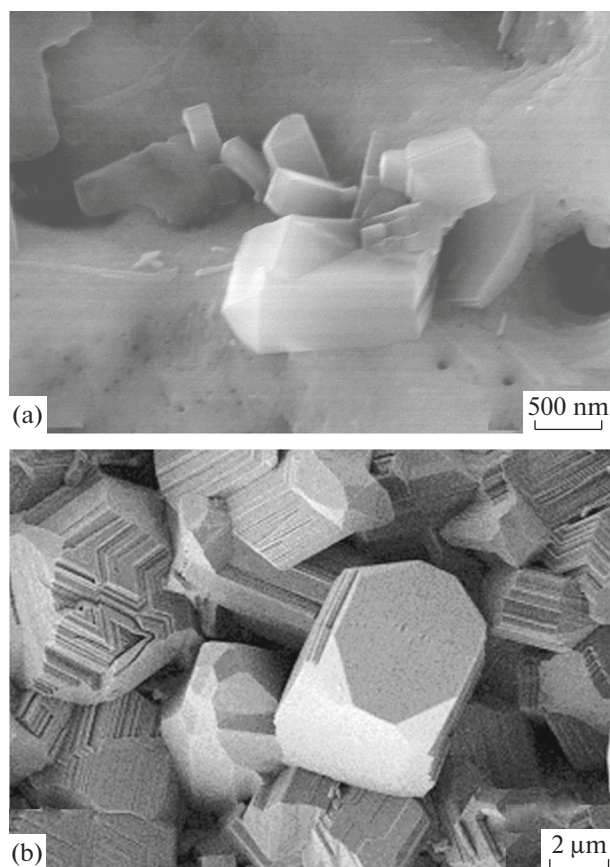


Fig. 7. The output (diffusion) of titanium to the surface with the formation of nano- and microcrystals of rutile for non-modified samples with PEO coatings at the annealing temperature of 850–900°C [28, 29].

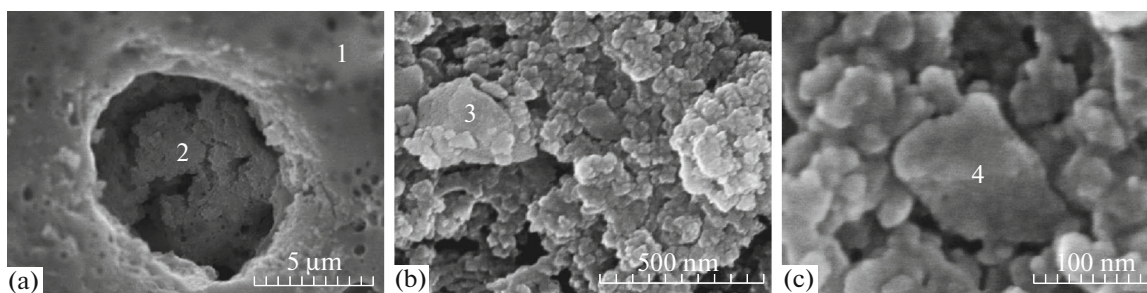


Fig. 8. Crystallites in the pores of the coatings formed on titanium by PEO technique in PBW electrolyte with addition of iron (III) oxalate [30].

tion is how the base electrolyte's composition and the ability of the formed PEO coating to interact with the impregnating solution (coatings with different water capacities, hydrophilic hydrophobic surface balance, etc.) will affect the compositions of growing nano- and microcrystals and nanowires.

5. CONCLUSIONS

To sum up, on the surface of PEO coatings formed in the PBW CuNi-electrolyte and modified by the

nickel and copper oxides, copper-enriched nanosized crystals of triangular shape were formed and accumulated in pores and their surroundings as a result of impregnation in nitrate solutions and annealing in air at 500–700°C. The annealing temperature increase leads to the copper diffusion into the depth of the coatings, transformation of triangular nanoformations into rectangular ones (750–800°C) containing nickel tungstate, and then to the emergence of nickel–titanium oxide nanowhiskers (above 850°C). The increase in the impregnation solution's concentration

contributes to a decrease of the length and diameter of the nanowhiskers formed at 900°C and to a more compactly filled (by them) surface at annealing. All the annealed coatings have a layered structure: a layer of nanocrystals, whose composition is determined by the annealing temperature, is located on the main matrix of a dense oxide coating.

The results of the present work, along with the data of [16, 17, 22–24], show that the combination of PEO in the PBW electrolyte with impregnation and subsequent annealing, or with just annealing, comprises an original method of a controlled fabrication of oxide systems with the developed surface architecture.

Coatings with surface developed at the nano- and microlevels are of interest for various practical applications, for instance, for application in catalysis and in medicine at deposition on implants, as coatings with specific capacity for absorption and scattering of different radiations, and as samples with specific magnetic characteristics.

FUNDING

The present work was partially supported by grant from the Russian Foundation for Basic Research no. 18-03-00418.

REFERENCES

- Yu, X.W., Chen, L., He, Y.Y., and Yan, Z.C., *Surf. Coat. Technol.*, 2015, vol. 269, pp. 30–35.
- Papurello, R.L., Cabello, A.P., Ulla, M.A., Neyertz, C.A., and Zamaro, J.M., *Surf. Coat. Technol.*, 2017, vol. 328, pp. 231–239.
- Domínguez, M.I., Pérez, A., Centeno, M.A., and Odriozola, J.A., *Appl. Catal., A*, 2014, vol. 478, pp. 45–57.
- Rafieerad, A.R., Ashra, M.R., Mahmoodian, R., and Bushroa, A.R., *Mater. Sci. Eng., C*, 2015, vol. 57, pp. 397–413.
- Shibli, S.M.A. and Mathai, S., *J. Mater. Sci.: Mater. Med.*, 2008, vol. 19, no. 8, pp. 2971–2981.
- Zhao, R.R., Xu, M.Z., Wang, J.A., and Chen, G.N., *Electrochim. Acta*, 2010, vol. 55, no. 20, pp. 5647–5651.
- Marinina, G.I., Vasilyeva, M.S., Lapina, A.S., Ustinov, A.Y., and Rudnev, V.S., *J. Electroanal. Chem.*, 2013, vol. 689, pp. 262–268.
- Jiang, X.C., Herricks, T., and Xia, Y.N., *Nano Lett.*, 2002, vol. 2, no. 12, pp. 1333–1338.
- Sun, Y., Xu, R., Yang, J.Y., He, L., Nie, J.C., Dou, R.F., Zhou, W., and Guo, L., *Nanotechnology*, 2010, vol. 21, no. 33, Paper 335605.
- Neyertz, C.A., Gallo, A.D., Ulla, M.A., and Zamaro, J.M., *Surf. Coat. Technol.*, 2016, vol. 285, pp. 262–269.
- Hahn, R., Brunner, J.G., Kunze, J., Schmuki, P., and Virtanen, S., *Electrochem. Commun.*, 2008, vol. 10, no. 2, pp. 288–292.
- Jitaru, M., Toma, A.M., Tertis, M.C., and Trifoi, A., *Environ. Eng. Manage. J.*, 2009, vol. 8, no. 4, pp. 657–661.
- Say, W.C. and Chen, C.C., *Jpn. J. Appl. Phys., Part 1*, 2007, vol. 46, no. 11, pp. 7577–7580.
- Chen, C.-C., Fang, D., and Luo, Z.P., *Rev. Nanosci. Nanotechnol.*, 2012, vol. 1, pp. 229–256.
- Bayati, M.R., Molaei, R., Zargar, H.R., Kajbafvala, A., and Zanganeh, S., *Mater. Lett.*, 2010, vol. 64, pp. 2498–2501.
- Jiang, X., Zhang, L., Wybornov, S., Staedler, T., Hein, D., Wiedenmann, F., Krumm, W., Rudnev, V., and Lukiyanichuk, I., *ACS Appl. Mater. Interfaces*, 2012, vol. 4, no. 8, pp. 4062–4066.
- Rudnev, V.S., Wybornov, S., Lukiyanichuk, I.V., Staedler, T., Jiang, X., Ustinov, A.Yu., and Vasilyeva, M.S., *Appl. Surf. Sci.*, 2012, vol. 258, pp. 8667–8672.
- Rudnev, V.S., Tyrina, L.M., Ustinov, A.Yu., Vybornova, S., and Lukiyanichuk, I.V., *Kinet. Catal.*, 2010, vol. 51, no. 2, pp. 266–272.
- Rudnev, V.S., Gordienko, P.S., Kurnosova, A.G., and Orlova, T.I., RF Patent 1783004, *Byull. Izobret.*, 1992, no. 47.
- Rudnev, V.S., Gordienko, P.S., Yarovaya, T.P., Zavidnaya, A.G., and Zheleznov, V.V., *Russ. J. Appl. Chem.*, 1994, vol. 67, no. 8, pp. 1128–1131.
- Nalbandyan, V.B., *J. Solid State Chem.*, 2017, vol. 249, pp. 27–28.
- Jiang, Y.A., Liu, B.D., Yang, L.N., Yang, B., Liu, X.Y., Liu, L.S., Weimer, C., and Jiang, X., *Sci. Rep.*, 2015, vol. 5, p. 14330.
- Jiang, Y.N., Liu, B., Zhai, Z., Liu, X., Yang, B., Liu, L., and Jiang, X., *Appl. Surf. Sci.*, 2015, vol. 356, pp. 273–281.
- Jiang, Y.N., Liu, B.D., Yang, W.J., Yang, B., Liu, X.Y., Zhang, X.L., Mohsin, M.A., and Jiang, X., *CrystEngComm*, 2016, vol. 18, pp. 1832–1841.
- Lukiyanichuk, I.V., Rudnev, V.S., Serov, M.M., Krit, B.L., Lukiyanichuk, G.D., and Nedorozov, P.M., *Appl. Surf. Sci.*, 2018, vol. 436, pp. 1–10.
- Preparative Inorganic Reactions*, Jolly, W.L., Ed., New York, London, Sydney: Interscience Publishers, 1964.
- Rudnev, V.S., Lukiyanichuk, I.V., Adigamova, M.V., Morozova, V.P., and Tkachenko, I.A., *Surf. Coat. Technol.*, 2015, vol. 269, pp. 23–29.
- Vasilyeva, M.S., Rudnev, V.S., Wiedenmann, F., Wybornov, S., Yarovaya, T.P., and Jiang, X., *Appl. Surf. Sci.*, 2011, vol. 258, no. 2, pp. 719–726.
- Rudnev, V.S., Malyshev, I.V., Lukiyanichuk, I.V., and Kuryavii, V.G., *Prot. Met. Phys. Chem. Surf.*, 2012, vol. 48, no. 4, pp. 455–461.
- Rudnev, V.S., Adigamova, M.V., Lukiyanichuk, I.V., Ustinov, A.Yu., Tkachenko, I.A., Kharitonovskii, P.V., Frolov, A.M., and Morozova, V.P., *Prot. Met. Phys. Chem. Surf.*, 2012, vol. 48, no. 5, pp. 543–552.

Translated by D. Marinin