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> NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

# Growth of Nanowires on the Surfaces of Multicomponent Oxide Coatings on Titanium

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**Abstract**—The thermal behavior of Ni- and Cu-containing coatings on titanium formed by plasma electrolytic oxidation and additionally modified with nickel and copper oxides is studied. Annealing of the produced multiphase coatings in air at a temperature of 750°C or higher is shown to result in the growth of surface nanowires, the main components of which are nickel, oxygen, and titanium. The sizes of nanowires depend on the temperature of annealing, and the diameters can be as large as tens or hundreds of nanometers at a length of several to tens of microns. Experimental and literature data show that the combination of plasma electrolytic oxidation with impregnation and annealing is promising for the production of both nanowires bound to metal-oxide substrates and individual nanostructures of certain compositions.

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# **INTRODUCTION**

In the last few decades, plasma-electrolytic oxidation (PEO), which is anodizing in electrolytes at voltages of spark and arc electric discharges, has been successfully used for the surface formation of complex oxide systems on metals and alloys [1-12], such as biocompatible layers that involve calcium phosphate [1, 2]; iron-containing coatings that absorb electromagnetic radiation in certain spectral ranges [3] or are ferromagnetic [4]; catalytically active layers that involve nickel, copper, and molybdenum oxides [5-8], etc.

In particular, Ni- and Cu-containing PEO layers on aluminum and titanium, which are active with respect to CO oxidation to CO<sub>2</sub> at temperatures above  $300^{\circ}$ C, were obtained in a Na<sub>3</sub>PO<sub>4</sub> + Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> +  $Na_2WO_4 + Ni(CH_3COO)_2 + Cu(CH_3COO)_2$  electrolyte [6, 7]. As was shown in the same works, additional impregnation of the coatings in an aqueous  $Cu(NO_3)_2 + Ni(NO_3)_2$  solution followed by annealing in air at 500°C results in a decrease in the content of oxygen-containing copper and nickel compounds in the modified coatings and the substantial increase in their catalytic activity. In the latter case, oxidation of CO to CO<sub>2</sub> proceeds at a temperature above  $150^{\circ}$ C. Functional properties of such complex oxide systems, which involve not only oxides of the metal treated, but also oxides of other metals, on the metals depend on many factors, including the surface structure and composition.

The object of this work was to study temperatureinduced changes in air in the surface structure and composition of systems that involve nickel and copper oxides on titanium, since the systems are considered to be promising in catalysis.

#### **EXPERIMENTAL**

Similarly to as in [6], plasma–electrolytic treatment of titanium specimens was carried out under galvanostatic conditions (at current density  $i = 0.1 \text{ A/cm}^2$ for 10 min) in an aqueous electrolyte of the following composition (M): 0.066 Na<sub>3</sub>PO<sub>4</sub> + 0.034 Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> + 0.006 Na<sub>2</sub>WO<sub>4</sub> + 0.1 Ni(CH<sub>3</sub>COO)<sub>2</sub> + 0.025 Cu(CH<sub>3</sub>COO)<sub>2</sub>. Coatings were formed on specimens made of sheet technical titanium of VT1-0 grade (0.2 Fe, 0.1 Si, 0.07 C, 0.04 N, 0.12 O, 0.01 H, >99.6% Ti at an admissible Al content of up to 0.7%) with a size of 20 × 20 × 1 mm or on a wire made of the same titanium with a diameter of about 1.5 mm. The set for the plasma electrolytic treatment, conditions of pretreatment and oxidation of specimens, the current source, and other experimental details can be found in [6].

Additional modification of PEO coatings was carried out similarly to as in [6] by exposing the specimens for an hour to an aqueous solution that contained 1 mol/L Cu(NO<sub>3</sub>)<sub>2</sub> and 1 mol/L Ni(NO<sub>3</sub>)<sub>2</sub>. Impregnated specimens were dried over an electric range and annealed in a furnace (SNOL 7.2/1100) at 500°C for 4 h in air.



**Fig. 1.** Surface of (a) original PEO coating, (b) PEO coating modified by impregnation and annealing at  $500^{\circ}$ C, and (c-f) modified coating additionally annealed at (c) 650, (d) 750, (e) 850, and (f) 950°C.

The modified PEO coatings obtained were additionally annealed in air for an hour at a temperature in a range from 650 to 950°C. In this case, specimens were placed in a cold furnace and taken away only upon natural cooling of the furnace to 100-150°C.

High-resolution surface images of the coatings were obtained and elemental analysis of the composition of coatings and threadlike crystals was carried out with an ULTRA 55 electron microscope (Carl Zeiss NTS GmbH, Switzerland) equipped with a special detector.

X-ray patterns of the coatings were recorded with a D8 ADVANCE X-ray diffractometer (Germany) in  $CuK_{\alpha}$  radiation. For phase analysis, the EVA search program and PDF-2 database were used.

## **RESULTS AND DISCUSSION**

Figure 1 shows the surface morphology of original PEO coatings (Fig. 1a), as well as modified Ni- and

Cu-containing coatings annealed in air at  $500^{\circ}$ C (Fig. 1b) and others additionally annealed at 650, 750, 850, or 950°C (Figs. 1c–f). On the surfaces of original coatings (immediately after PEO), one can see alternating protuberances with pores with a diameter of up to 10 µm on their tops and deeper areas (valleys) between them. Pores are chaotically arranged in valleys. Upon modification (impregnation and annealing at 500°C, Fig. 1b), valleys are filled with compounds based on the components of the impregnating solution and the surface relief becomes smoother.

Elemental and phase compositions, as well as thicknesses of the original and modified coatings, are listed in Table 1. According to the data, the mean thicknesses of the original and modified coatings are the same. The result confirms the above statement that components of the impregnating solution fill chiefly large pores and valleys. In contrast to the original coatings, the content of nickel in the modified coatings is nearly twice as large, while that of copper is four times as large. Moreover, crystalline NiO and CuO phases are present in the modified coatings. This means that the surface parts formed upon impregnation and annealing consist chiefly of nickel and copper oxides. Note that both original and modified Ni- and Cu-containing PEO coatings are active as catalysts with respect to CO oxidation at temperatures above 300-350 and 150-200°C, respectively [6, 7].

The modified wire specimens were additionally annealed in air at temperatures of 650, 700, 750, 800, 850, 900, or 950°C for an hour.

Upon additional annealing in air at temperatures of 650 and 700°C, a shell composed of components of the impregnating solution and containing nickel and copper oxides that was formed in valleys of the original coating becomes less pronounced (Fig. 1c). Probably due to the diffusion processes, components of the shell penetrate deeply into the original coating to form the corresponding alloys. In this case, the surface becomes cracked (Fig. 1c).

Starting from an annealing temperature equal to  $\sim$ 750°C, nanowires begin to grow on the surfaces of modified coatings (Fig. 1d). The initial growth of nanowires often takes place in the vicinity of pores and cracks. However, when the temperature of annealing is further increased, nanowires cover the whole surface of the coating (Figs. 1e, 1f). The surfaces of coatings

Table 1. Thickness and elemental (X-ray spectrum analysis data) and phase compositions of coatings

Composite	<i>h</i> , μ	Phase composition	Elemental composition, at %						
			Ni	Cu	Р	Ti	0	W	Na
PEO/Ti	40 ± 2	$TiO_2(r)$ $TiO_2(a)$	11.9	3.2	8.3	9.5	62.4	1.0	3.7
*PEO/Ti	40 ± 2	$\begin{array}{c} \text{TiO}_2(r) \\ \text{TiO}_2(a) \\ \text{NiO}, \text{CuO} \end{array}$	20.8	12.4	4.5	6.2	55.6	0.5	_

\* PEO coatings modified by additional impregnation and annealing at 500°C in air, (r)- rutile, (a) - anatase.

that were annealed at 950°C are nearly continuously covered with a nanowire brush. Depending on the temperature of annealing, nanowires have diameters of tens to hundreds of nanometers at lengths of several to tens of microns.

Note that, upon treatment at a temperature above 850°C, one can see splits and spalls of the coating, which partially exfoliates from the titanium substrate. The latter peculiarity seems to be caused both by the different coefficients of thermal expansion of the coating and titanium and by intense oxidation of titanium by oxygen from air that penetrates deeply toward the base substrate via cracks formed. The oxidation was confirmed in the case of  $ZrO_2 + TiO_2$  PEO coatings on titanium [10].

Analysis of the composition of nanowires was carried out on surface spots of  $50 \times 50 \text{nm}^2$  (Fig. 2) with the use of the energy-dispersive detector with which the ULTRA 55 microscope was equipped. The composition of the base coating was also determined (site 3in Fig. 2a). The data obtained are listed in Table 2. The results of the elemental analysis enable us to conclude that nanowires are composed chiefly of nickel oxide with admixtures of titanium, phosphorus, carbon, and aluminum compounds. Nanowires have nearly the same composition as the base coating material (base coating, Table 2) except for titanium. Similarly to the original surface, titanium is absent on the annealed surface. At the same time, the titanium content in nanowires is substantial (about 5.1–9.6 wt %), seemingly due to the diffusion from the depth of the coating to the growing nanowires.

Note that the analysis provides the composition of the bulk, which includes both nanowires and, partially, the coating material. This means that the results obtained in this work can by no means be related to the composition of nanowires solely. The relation is only qualitative.

As follows from the data (Table 2), copper is absent in nanowires and on the surfaces of specimens annealed at 850°C. We can suppose that copper diffuses from the surface deeply into the oxide coating at increased temperatures.

According to the results of X-ray phase analysis (XPA) (Table 1), specimens that were impregnated

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Fig. 2. Surface images of specimens covered with modified coatings annealed at  $850^{\circ}$ C for 1 h and sites where the composition of nanowires was determined.

and annealed at 500°C contain crystalline nickel, titanium, and copper oxides. Further annealing at still higher temperatures results in a decrease in signals of crystalline nickel and copper oxides and an increase in the intensity of signals of crystalline  $TiO_2$  in rutile and anatase modifications.

The XPA data correspond to the whole nanowireson-coating system, and we can scarcely formulate a definite conclusion about the phase composition of individual nanowires. Analysis of the elemental composition (Fig. 2, Table 2) shows that the main components of nanowires are oxygen, nickel, and titanium, with the mean atomic ratios (calculated from the data of Table 2) being Ni/Ti  $\approx$  4.2 and O/Ti  $\approx$  16.8. Nanow-

Flement wt %		Base coating			
Element, wt 70	Site 1 in Fig. 2a	Site 2 in Fig. 2a	Site 2 in Fig. 2b	Site 3 in Fig. 2b	Site <i>3</i> in Fig. 2a
С	1.9	2.1	3.0	3.0	3.5
0	42.9	44.4	41.4	39.6	45.9
Al	2.3	3.0	2.2	1.5	2.2
Si	_	_	_	0.3	—
Р	4.6	9.4	3.9	1.5	10.6
Ti	8.4	5.1	9.2	9.6	—
Ni	39.9	36.1	40.3	44.5	37.9

 Table 2. Composition of nanocrystals and base coating

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ires probably involve a complex oxygen-containing compound of nickel and titanium.

Thus, annealing a PEO coating, which was formed on titanium and modified with nickel and copper oxides, at a temperature of 750°C or higher in air results in the surface growth of nanowires, the main components of which are nickel, oxygen, and titanium. The sizes of nanowires depend on the temperature of annealing. The diameters of nanowires may be from tens to hundreds of nanometers at lengths of several to tens of microns.

Covering the surface, nanowires substantially increase the active surface of specimens, which is especially important for catalysis. Insofar as nanowires involve nickel (predominantly) and titanium oxides or complex binary oxides of nickel and titanium, they can be catalytically active with respect to redox processes. Catalysts based on nickel-oxide nanowires bound to a titanium oxide substrate are promising for the conversion of organic compounds. In particular, German researchers have shown recently that the modified NiO + CuO/TiO<sub>2</sub>/Ti systems studied in this work are catalytically active in the conversion of naph-thalene [13].

Judging from the thermal stability of the systems produced, they can be used at temperatures up to 800°C. At a higher temperature, some surface parts begin to exfoliate from the titanium substrate.

At the same time, the discovered growth of nanowires on the surfaces of modified PEO coatings can be used for production of individual nanowires by means of their mechanical separation from an oxide substrate.

Note that no sign of the growth of nanowires was noticed during the investigation of the thermal behavior of Ni- and Cu-containing PEO layers, which were formed [9] in accordance with the same technique (electrolyte composition and conditions of formation), but without additional impregnation, and then annealed in air at temperatures up to 900°C. On the other hand, individual nanoribbons composed chiefly of zirconium and titanium were observed on the surfaces of coatings formed on titanium in an electrolyte containing  $Zr(SO_4)_2$  upon plasma electrolytic oxidation [10]. Nanowires were also present on the surfaces of PEO coatings formed on titanium in a Na<sub>2</sub>SiO<sub>3</sub>containing electrolyte and then impregnated in a manganese-nitrate solution and annealed in air at a temperature of 500°C [11]. At the same time, there were no nanowires upon annealing at 800-900°C. This means that nanowires composed seemingly of manganese oxides can be formed and are stable only within a certain temperature range. The formation of nanorods was observed also on the surfaces of PEO coatings formed in an electrolyte suspension based on Na<sub>2</sub>SiO<sub>3</sub> + NiO either individual or containing  $C_{18}H_{33}NaO_2$  surfactant additive upon annealing in air for a 24 day [12].

Thus, the results obtained in this work and independent literature data confirm the idea that PEO technique, including its combination with impregnation and annealing, can be used for creating nanostructures bound to metal-oxide substrates or for producing individual nanosystems of certain compositions. The conditions of the formation of nanostructures with a desirable structure and composition with the use of the method described may be clarified in forthcoming investigations.

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