

Composition, Surface Structure and Catalytic Properties of Manganese- and Cobalt-Containing Oxide Layers on Titanium

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Abstract. Silicon-containing oxide layers deposited on titanium using the plasma electrolytic oxidation (PEO) method were modified with manganese and cobalt compound through impregnation followed by annealing. The obtained manganese composites are catalytically active in the process of oxidation of CO at 100°C, while cobalt-containing structures demonstrate this type of activity at temperatures above 200°C. The composition and surface structure of the obtained systems were investigated by means of X-ray phase and energy dispersive analyses and by high resolution scanning electron microscopy (SEM). Granule-like particles with diameters of a few dozens of nanometers were observed on the surface of oxide-cobalt layers on titanium, whereas the surface of oxide-manganese layers was coated by nano-whiskers of diameters <50 nm and length <1 μm. The presence of manganese-containing nano-whiskers substantially increases the catalyst specific surface, thus facilitating the attainment of higher degree of transformation of initial gaseous substances.

Introduction

Recently, transition metal oxides, including those deposited on different substrates, have been extensively used as heterogeneous catalysts in chemistry and oil-refining industry as well as in the processes of treatment of gaseous waste of factories/plants and exhaust gases of motor vehicles [1,2].

The method of plasma electrolytic oxidation (PEO) – deposition of oxide layers on metal surface under effect of spark and arc discharges at the metal/electrolyte interface – comprises one of the unconventional and prospective methods of producing catalytically active materials with controlled composition, porosity, and surface structure [3-7]. The formed systems MO_x/M or $EO_y + MO_x/M$, where M – the treated metal, EO_y – oxides on the basis of electrolyte components, are investigated, in particular, as substrates for catalytically active compounds [4] and, if E is a transition metal, as catalysts of various processes [5-7].

In virtually all the published works the catalytic activity of plasma-electrolytic layers is studied in correlation to the surface chemical composition, active sites concentration, and catalyst surface structure on micro- and macro-levels, whereas the structure of such coatings on nano-level and its effect on the coatings catalytic properties have not yet been studied in sufficient detail.

The objective of this work was to investigate the composition and structure of the surface (also on nano-level) and catalytic activity in the process of CO oxidation into CO_2 of some of the most active oxide catalysts of CO and hydrocarbons oxidation – oxide-manganese and oxide-cobalt structures obtained through impregnation of PEO-pre-deposited silicon-containing layers on titanium.

Experimental

Titanium plates (2.5 cm × 0.5 cm × 0.1 cm in size) and titanium wire (l = 32 cm and $\varnothing = 0.1$ cm) of VT1-0 alloy were used as a substrate. Prior to anodizing the metallic substrates were etched by using

a mixture of concentrated acids HF: HNO₃ (1:3 volume ratio), at 60–80°C for 2–3s, and then rinsed in distilled water and dried in air.

PEO process was carried out in a thermal glass of 500 ml in volume. The electrolyte in a glass was mixed using a magnetic mixer. Thyristor unit TER4-63/460H (Russia) with unipolar pulse current was used as a power source. The silicon-containing oxide coatings SiO₂/TiO₂/Ti were formed at effective current density 10 A dm⁻² for 10 min in aqueous solution containing 0.1 MNa₂SiO₃. Then the samples were rinsed with distilled water and dried on air.

Supported manganese or cobalt catalysts were prepared by the impregnation of SiO₂/TiO₂/TiPEO-systems with the aqueous solution containing 1 MMn(NO₃)₂ or 1 M Co(NO₃)₂ accordingly. Then, samples were dried and calcined in air at 500°C in a for 4 h.

The structure and element composition of the samples surface were studied on the ultra high resolution field emission scanning electron microscope ULTRA 55 (FESEM) by ZEISS. The Energy Dispersive X-ray Spectrometer (EDX) of the company Thermo Scientific for qualitative and quantitative element control was integrated in the REM.

The phase composition of the coatings was determined by a D8 ADVANCE X-ray diffractometer (Germany) in CuK_α-radiation. X-ray diffraction (XRD) analysis was performed using the EVA retrieval program with the PDF-2 database.

Catalytic activity of the composites was investigated in the CO oxidation reaction using a BI-CATflow catalytic installation (Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk). Four plane titanium plates (25 mm x 25 mm x 1 mm) with the cobalt compounds sprinkled with quartz filling agent were placed into a quartz reactor of 3 cm³ volume. The starting reaction mixture consisted of 79% Ar, 20% O₂, and 1% CO. The gas flow rate was 70 ml·min⁻¹. The measurements were performed in the range from the room temperature to 500°C. The rate of temperature change in the reactor was 10°C·min⁻¹. The quantitative determination of the composition of the gaseous products was performed by means of a PEM-2M gas analyzer (Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk).

Results and discussion

Catalytic activity results for the oxidation of CO by O₂ over supported oxide catalysts are presented in Fig. 1. It was established that although both systems were active in CO oxidation, the manganese-containing structures manifested higher activity as compared to cobalt-containing systems. The temperature of CO semi-conversion of oxide-manganese systems T₅₀ is 100°C lower than that of cobalt-containing systems (Fig. 1, Table).

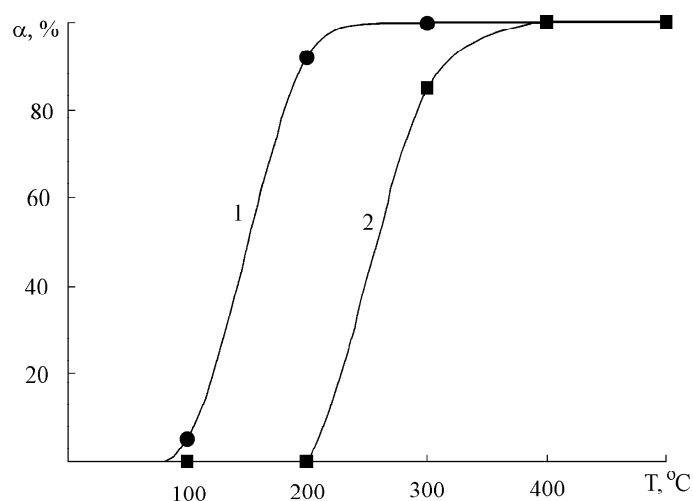


Fig. 1. Temperature dependence of the degree of conversion from CO to CO₂ (α, %) for manganese- (curve 1) and cobalt-containing (curve 2) structures on titanium.

Table. Phase, element composition and CO semi-conversion temperature for cobalt- and manganese-containing oxide layers on titanium

System	Phase composition	Element composition [at.%]						T ₅₀ [°C]
		C	O	Si	Ti	Co	Mn	
CoO _x /SiO ₂ /TiO ₂ /Ti	TiO ₂ (r, a)	2.6	66.2	19.5	3.1	8.7	-	250
MnO _x /SiO ₂ /TiO ₂ /Ti	Ti, TiO ₂ (r), Mn ₂ O ₃	3.1	63.8	17.3	3.5	-	11.9	150

Note: r–rutile, a–anatase.

The manganese and cobalt oxides deposited on different substrates are known to be among the most active catalysts of oxidation of CO and hydrocarbons and capable to catalyze this type of reaction even at negative [Celsius] temperatures [8]. At the same time, the activity of the deposited catalysts depends on the surface structure and composition, which, in their turn, are determined by the synthesis conditions. According to the opinion of the authors of [9, 10], the reaction limiting stage is related to breakage of the bond oxygen-catalyst. In this case there exists the correlation between the catalytic activity and the oxygen bond energy as for simple oxides as for more complex compounds. As was shown in [11], the catalytic activity of Co₃O₄ is higher than that of MnO₂. This regularity coincides with the trend of the oxygen bond energy increase on the oxide surface. The oxide activity in the processes of complete oxidation is related to easiness of restructuring, which facilitates the oxygen diffusion to the molecule to be oxidized [12]. In this case the deposited manganese-containing structures are more active in CO oxidation as compared to cobalt-containing ones. It appears possible that during deposition of active layers on silicon-containing oxide coatings there occurs some specific interaction of the substrate and precursor, which, in its turn, might affect the peculiarities of oxides crystal structures and defects character (electronic properties) of metal oxides. The latter is known to have a dominating role in catalytic properties of these types of solids [13].

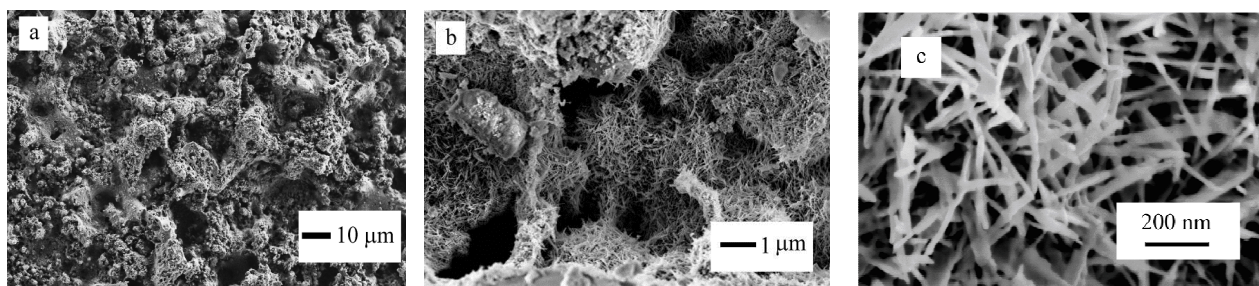


Fig. 2. SEM-images of manganese-containing oxide coatings on titanium (a, b, c).

Table shows the data on element and phase composition of cobalt- and manganese-containing oxide layers on titanium. According to the element analysis data, the surface layers of both systems contain insignificant amounts of carbon and titanium and quite substantial amounts of oxygen and silicon. The presence of high silicon concentration in the surface layers composition enables one to assume the presence of amorphous silicon compounds, most probably, silica. The cobalt-containing surface layers contain 8.7 at. % of Co, whereas the manganese-containing layers contain 11.9 at. % of Mn. Thus, it is evident that cobalt and manganese compounds are present on the surfaces of respective samples as well.

As was established by the X-ray phase analysis method, the titanium dioxide in the rutile modification and manganese oxide Mn₂O₃ were crystallized on the manganese-containing samples surfaces. The crystalline TiO₂ in rutile and anatase modifications was exclusively found on the cobalt-containing samples surfaces.

SEM images of the surface of the manganese-containing oxide layers on titanium are presented in Fig. 2. At small magnification values (Fig. 2a) one can see that the surface of manganese-containing layers on titanium is heterogeneous and has relatively smooth parts, complex formations, and pores of different sizes. At larger magnification values it is seen that there are also the parts coated by a dense layer of thin “feather-like” nanocrystals of diameters less than 50 nm and lengths less than 1 μm (nano-whiskers) (Fig. 2 b, c). Nano-whiskers are localized preferentially in the pores and deepened parts of the surface between coral-like formations (Fig. 2b). The latter affects the distribution of active centers over the surface and, therefore, the catalysts reactivity. One should mention that the formed nanostructures are stable and preserved on the surface in an intact form after prolonged annealing at a temperature 500°C.

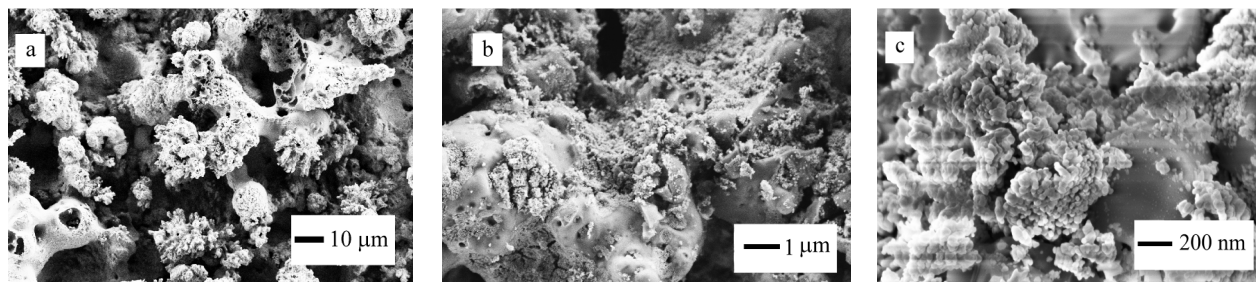


Fig. 3. SEM-images of cobalt-containing oxide coatings on titanium (a, b, c).

SEM images of the surface of the cobalt-containing layers on titanium are presented in Fig. 3. According to the images (Fig. 3 a, b, c), the surface of cobalt-containing layers on titanium consists of smooth parts, coral-like structures and cavities; it also has relatively large pores and relatively smooth parts and areas containing a bulk of nanosize round-shape particles.

Analysis of the performed studies enables us to conclude on substantial differences in surface structures of oxide-manganese and oxide-cobalt layers formed by impregnation of silicon-containing oxide layers on titanium.

Conclusions

To sum up, manganese- and cobalt-containing oxide layers on titanium, which are catalytically active in CO oxidation, were obtained by impregnation of silicon-containing PEO-layers on this metal. The manganese-containing layers catalyze the conversion CO into CO_2 in the temperature range above 100°C, whereas cobalt-containing layer manifest such an activity at temperatures above 200°C. The formed coatings are distinguished by the surface organization on different levels. Nanosize particles were found on coatings surfaces for both systems under study. In the case of oxide-cobalt layers on titanium, their surface contains granule-like particles of diameters of a few dozens nm, whereas the so-called nano-whiskers were found on the oxide-manganese layers surfaces. The “feather-like” nanocrystals comprise one of the most prospective classes of crystallographic materials with a unique complex of properties. One of the main advantages of the latter structures comprises a substantial factor of shape which dramatically increases the catalyst surface area, promotes high accessibility of its surface and higher degree of transformation of initial gaseous substances in final products.

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