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

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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/TiO₂/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.

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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/Al₂O₃/Al, CrO_x/Al₂O₃/Al [5], MnO_x/TiO₂/Ti [8], CoO_x/TiO₂/Ti [9], CeO_x+ZrO₂/TiO₂/Ti [10], Pt+CeO_x+TiO₂/Ti, Pt+Al₂O₃/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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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/TiO₂/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 Na₃PO₄ + 0.034 M Na₂B₄O₇ + 0.006 M Na₂WO₄ + 0.1 M Ni(CH₃COO)₂ + 0.025 M Cu(CH₃COO)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 cm². 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:HNO₃ = 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(NO₃)₂ and 0.1 mol/L Ni(NO₃)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) multi-purpose 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 cm²) 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 CO₂ 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 CO₂ sorption) as well as (3) a surface contamination.

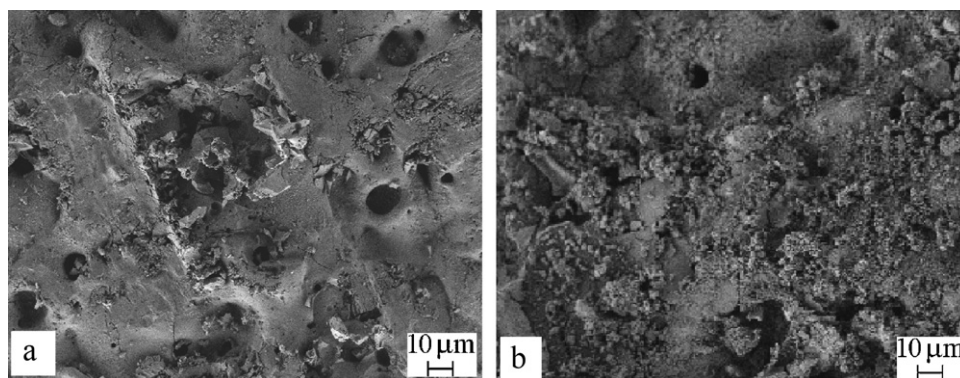


Fig. 1. Surface morphology of initial (a) and modified (b) oxide coatings on titanium.

Table 1

Thickness h , elemental and phase composition of coatings (XSA and XRD data).

Composite	h (μm)	Phase composition	Elemental composition (at%)						
			Ni	Cu	P	Ti	O	W	Na
PEO/Ti	40 ± 2	TiO ₂ (rutile) TiO ₂ (anatase)	11.9	3.2	8.3	9.5	62.4	1.0	3.7
PEO/Ti ^a	40 ± 2	TiO ₂ (rutile) TiO ₂ (anatase) NiO, CuO	20.8	12.4	4.5	6.2	55.6	0.5	–

^a PEO coatings, modified by additional impregnation and air annealing.

Table 2

Elemental composition of coatings (data of XPS).

Composite	Elemental composition, at %							
	Ni	Cu	P	O	C	Na	Ti	
PEO/Ti	5.5	5.9	7.5	42.9	36.3	1.9	–	
	8.8	9.8	9.6	47.1	17.0	7.8	–	
PEO/Ti ^a	21.0	16.7	1.5	42.8	18.0	–	–	
	32.9	18.6	0.8	35.9	11.8	–	–	

^a PEO coatings, modified by additional impregnation and air annealing. The numerator specifies the content of elements at the surface and the denominator indicates the content of elements after surface processing by high energy argon beam for 5 min.

3.2. Thermal treatment effect

The additional annealing of modified structures in air at temperatures above 650 °C results in surface cracking (Fig. 2). This,

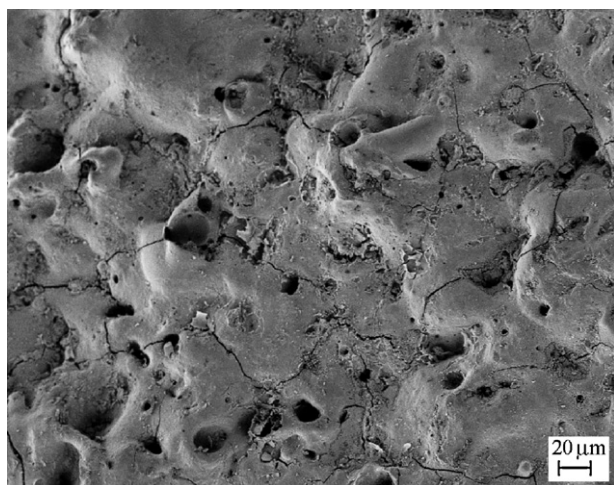


Fig. 2. Surface morphology of modified (b) coating after its annealing in air at 650 °C.

however, has no significant effect on the general surface topography. Above 700 °C an onset of growth of filiform nanocrystals featuring a pseudo-ordered structure (Fig. 3) is observed. For the first time the growth of filiform nanocrystals under thermal treatment of such modified PEO structures was founded out by our colleagues from Institute of Materials Engineering (University Siegen). The average diameter of these whiskers is 50–200 nm while their length does not exceeds 10 μm . In this context the surface topography plays a key role as protuberances and pores act as nucleation centers of the whiskers. For this reason the growth of nanostructures is found not only on the surface of modified coatings but also on the surface of initial coatings as well as in pores and their vicinity.

At temperature above 850 °C some delamination of the coatings from its titanium substrate is noted. Besides differences in the thermal expansion coefficients of titanium and coating material a severe oxidation of titanium owing to an oxygen penetration through cracks in the film to the film-substrate interface might explain these findings.

The results of a point elemental analysis of the filiform nanocrystals (points 1 and 2, Fig. 4) and of the base coating material (point 3) are presented in Table 3. The whiskers mainly consist of nickel, titanium and oxygen. Phosphorus, carbon and aluminum signal registration may arise from the base coating material. According to using analysis techniques, the coating surface (point 3, Table 3)

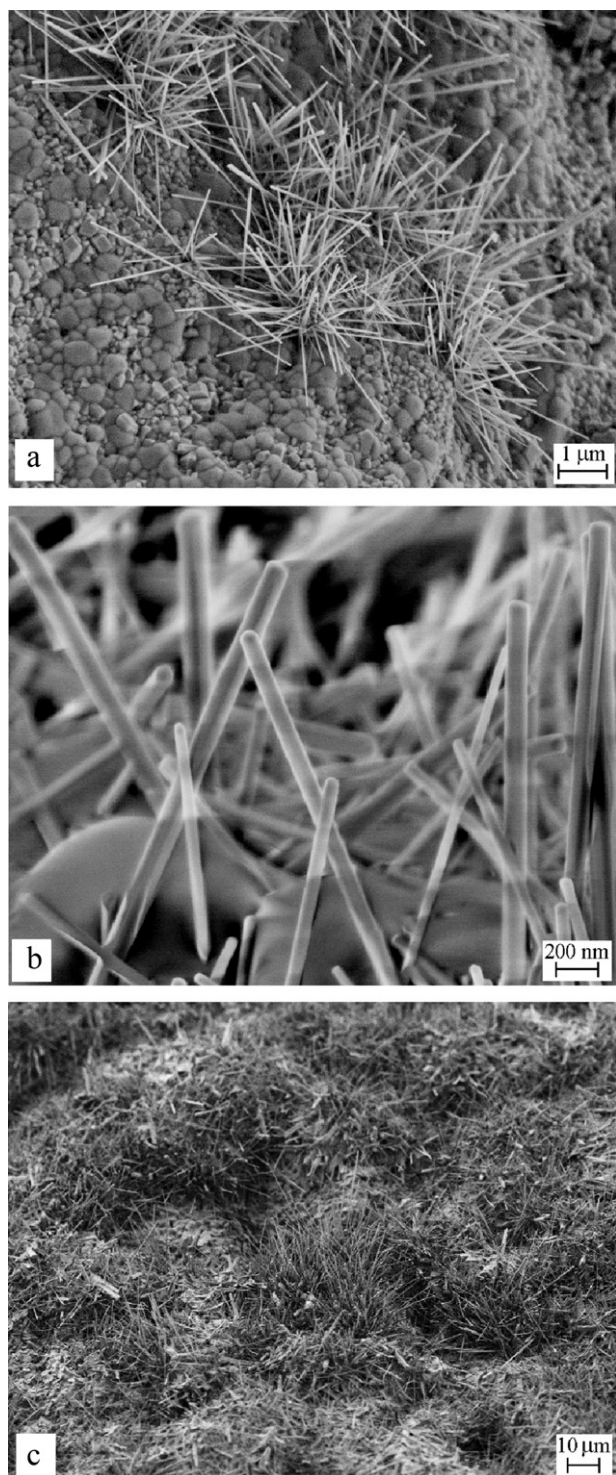


Fig. 3. SEM images of modified Ni-, Cu-containing coatings with grown filliform nanocrystals: (a) the beginning of nanocrystal growth (750 °C); (b) at 850 °C; (c) the brush from filliform nanocrystals (950 °C).

shows almost the same elemental composition as the whiskers with the exception of titanium, which is absent at the annealed as well as the initial surface. Analyzing the whiskers' composition allows us to propose that the nucleation of the nanostructures is initiated at nickel containing surface sites. The surface of the layers annealing at 950 °C is completely coated by filiform nanocrystals and it looks as a uniform brush from whickers (Fig. 3c).

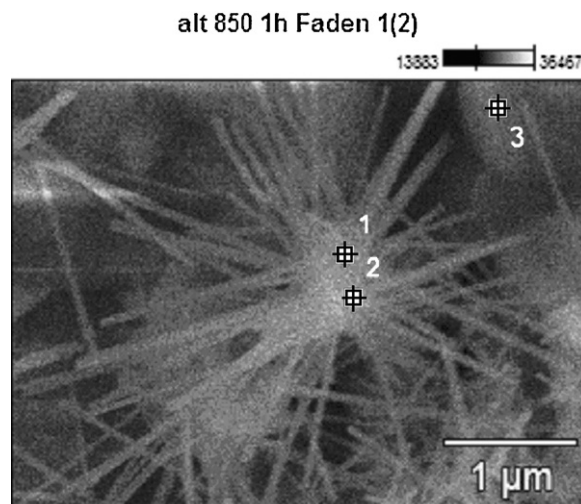


Fig. 4. The wickers grown at the surface of modified coatings.

The lack of copper in the nanofibers as well as it the surface layer of samples annealed at 850 °C might be explained by diffusion of the copper away from the surface deep into the oxide layer.

The XPS and XRD results of the annealed modified coating surfaces are summarized in Tables 4 and 5. The data of XPS has to be regarded as qualitative as our resolution is not sufficient to distinguish between the individual sources of the signals, whiskers and coating, respectively.

The analysis of XPS data (Table 4) shows that annealing in air at 700 °C results in drastic (one third) decrease of the copper content at the coating surface, confirming our hypothesis about its diffusion into deeper layers of the coating. Additionally, decreasing nickel content at the surface with increasing annealing temperature is observed. In contrast to this, phosphorus and oxygen concentrations increase with increasing annealing temperature. The carbon detected at the surface features C–H bonds as well as C–M bonds (M= metal).

According to our XRD data (Table 5) the modified coatings contain crystalline oxides of nickel, titanium and copper. The coatings annealed at increased temperatures show a decreasing crystalline nickel and copper oxide content while at the same time the content of crystalline titanium oxide (rutile and anatase) increased. Once the annealing temperature is raised above 700 °C, metal phosphates are found in the coatings.

All analytical results presented here are in good agreement. In principle it was found that the copper content at the surface decreases with increasing annealing temperature. At the same time the content of crystalline nickel and copper oxides also decreases while the concentration of crystalline titanium oxides, such as rutile and anatase, increases in the

Table 3
Elemental composition of whiskers and of base coating (Fig. 4).

Element	Elemental concentration (wt%)		
	In whiskers		In base coating
	Point 1	Point 2	Point 3
C	1.9	2.1	3.5
O	42.9	44.4	45.9
Al	2.3	3.0	2.2
P	4.6	9.4	10.6
Ti	8.4	5.1	–
Ni	39.9	36.1	37.9

Table 4
Annealing temperature effect on surface coating composition (XPS data).

T(°C)	Elemental concentration (at%)						
	Cu	Ni	O	Ti	C	Na	P
500	16.7	21.0	42.8	–	18.0	–	1.5
	18.6	32.9	35.9		11.8		0.8
700	5.1	15.9	52.3	1.0	17.2	4.9	3.7
	5.5	26.0	48.8	1.3	10.7	5.1	2.7
850	4.3	6.6	58.3	2.8	19.6	1.7	6.8
	5.6	10.8	63.0	4.7	4.9	2.0	9.0

The numerator specifies the composition of initial surface and the denominator indicates the content of elements after surface processing by high energy argon beam.

Table 5
Annealing temperature effect on phase coating composition (XRD data).

T(°C)	Coating color	Phase composition
500	Black	TiO ₂ (rutile + anatase) + NiO + CuO (tenorite)
700	Brown	TiO ₂ (rutile + anatase) + NiO + CuO (tenorite) + NaTi ₂ (PO ₄) ₃ + Ni ₃ (PO ₄) ₂
850	Yellow-green	TiO ₂ (rutile + anatase) + NaTi ₂ (PO ₄) ₃ + CuPO ₃ + Ni ₃ (PO ₄) ₂

coating. Metal phosphates are crystallized at temperatures above 700 °C.

3.3. Catalytic tests

Fig. 5 shows the effect of annealing temperature on the appropriate catalytic activity in CO oxidation of the coatings. It is obvious that the coating activity in CO oxidation into CO₂ decreases with increasing annealing temperature, reaching its minimum for samples treated at 750 and 850 °C. The deactivation of the samples can be explained by changes in the coating structure and surface composition. It is well known that binary nickel–copper oxide systems are more active in CO oxidation than free nickel and copper oxides [12,13]. So the deactivation of the samples after their annealing in air is possibly associated with the growth of whiskers and the drop of copper concentration at the surface as well as with the simultaneous formation of nickel and copper phosphates, which are inactive in CO oxidation.

However, the samples featuring the filiform nanocrystals may be promising candidates in the catalysis of organic compounds. So, colleagues from Siegen University showed that the resulted nanoarchitected compound composite is outstandingly active as catalyst and appears most suitable for high temperature operation in biomass gasification [18].

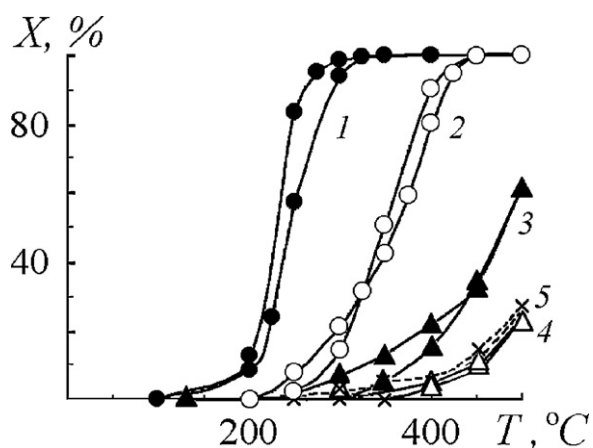


Fig. 5. The temperature dependence of the conversion of CO(X) for modified coatings annealed in air at the temperatures (°C): 500–curve 1, 600 – 2, 700 – 3, 750 – 4 and 850 – 5.

Additionally, the synthesis process of whiskers described here can be utilized to prepare the appropriate nanofibers for other applications. This would possibly require a subsequent removal of the fibers, for example, by mechanical means.

The systems studied in this work featured a thermal stability up to 850 °C. Thermal treatment at temperatures higher than that results in partial coating delamination from the titanium substrates used here.

4. Conclusion

In this paper the effect of annealing temperature in air on composition, surface structure as well as catalytic activity in CO oxidation into CO₂ of Ni- and Cu-containing oxide coatings has been studied in the temperature regime between 650 and 950 °C. A decreasing copper content at the surface was observed for annealing temperatures above 700 °C, which was explained by a diffusion of the copper into lower coating regions. High temperature annealing in air leads to a deactivation of the oxide structures in catalytic CO oxidation. A clear relationship between increasing annealing temperature and decreasing activity is shown. The decreasing catalytic activity is possibly related to copper diffusion from the surface into deep layers as well as to nickel and copper phosphate formation. Annealing of the film/substrate systems presented here at temperatures above 700 °C causes the growth of filiform nanocrystals which show a pseudo-ordered structure. The average diameter of these whiskers is 50–200 nm and they feature lengths below 10 μm.

These nanostructures containing nickel and titanium oxides are promising candidates for catalytic applications which are based on this material already as they provide the option of a dramatic increase of surface area. The process established in this work might form the basis for an appropriate synthesis of free nanocrystals.

The systems discussed here proved to be thermally stable for 1 h at temperatures up to 850 °C. Long term studies of thermal stability as well as catalytic activity are still required.

The synthesis strategy for filiform crystals presented here might serve as kind of template for the preparation of various whiskers from other metal oxycompounds.

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