

MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Deposition of Cobalt-Containing Films on Titanium by Plasma Electrolytic Oxidation

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Abstract—The possibility of forming Co-containing coatings on titanium by plasma electrolytic oxidation and by a combination of oxidation and impregnation methods using an aqueous solution of sodium silicate as the base electrolyte was examined. Comparative analysis of the composition and structure of the systems obtained and of their activity in oxidation of CO to CO₂ was performed.

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For catalysis, in particular, for photo- and electro-catalysis, of much interest are layers on titanium that contain, along with TiO₂, oxides of transition and rare-earth metals, including cobalt oxides [1]. At the same time, coatings with cobalt and cobalt oxides can exhibit magnetic properties. For example, incorporation of cobalt nanoparticles into oxide layers on titanium imparts ferromagnetic properties to the surface oxide structures [2].

One of methods for preparing cobalt-containing oxide coatings on the surface of titanium specimens is plasma electrolytic oxidation (PEO) in aqueous electrolytes [2–5]. For example, X-ray amorphous coatings containing up to 45 wt % cobalt depending on the forming conditions were prepared by plasma electrolytic treatment of a titanium alloy in an aqueous electrolyte containing salts of phosphoric, boric, and tungstic acids (PBW) and up to 30 g l⁻¹ Co(CH₃COO)₂ [3]. After annealing in air at 800°C, the CoO, Co₂O₃, Co₃O₄, CoWO₄, Na₂TiO₃, and Na₃Co₉(PO₄)₇ phases crystallized in the coatings. In [4, 5], the coatings were formed from electrolytes with Co²⁺ polyphosphate complexes. On titanium and aluminum, layers containing from 18 to 27 wt % cobalt and crystalline phases of Co(II)Co(III)Ti(PO₄)₃, Co₂O₃, and TiO₂ (on Ti) and of Co₂O₃, CoAl₂O₄, and AlPO₄ (on Al) were obtained. However, the functional properties of the oxide

systems obtained were not studied.

One of the most widely used electrolytes for PEO of valve metals and alloys is an aqueous solution of sodium silicate [6]. In addition, it was shown that the coatings formed in this electrolyte by PEO are convenient for modification by impregnation [7].

This study was aimed to form Co-containing coatings on titanium by PEO alone and in combination with impregnation, using an aqueous solution of sodium silicate as the base electrolyte, and to compare the composition and structure of the systems obtained and their activity in the oxidation of CO to CO₂.

EXPERIMENTAL

Plasma electrolytic oxidation experiments were performed with plates of VT1-0 grade titanium of sizes 0.5 × 2.5 × 0.1 and 2.2 × 2.2 × 0.1 cm. The specimens were subjected to mechanical polishing and chemical etching in the HF : HNO₃ = 1 : 3 acid system at 60–80°C for 2–3 s, after which they were washed with distilled water and dried in air.

As power source we used a TER4-63/460N-2-2-UKhL4 thyristor aggregate with the unipolar pulse current. The coatings were formed under galvanostatic condi-

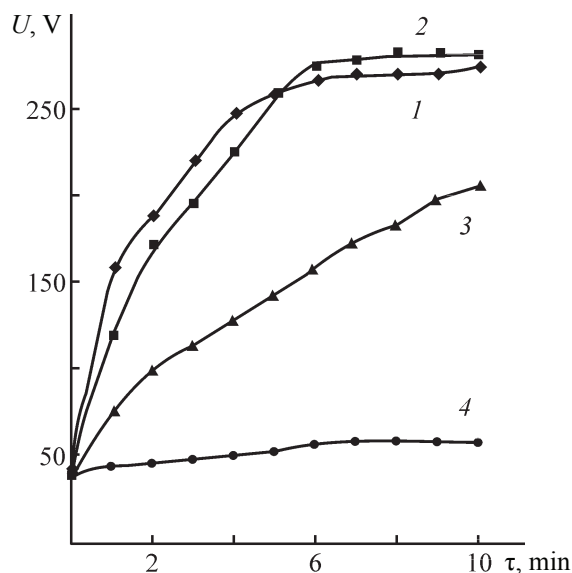


Fig. 1. Voltage U as a function of time τ of formation of PEO layers. Electrolyte: 0.05 M Na_2SiO_3 + additives. Additive, M: (1) none, (2) 0.012 $\text{Co}(\text{CH}_3\text{COO})_2$, (3) 0.012 $\text{Co}(\text{CH}_3\text{COO})_2$ + 0.075 NaOH, and (4) 0.1 $\text{Co}(\text{CH}_3\text{COO})_2$.

tions at the effective current density $i = 0.1 \text{ A cm}^{-2}$. To prepare the electrolytes, we used pure grade $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, analytically pure grade $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, NaOH, and distilled water. The treatment time was 10–20 min. After the PEO, the specimens were washed with distilled water and dried in air at room temperature. The coatings obtained were additionally modified by impregnation for 1 h in aqueous solutions containing 1 M $\text{Co}(\text{CH}_3\text{COO})_2$ or 1 M $\text{Co}(\text{NO}_3)_2$, followed by annealing for 4 h in a muffle furnace in air at 500°C .

The phase composition was determined with a D8 ADVANCE diffractometer (Germany) by the standard procedure using $\text{CuK}\alpha$ radiation. The components of the specimens were identified in the EVA automatic search mode using PDF-2 database.

To determine the catalytic activity of the specimens, we used BI-CAT flow 4.2(A) multi-purpose flow-type system (Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk). Gaseous components were analyzed with a PEM-2M gas analyzer (Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk). The gas flow rate was 70 ml min^{-1} . The initial reaction mixture contained 79% Ar, 20% O_2 , and 1% CO.

Figure 1 shows that the process course and the final forming voltage strongly depend on the electrolyte composition. In the series of the systems examined, the highest rate of the voltage growth on the electrodes, $dU/d\tau$, is observed in oxidation in the silicate electrolyte. With an increase in the concentration of cobalt acetate or sodium hydroxide in the solution, the final voltage at a given time decreases.

Data on the phase and elemental composition of the coatings formed under different conditions are given in the table. As can be seen, with an increase in the cobalt acetate concentration in the electrolyte, the cobalt content of the coatings formed increases also. Simultaneously, CoO is detected in the coatings. Impregnation of the coatings formed in the silicate electrolytes also makes the cobalt content of the coatings noticeable (3–8 at. %). However, in this case crystalline Co-containing phases

Preparation conditions and composition of PEO layers on titanium (forming time 10 min)

Specimen no.	Preparation conditions		Phase composition ^a	Elemental composition, at %			
	electrolyte for PEO, M	impregnating solution, M		Na	Si	Ti	Co
1	0.05 Na_2SiO_3	–	r/a	0.2	11.3	13.5	–
2	0.05 Na_2SiO_3 + 0.012 $\text{Co}(\text{CH}_3\text{COO})_2$	–	$\text{TiO}_2(\text{r})$	0.3	2.5	23.6	0.3
3	0.05 Na_2SiO_3 + 0.012 $\text{Co}(\text{CH}_3\text{COO})_2$ + 0.075 NaOH	–	$\text{TiO}_2(\text{r})$, CoO, CoTiO_3	0.7	8.9	11.1	1.9
4	0.05 Na_2SiO_3 + 0.1 $\text{Co}(\text{CH}_3\text{COO})_2$	–	$\text{TiO}_2(\text{r})$, CoO	0.8	10.9	7.5	11.7
5	0.05 Na_2SiO_3	1.0 $\text{Co}(\text{CH}_3\text{COO})_2$	$\text{TiO}_2(\text{a})$	0.4	9.9	3.2	3.1
6	0.05 Na_2SiO_3	1.0 $\text{Co}(\text{NO}_3)_2$	$\text{TiO}_2(\text{r} + \text{a})$	0.4	13.1	7.9	7.8

^a (r) Rutile and (a) anatase.

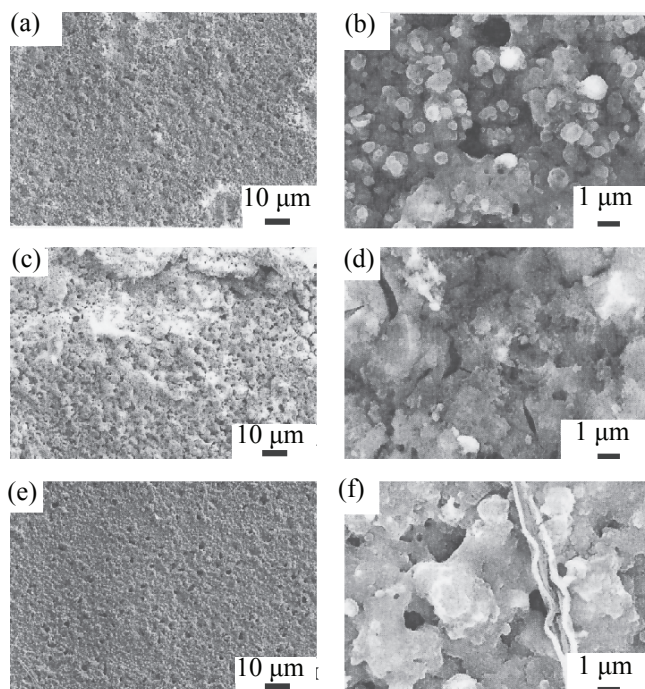


Fig. 2. SEM images of the surface of coatings formed by (a, b) PEO in 0.05 M Na_2SiO_3 , (c, d) PEO in 0.05 M Na_2SiO_3 + 0.1 M $\text{Co}(\text{CH}_3\text{COO})_2$, and (e, f) combination of PEO in 0.05 M Na_2SiO_3 , impregnation in 1 M $\text{Co}(\text{CH}_3\text{COO})_2$, and annealing.

are not detected in the coatings.

According to data of electron microscopy, the conditions for preparing Co-containing coatings appreciably affect the morphology of their surface (Fig. 2). The PEO coating prepared in the silicate electrolyte has a developed surface with numerous protrusions approximately 1 μm in diameter (Fig. 2b). Addition of 0.1 M $\text{Co}(\text{CH}_3\text{COO})_2$ to the silicate electrolyte leads to the formation of dense “crust-like” areas arranged as separate islets on the surface of the PEO coatings (Figs. 2c, 2d). Impregnation of the silicate coatings with cobalt in a 1 M $\text{Co}(\text{CH}_3\text{COO})_2$ solution, followed by annealing, on the contrary, leads to the formation of a thin layer of the compounds based on the impregnation solution components, which follows from comparison of the images in Figs. 2a and 2e, 2b and 2f. In the latter case, it is seen that, although the protrusions are preserved, they became larger. In addition, on protrusions of coatings in Fig. 2f one can see formations of smaller size.

The results of catalytic tests (Fig. 3) show that the catalytic activity in CO oxidation of the specimens formed solely by PEO increases with an increase in the Co content (specimen no. 2 < specimen no. 3 < specimen no. 4). At the same time, the most active in the CO oxidation to CO_2 are the coatings formed by a combination of PEO and impregnation methods (specimen nos. 5, 6). Their activ-

ity is independent on whether the impregnating solution contained cobalt(II) acetate or nitrate. Specimen nos. 5 and 6, according to the results of microprobe analysis, contain 3 to 8 at. % cobalt, which is lower than, e.g., in specimen no. 4 prepared solely by PEO.

Different activity in CO oxidation may be due to several factors. In the coatings prepared by PEO, cobalt can

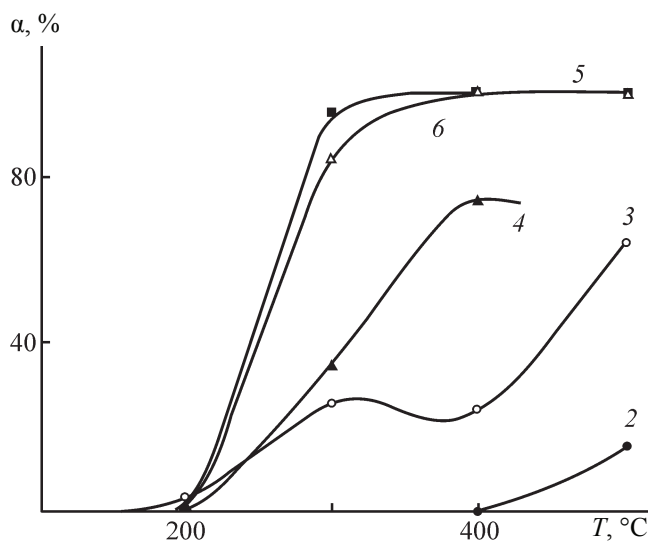


Fig. 3. Effect of temperature T on the CO conversion α on cobalt-containing specimens prepared under different conditions. Figures at curves are specimen nos. in the table.

be distributed throughout the thickness, whereas in the impregnated PEO coatings it is concentrated practically on the surface. At the same time, the impregnated coatings have a more developed surface, which also positively affects their activity. We also should not rule out the effect exerted by annealing of the impregnated specimens in air on the structure of their surface, on the cobalt chemical form in them, on the cobalt oxidation state, and ultimately on their activity in the CO oxidation.

CONCLUSIONS

(1) Coatings containing up to 10 at. % cobalt in the area examined by microprobe analysis were formed on titanium in a silicate electrolyte by plasma electrolytic oxidation used alone and in combination with impregnation.

(2) The specimens formed by the combination of the methods are appreciably more active in catalysis of the CO oxidation to CO₂. This fact is due to differences in the surface structure and amount of Co-containing catalytically active centers.

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