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Thermally Stimulated Transformation of the Surface Nanoarchitecture of Ni-and Cu-Doped Oxide Coatings on Titanium

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Abstract. It has been shown that triangular nanocrystals with a thickness of ~ 50 nm and a height of ~ 500 nm, mainly containing copper oxides, are formed on the surface of Ni- and Cu-doped plasma electrolytic oxide (PEO) coatings on titanium during air annealing at 500-700 °C. Upon the annealing at 750-850 °C, rectangular nano- and micro-sized crystals presumably consisting of nickel tungstate cover the coating surface. At annealing temperatures above 850 °C, the brushes of Ni_5TiO_7 whiskers having a diameter of tens to 200 nm and a length up to 10 μm are formed on the surface. The thermally stimulated change in the surface nanoarchitecture and the composition of nano-formations explains the change in the catalytic activity of the formed composites in oxidation of CO into CO_2.

Introduction

'Metal / oxide coating' composites are widely used in catalysis, medicine, sensorics [1-3]. In order to enhance the functional properties, a special attention has recently been paid to forming the ensembles of nanosized particles of a certain composition on the surface of such composites.

Metal oxide nanostructures fixed on the surface of metals can be obtained by various methods: thermal oxidation of metal substrates [4], treatment with NH_3-H_2O_2 vapors [5], template synthesis [6], anodic oxidation [7], plasma electrolytic oxidation (PEO) [8].

A new approach was first proposed in [9, 10] to produce Ni-containing oxide nanowhiskers on titanium surface. Titanium was subjected to PEO treatment (electrochemical oxidation under spark and microarc electric discharges) in alkaline phosphate-borate-tungstate electrolyte (PBW) with colloidal particles of Cu (II) and Ni (II) hydroxides. Then 'PEO coating/ Ti' composites were impregnated in the solution of $Ni(NO_3)_2$ and $Cu(NO_3)_2$ and air-annealed at 500 °C. After repeated annealing in air at a temperature above 850 °C, the surface of the composites was covered with ensembles of Ni_5TiO_7 whiskers of a diameter from tens to 200 nm and a length of up to 10 μm.

The development of this approach was continued in works [11-13]. Using the same strategy, zinc and nickel tungstates in the form of nanorods, nanoscreens, nanowires or nanobands were obtained on the surface of titanium at annealing temperatures of 650-850 °C [12]. The PEO, impregnation and annealing steps were used to obtain $ZnWO_4/TiO_2/Ti$ and $NiWO_4/TiO_2/Ti$ composites, while for the step of impregnation in the nitrate solution was excluded during the synthesis of $MnWO_4/TiO_2/Ti$ composites [13]. In the last case, the electrolyte for PEO served as the impregnating solution. The authors of [12, 13] believe that $ZnWO_4$, $NiWO_4$, $MnWO_4$ tungstates in the amorphous state were already present in the initial PEO coating and served as a seed for the subsequent growth of corresponding nanoformations at elevated temperatures. The described examples show the prospect of using the PEO layers formed in PBWM-electrolyte, where M is transition metal salt, as the basis for the thermally stimulated growth of nanoobjects of a certain composition fixed on their surface. Comparison of the data on the obtaining the nanoformations of $NiWO_4$ [12] and Ni_5TiO_7 [11] shows that the annealing temperature affects the composition of nano- and microcrystals formed on the surface of Ni-, Cu -modified PEO coatings.

In this work, the change in the architecture of the surface of the formed composites at the nano and microlevels is studied in more detail at intermediate annealing temperatures.

Experimental

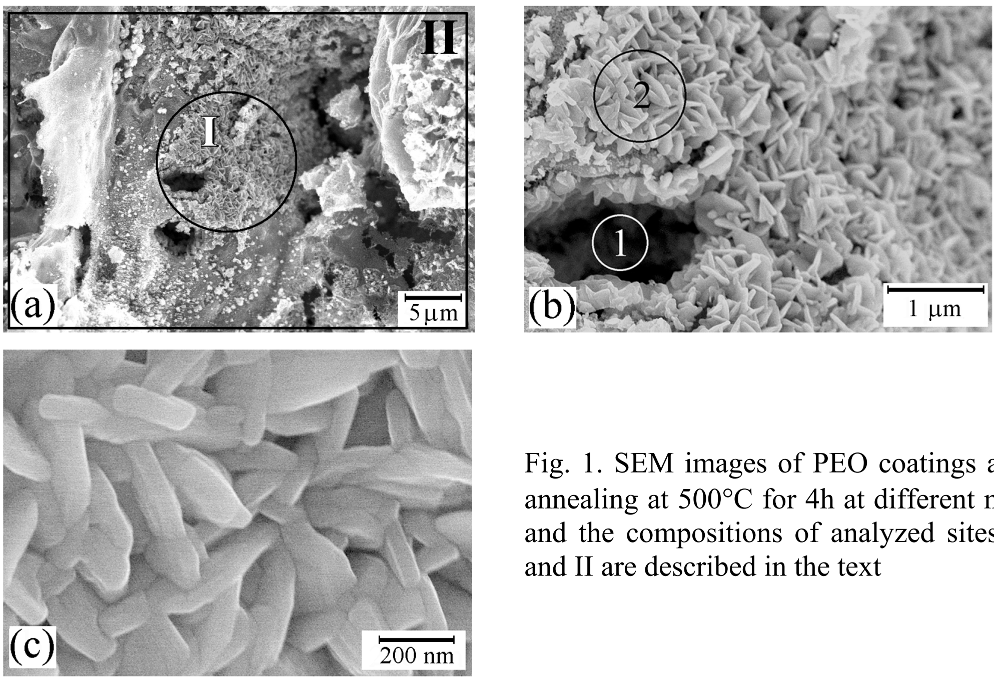
PEO layers containing nickel and copper compounds were formed on titanium plates and wires as in [9, 10] in the galvanostatic mode under anodic polarization for 10 min in an aqueous electrolyte of a composition, mol/L: 0.066 Na_3PO_4 + 0.034 $Na_2B_4O_7$ + 0.006 Na_2WO_4 + 0.1 $Ni(CH_3COO)_2$ + 0.025 $Cu(CH_3COO)_2$ (hereinafter, PBWNiCu-electrolyte).The obtained samples with PEO coatings of a thickness of about 15 μm were immersed into the aqueous solution containing 1 mol/L $Cu(NO_3)_2$ and 1 mol/L $Ni(NO_3)_2$ and held therein for 1 h. Then the samples were annealed in air at 500 °C for 4 h to decompose the nitrates and form nickel and copper oxides. Finally, the prepared samples were annealed in air at temperatures of 700, 750, 800, 850, 900 and 950 °C.

X-ray diffraction (XRD) patterns of the titanium plates with coatings were obtained on an D8 ADVANCE X-ray diffractometer (Germany) using CuK_α radiation. The XRD analysis was carried out with help of the Eva retrieval programm based on the PDF-2 database. The morphology and surface composition were studied using a high-resolution Hitachi S5500 scanning electron microscope (SEM) (Japan) equipped with an energy dispersive spectrometer (Therma Scientific, USA). To prevent the surface charging, samples were preliminarily sputtered with gold.

The catalytic tests in the reaction of CO oxidation into CO_2 were conducted on a BI-CATflow 4.2(A) flow type universal catalytic system (Institute of Catalysis, SB RAS, Novosibirsk) in the temperature range of 20–500°C. In this case, titanium wire samples cut into pieces were used. The geometric surface area of the sample placed into the active zone (0.9 cm in diameter and 3 cm in height) of a tubular quartz reactor was 20 cm^2.The initial reaction mixture contained 5% CO and air. The gas flow rate was 50 mL/min. The CO and CO_2 concentrations were defined with a PEM-2 IR gas analyzer.

Results

Surface of modified PEO coatings. The surface morphology of PEO coatings after impregnation and annealing at 500 °C for 4 h is given in Fig. 1.



Element composition, at. %

	site 1	site 2
C	-	10.4
O	15.5	35.6
Ti	6.5	3.7
Ni	20.4	6.6
Cu	71.5	46.5

Fig. 1. SEM images of PEO coatings after impregnation and annealing at 500°C for 4h at different magnifications (a, b, c) and the compositions of analyzed sites 1 and 2 (b). Areas I and II are described in the text

The agglomerates of triangular crystals with a thickness of ~ 50 nm and a height of ~500 nm are formed in individual sites of the surface, Fig. 1. The average compositions of the coating surface (area II, Fig. 1a), including with systems of triangular formations, as well as that of triangular crystals (area I), according to the energy-dispersive analysis, are given in Tables 1 and 2.

The data on the elemental composition of nanocrystals (Table 2, 500 °C) suggest the presence in their composition of oxides of titanium, nickel and copper with a significant predominance of the latter. Meanwhile, nickel and copper concentrations measured for large sites (40×60 μm) are approximately the same, Table. 1.

As can be seen from images in Fig. 1a, b, the crystals grow near the pores. Apparently, components of the impregnating solution are accumulated in the pore and around it. The crystals are located not only around the pore, but also inside it, Fig. 1b. Analysis of the composition of the crystals of the inner part of the pore (site 1) and around the pore (site 2) confirms that the copper content in crystals is sharply increased (Fig. 1b).

Table 1. Effect of the annealing temperature on the element composition (at. %) of coating surface

T_{ann} [°C]	Element composition [at. %]						
	C	O	P	Ti	Ni	Cu	W
500	-	48.8	0.9	4.3	20.4	26.6	-
700	7.6	49.3	0.7	3.0	18.4	20.7	0.3
750	12.4	59.9	1.9	4.7	14.5	6.0	0.6
800	10.5	68.5	4.9	4.9	7.5	-	3.7
850	28.2	54.0	3.8	5.2	7.7	-	1.1

Table 2. Effect of the annealing temperature on the element composition (at. %) and shape of crystalls

T_{ann} [°C]	Element composition [at. %]						Shape of micro- and nanocrystalls
	C	O	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 crystals + individual whickers
900	-	57.0	11.0	32.0		-	Whisckers

Surface morphology after annealing in the temperature range from 500 to 900 °C. As can be seen from the comparison of Fig. 1b, c and Fig. 2a, the surfaces of the samples annealed at 500 and 700 °C are similar. In both cases, triangular nanocrystals cover part of the surface. Accordingly, a large amount of copper is present in both coating and triangular nanocrystals, Table 2. Annealing at 750 °C leads to a sharp decrease in the average copper content in the coating composition, and after annealing at 800 and 850 °C, copper is not detected in a surface layer of thickness of ~ 1 μm (analysis depth). Because of thermal diffusion in the temperature range 700 – 750 °C copper leaves the surface and goes to the depth of the oxide layer.

The geometry of nano- and microformations that occupy part of the surface changes with annealing temperature too. Rectangular crystals of ~ 1 μm in length are formed after annealing at 750 and 800 °C (Fig. 2b, c). With increasing annealing temperature up to 850 °C, the content of nickel and tungsten in rectangular crystals is markedly increased, Table 2. Along with these microcrystals, the individual whiskers of a thickness of several microns and a length of up to 8 microns are formed on the surface after air annealing at 850 °C, Fig. 2d. Annealing in air at 900-950 °C results in preferential formation of whiskers (Fig. 2e), whose shape and sizes are similar to those observed in Refs [9, 10].

Taking into account the data of [9-12, 14], one can assumed that the annealing at 850 °C results in both Ni_5TiO_7 (or $Ni_5TiO_4(BO_3)_2$) and $NiWO_4$ crystals, while the annealing at 900 °C leads to preferred growth of nickel titanates or titanoborates.

In order to establish the crystal compositions, an XRD pattern was obtained for the coated sample annealed at 850 °C, Fig. 3. XRD analysis shows that titanium dioxide in form of rutile, nickel titanophosphate and nickel tungstate are present in the coating, while nickel titanate and titanoborate are not detected.

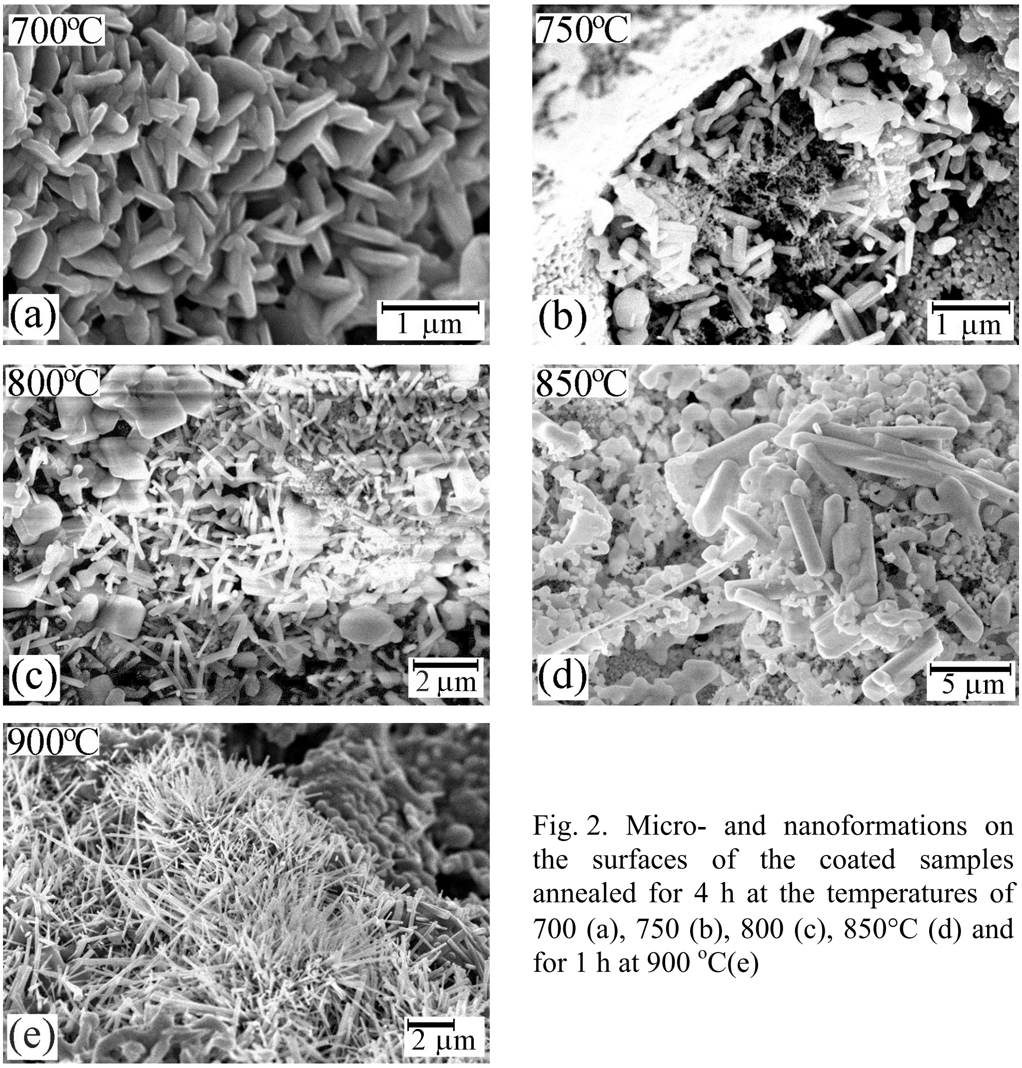


Fig. 2. Micro- and nanoformations on the surfaces of the coated samples annealed for 4 h at the temperatures of 700 (a), 750 (b), 800 (c), 850°C (d) and for 1 h at 900 °C(e)

Correlation between the surface structure and catalytic activity in CO oxidation. As shown above, with annealing at a given temperature, it is possible to control obtaining a whole spectrum of nanoformations of a certain geometry and composition on the surface of the coatings under study. This should be manifested in the properties of the coatings formed. Indeed, the architecture and composition of micro and nanoformations on the coating surface, Table 2 and Fig. 2, correlate well with their ability to catalyze the oxidation of CO into CO_2, Fig. 4. Transformation of triangular nanoformations with an increased content of copper into rectangular ones with an increased content of nickel leads to a decrease in activity. Samples annealed at 850 °C are inactive in CO oxidation.

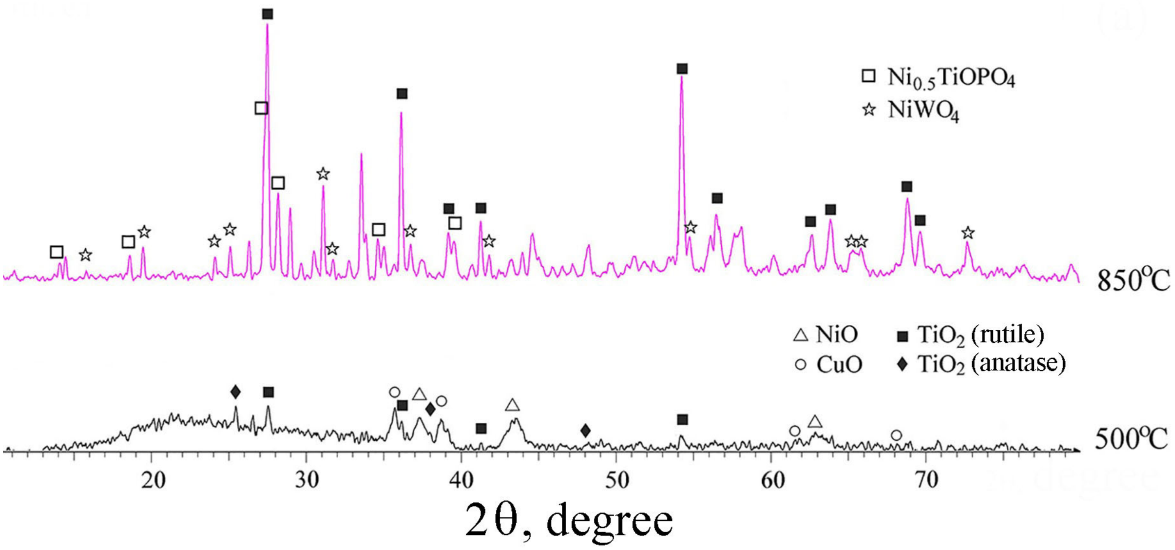


Fig. 3. X-ray patterns of the samples with modified PEO coatings annealed at 500 and 850°C for 4 h

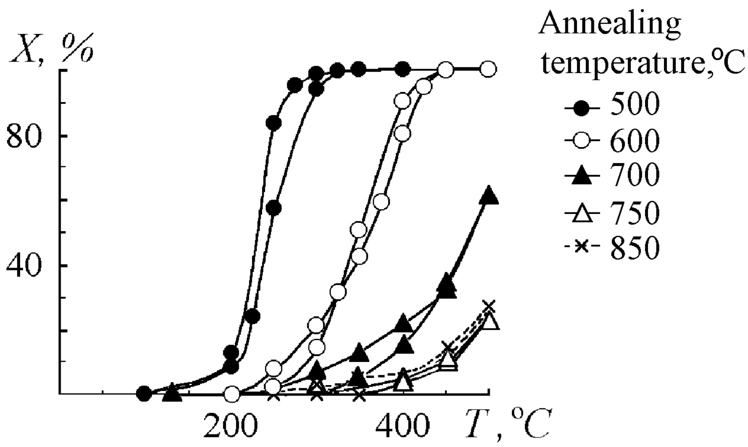


Fig. 4. Temperature dependences of CO conversion (*X*) for the samples with modified PEO coatings annealing in air at the temperatures of 500, 600, 700, 750 and 850°C

Discussion

The formation of nanowires, Fig. 3e, occurs in the same temperature range as the yield of titanium to the surface of unmodified PEO coatings [15, 16]. As these studies showed, at temperatures above 850 °C titanium diffuses through the pores to the coating surface, where it forms regular nano- and microcrystals of rutile. Furthermore, it is known [17] that when PEO coatings are obtained in the alkaline PBW-electrolyte (mol/L: 0.066 Na_3PO_4 + 0.034 $Na_2B_4O_7$ + 0.006 Na_2WO_4) with the addition of nickel, iron or cobalt acetates, the agglomerates of crystallites with an increased content of these metals are formed in the coating pores. In this case, the walls and the bottoms of the pores also contain increased concentrations of the metals from the electrolyte. It is possible that at annealing temperatures greater than or equal to 850 °C, the thermally stimulated diffusion of titanium through the coating pores to the surface leads to its interaction with nickel concentrated in the pores, followed by the formation of nickel titanates on the surface.

Conclusion

The study has shown that by setting the annealing temperature it is possible to control a whole spectrum of nanoformations of a certain geometry and composition on the surface of coatings formed in PBWNiCu-electrolyte and modified with nickel and copper oxides as a result of impregnation in nitrate solutions and annealing in air at 500 °C. At an annealing temperature of up to 700 °C, copper-enriched nano-sized crystals of triangular shape are accumulated in the pores and in the vicinity of the pores. An increase in the annealing temperature leads to the copper diffusion into the depth of the coatings, formation of rectangular nanocrystalls (750-800 °C) containing nickel tungstate and appearance of nickel titanate nanowhiskers (above 850 °C) on the surface.

All annealed coatings have a layered structure: a layer of nanocrystals is located on the main matrix of a dense oxide coating, the composition of which is determined by the annealing temperature.

The results of this work, as well as the data of [9-12, 14] show that the combination of PEO treatment in the PBWM-electrolyte with impregnation and subsequent annealing, or with only annealing is the original way of controlled production of oxide systems with a developed surface architecture.

Acknowledgements

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