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Thermal behavior of Ni- and Cu-containing plasma electrolytic oxide coatings on titanium

V.S. Rudnev[a,b,*], S. Wybornov[c], I.V. Lukiyanchuk[a], T. Staedler[c], X. Jiang[c], A.Yu. Ustinov[a,b], M.S. Vasilyeva[a,b]

[a] Institute of Chemistry, Far Eastern Branch of Russian Academy of Sciences, Vladivostok, 690022, Prosp. 100-letya Vladivostoka, 159, Russian Federation
[b] Far Eastern Federal University, Vladivostok, 690950, Sukhanova str., 8, Russian Federation
[c] Institute of Materials Engineering, Chair of Surface and Materials Technology, University of Siegen, 57076 Siegen, Paul-Bonatz-Str. 9-11, Germany

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ABSTRACT

In this work the effect of thermal annealing on the surface composition, structure and catalytic activity in CO oxidation of NiO + CuO/TiO_2/Ti composites is studied. The composites have been obtained by a plasma electrolytic oxidation (PEO) technique, followed by impregnation in a solution of nickel (II) and copper (II) salts and air annealing. The structures contain ~20 at% Ni and ~12 at% Cu. It has been shown that the additional air annealing of such structures at temperature above 750 °C results in phosphate crystallization in the coatings and decreasing of Cu concentration in the surface layers. A growth of filiform nanocrystals containing mainly oxygen compounds of nickel and titanium on the coating surface takes place at the temperatures above 700 °C. The nanocrystals have a diameter of 50–200 nm and lengths below 10 μm. Such changes result in decreasing of catalytic activity of the composites in CO oxidation. At the same time the ascertained regularities may be of interest for obtaining the Ni-containing oxide catalysts with an extended surface, perspective for usage in organic catalysis or for preparing oxide nanofibers.

1. Introduction

One of the methods of catalysts preparation consists in deposition of catalytically active compounds on a metal substrate [1–3]. The advantages of a metal substrate in this regard are concerned with its high thermal conductivity combined with mechanical strength. As a rule, in order to attach catalytically active compounds on a metal substrate, an appropriate surface layer needs to be synthesized beforehand: for instance, an oxide surface layer formation is used for valve metals. To obtain an oxide layer on the surface of a valve metal, one can apply the plasma electrolytic oxidation (PEO) technique [4]. This technique features anodization under high voltages resulting in electric spark or arc discharges at the electrode–electrolyte interface. PEO enables one not only to form layers of a specific phase composition from treated metal oxides with a developed surface, but also to modify the formed oxide layer composition as a result of electrolyte component incorporation. Utilizing the single-stage PEO technique, the following catalytically active composites have been formed: NiO/MO_x/M (where M = Al, Mg, and Ti) [5–7], MoO_x/Al_2O_3/Al, CrO_x/Al_2O_3/Al [5], MnO_x/TiO_2/Ti [8], CoO_x/TiO_2/Ti [9], CeO_x + ZrO_2/TiO_2/Ti [10], Pt + CeO_x + TiO_2/Ti, Pt + Al_2O_3/Al [11]. These systems were active in oxydehydrogenation of cyclohexane to cyclohexene [5], naphthalene destruction [10], and CO oxidation [6–9,11]. The composites without noble metals, particularly, Ni- and Cu-containing PEO layers are of specific interest, because nickel and copper oxides are applied in industry as the catalysts of redox reactions [12–14]. The Ni- and Cu-containing coatings on aluminum and titanium obtained by the single-stage PEO technique were studied in [6,7]. They were active in deep CO oxidation at temperatures above 300 °C. It has been demonstrated that the catalytic activity of the PEO coatings substantially increases upon an additional impregnation in aqueous solutions of nickel (II) and copper (II) nitrates followed by thermal annealing [15,16]. Such a treatment results in the increase of nickel and copper oxide concentration on the surface of Ni-, Cu-containing PEO coatings [16]. The above systems could be promising for application in high-temperature catalysis, for example, in organic compound oxidation and exhaust gas afterburning. Meanwhile, high-temperature behavior (composition, structure and catalytic properties) of such systems are not yet studied in detail. The only available data are related to the effect of high-temperature air annealing on the composition and structure of Ni-, Cu-containing PEO coatings on titanium (without impregnation) [17]. The crystallites of a size of ~1 μm were found on the

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* Corresponding author at: Far Eastern Branch of Russian Academy of Sciences, Institute of Chemistry, Prosp. 100-letya Vladivostoka 159, 690022 Vladivostok, Russian Federation.
E-mail address: rudnevvs@ich.dvo.ru (V.S. Rudnev).

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surface of PEO layers upon their air annealing at a temperature above 800 °C. It is still unclear how similar systems, i.e. those with higher nickel and copper oxides content, would behave upon impregnation. The objective of this paper was to study the thermal behavior of NiO + CuO/TiO_2/Ti impregnated composites and the change of their element composition, surface morphology, and catalytic properties at temperatures up to 950 °C.

2. Experimental details

2.1. Coating preparation by PEO technique

As reported in [16], the oxide layers with nickel and copper compounds were formed by PEO in an aqueous electrolyte containing 0.066 M Na_3PO_4 + 0.034 M $Na_2B_4O_7$ + 0.006 M Na_2WO_4 + 0.1 M $Ni(CH_3COO)_2$ + 0.025 M $Cu(CH_3COO)_2$. As substrate material a titanium alloy, VT1-0 (0.2 Fe, 0.1 Si, 0.07C, 0.04N, 0.12 O, 0.01H and Ti > 99.6%, Al content is allowed up to 0.7%), was utilized in two geometrical configurations: type 1 was a sheet geometry (40 mm × 10 mm × 1 mm) and type 2 was a coil-shaped titan wire (Ø 2 mm) with a geometric surface area of 20 cm^2. Type 2 was used for catalytic tests and for obtaining of high-resolution SEM images of the film surfaces as well as for energy dispersive X-ray (EDX) analysis. Type 1 was used otherwise.

Prior to coating deposition the substrates were polished chemically in a mixture of concentrated acids ($HF:HNO_3$ = 1:1, volume relation) at a temperature of about 70 °C. Multiple immersions into the polishing solution followed by a rinsing step in distilled water were carried out until a mirror like surface (surface finish classes 8–9) was achieved.

PEO coatings were formed on the titanium substrates being in an anodic polarization for 10 min at an effective current density of 0.1 A cm^{-2}. A computer-controlled thyristor TER4-100/460H (Russia) operating in unidirectional mode was used as the power source. The stainless tank body along with its cooling water jacket served as a counter electrode. The electrolyte itself was agitated by a mechanical stirrer. The electrolyte temperature was kept below 40 °C. Then, the samples were washed with distilled water and dried in air.

Additional modification of the PEO coatings was realized by means of impregnation of the coatings followed by annealing in air. In this context the PEO coated samples were exposed to an aqueous solution containing 0.1 mol/L $Cu(NO_3)_2$ and 0.1 mol/L $Ni(NO_3)_2$ for 1 h. The impregnated coating/substrate systems were aired above an electric stove and annealed in an oven (SNOL 7.2/1100) at a temperature of 500 °C for 4 h. The resulting samples with modified coatings were subsequently annealed for an additional hour at temperatures of 650, 700, 750, 800, 850, 900 and 950 °C, respectively.

2.2. Coating characterization

The thickness of coatings was determined using a vortex-current layer thickness meter.

High-resolution SEM images of the film surfaces as well as the elemental analysis of the coatings and the filiform crystals were acquired by a Carl Zeiss ULTRA 55 electron microscope equipped with a special detector from Carl Zeiss NTS GmbH (Switzerland), which provides a magnification of up to 900,000 and a resolution of 1 nm, at the chair of Surface and Materials of the Technology University (Siegen). Qualitative and quantitative analyses of the elemental composition of the surface averaged over an area of 100 × 100 μm and at local sites of ~50 × 50 nm was carried out with a Thermo Scientific X-ray spectrometer integrated in the microscope (EDX analysis).

Data concerning the elemental composition (X-ray spectrum analysis, XSA, average readings from areas 50 μm × 50 μm, 2–5 μm deep) were obtained by an electron probe micro-analyzer JXA 8100 (Japan) with an INCA energy spectrum analyzer (the United Kingdom). To prevent surface charging in this context, a thin graphite layer was deposited on the samples prior to measuring.

X-ray diffraction (XRD) patterns were studied with a D8 Advance X-ray diffractometer (Germany) using Cu Kα radiation. The corresponding analysis was carried out with the EVA retrieval program based on the PDF-2 database.

In addition, X-ray photoelectron spectroscopy (XPS) was used to characterize the surfaces. Here a Specs ultra high-vacuum system with a 150-mm electrostatic hemispherical analyzer was used. Ionization was realized by Mg Kα radiation. The spectra were calibrated utilizing the C1s line of hydrocarbon, which energy was assumed to be equal to 285.0 eV. The surface was etched by a bombardment with argon ions featuring energy of 5 keV.

2.3. Catalytic tests

Catalytic tests were performed using a BI-CAT flow 4.2(A) multipurpose flow-type system (Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences). Finely cut wire samples sized 3–5 mm with modified PEO coatings (the geometric surface area of the coating was 20 cm^2) were placed in the active zone (0.9 cm in diameter and 3 cm in height) of a quartz tube reactor. The initial reaction mixture contained 5% CO and air. While keeping the gas flow rate at 50 ml/min, the outlet concentration of CO and CO_2 were determined using a PEM-2 IR gas analyzer. The tests were carried out at temperatures ranging from 20 to 500 °C.

3. Results and discussion

3.1. Influence of surface modification

Fig. 1 shows the morphology of typical surface sites of the initial and modified Ni-, Cu-containing PEO coatings on a titanium substrate. The surface of the initial layers features fused convex-like formations. Additionally, pores with diameters up to 10 μm are observed (Fig. 1a). The modification results in a smoothing of initial coating relief (Fig. 1b).

The layer thickness as well as the phase and elemental composition (average readings from areas ~50 μm × 50 μm, 2–5 μm deep, JXA 8100 electron probe microanalyzer) are summarized in Table 1. According to our observations an additional modification of the coatings does not result in an increase layer thickness. This may be due to a combination of a partial dissolution of the oxide film surface and a filling of pores and valleys between surface asperities. In addition to that the modification results in an increased nickel and copper content in the coating surface along with the formation of NiO and CuO (Tables 1 and 2).

Table 2 lists the elemental composition of a surface layer (3 nm deep) of the initial and the modified coatings according to XPS. In general the surface elemental concentrations and their changes after modification agree with the XSA data (Table 1). In principle XPS indicates a significant amount of carbon, an increased copper content as well as a total lack of titanium at the surface of the samples. Additionally, a decrease in carbon and phosphorus concentration after the modification of a coating is observed. Three potential explanations for the presence of carbon at the sample surfaces exist: (1) adsorption of a carbon containing compound from the air or from (2) the aqueous solutions (acetate ions in PEO electrolyte and/or carbonate-ions as the result of CO_2 sorption) as well as (3) a surface contamination.