

Manganese-Containing Nanostructured Oxide Coatings on Titanium Formed by Plasma Electrolytic Oxidation

VASILYEVA Marina S.^{1,2,a*}, RUDNEV Vladimir S.^{1,2,b}

¹Far Eastern Federal University, 8 Sukhanova St., Vladivostok 690091, Russia

²Institute of Chemistry FEB RAS, 159, pr. 100-letya Vladivostoka, Vladivostok 690022, Russia

^avasileva.ms@dvfu.ru, ^brudnevvs@ich.dvo.ru

Keywords: plasma electrolytic oxidation; titanium; manganese oxide; acetonitrile; nanostructured coating; catalyst; photocatalyst

Abstract. Nanostructured manganese-containing oxide coatings on titanium were formed by method of plasma electrolytic oxidation in tetraborate aqueous electrolyte containing manganese acetate with and without the acetonitrile addition. These oxide layers with high content of manganese and coated by ordered "leaf-like" mesh nanostructures are formed in the electrolyte without acetonitrile addition. The oxide layers are displayed high activity towards oxidation CO and photoactivity in the degradation reaction of methylene blue. The addition of acetonitrile into electrolyte results in the change in the morphology of the coating surface, a significant reduction in the manganese content and, as a consequence, practical loss of activity in the oxidation of CO in CO₂ and a reduction in the photocatalytic activity in the decomposition of methylene blue.

Introduction

Recently, much attention has been devoted to the development and application of catalytic and photocatalytic systems for solving a number of environmental problems, such as the purification of waste water from organic pollutants, the purification of exhaust gases from combustion engines, and so on.

One of the most widely used catalysts of various chemical processes are manganese oxides, including those deposited on various carriers [1-3]. Plasma electrolytic oxidation (PEO) is one of the methods for technological generating multicomponent oxide coatings on metals [4, 5]. The functional properties of the oxide coatings on metals deposited by the method are determined primarily by their composition and morphology, which can be controlled by varying the process parameters and the electrolyte composition. For example, the addition of various organic compounds into aqueous electrolytes for PEO significantly changes the composition and morphology of the surface [6-9].

One of the interesting and poorly studied organic substances used to form anode films is acetonitrile CH₃CN. The high polarity of the nitrile group of acetonitrile determines the possibility of its adsorption on metallic surfaces followed by electrochemical conversion [10]. In addition, due to the good solubility of acetonitrile in water, its ability to form complex compounds by the donor-acceptor mechanism with transition metal salts [11], the addition of acetonitrile to aqueous electrolytes of various compositions may influence the mechanism and properties of PEO coatings. At the same time, this issue, as far as we know, was not considered in the scientific literature.

The purpose of this work was to study the effect of acetonitrile additives into aqueous electrolyte for PEO on the composition, morphology of the surface of manganese-containing coatings on titanium, their catalytic activity in CO oxidation, and photoactivity in the decomposition of methylene blue.

Experimental

Titanium plates of the grade VT1–0 of a size of 2.5×2.5 cm were used in plasma electrolytic oxidation. Prior to anodizing the samples were polished mechanically and chemically with a mixture of concentrated acids HF: HNO₃ (1:3), at 60–80°C for 2–3 s, and then rinsed in distilled water and dried in air.

PEO process was carried out in a thermal glass of 1000 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 Mn-containing oxide coatings on titanium were formed at effective current density 0.1 A/cm² for 10 min in an aqueous electrolyte containing 0.1 M Na₂B₄O₇ + 0.04 M Mn(CH₃COO)₂ (Electrolyte I) or 0.1 M Na₂B₄O₇ + 0.04 M Mn(CH₃COO)₂ + 3.0 vol. % CH₃CN (Electrolyte II).

The data on morphology and element composition of the surface were obtained using an S-5500 scanning electron microscope (Hitachi, Japan) with the system for energy-dispersive X-ray spectral microanalysis. The phase composition was determined by the method of X-ray diffraction analysis (XRD).

Catalytic activity of the manganese-containing composites was investigated in the CO oxidation reaction using a BI-CATflow catalytic installation (Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk).

The photocatalytic activity of the fabricated samples was determined through photodegradation of methylene blue (MB) dye in an aqueous solution (10 mg/L) under ultraviolet radiation for 2 h using SB-100P UV-lamp (radiation maximum at a wavelength of 365 nm). Changes in the dye concentration were controlled by a spectrophotometer Shimadzu UV mini-1240 (Japan) on changes in the intensity of the dye absorption peak. Measurements of the optical density of MB solutions before and after irradiation were carried out at a wavelength of 659 nm (light absorption maximum).

Results and Discussion

Base 0.1 M sodium borate electrolyte is a transparent true solution. The solution was dyed in white color with a pinkish shade after addition of manganese acetate. Addition of acetonitrile to the electrolyte did not lead to a visual change in the state of the electrolyte. In the process of electrolyte stirring the deposit was easily stirred and supported as a suspension.

In the process of oxidation, in both cases, during the first minutes of the process, a rapid increase in the voltage on the electrodes occurs, which reaches 75 V in the Electrolyte I and 130 V in the Electrolyte II for 4–6 minutes, and then changes insignificantly during the process time to 10 min.

As was established by the X-ray phase analysis method, the coatings formed in the Electrolyte I contain traces crystalline MnO₂. The crystalline TiO₂ in rutile and anatase modifications was exclusively found on the samples surfaces fabricated in the Electrolyte II.

Table shows the data on element composition of formed in electrolytes with and without addition of acetonitrile. The oxide layers formed in the aqueous electrolyte without the addition of acetonitrile (Electrolyte I) contain a high amount of manganese, oxygen, and also carbon and sodium. Titanium in the coatings is not detected. The addition of 3.0 vol. % acetonitrile to the electrolyte (Electrolyte II) results in a significant (in 10 times) decreasing of the amount of manganese in the coating. In addition a high amount of titanium is found in the coatings.

Table. Elemental composition of the samples

Electrolyte	Elemental composition [at. %]				
	Mn	Ti	Na	O	C
I	46.0	-	2.2	41.4	10.4
II	4.6	26.9	-	64.3	4.2

SEM images of the surface of the manganese-containing oxide layers on titanium are presented in Fig. 1. It is seen that sample surface formed in Electrolyte I are coated by ordered "leaf-like" mesh nanostructures (Fig. 1 a). The addition of acetonitrile into the tetraborate-acetate electrolyte leads to a marked change in the morphology of the coatings formed. On the surface of such coatings, crystal-like nanostructured objects localized on individual parts of the surface were found (Fig. 1 b). The objects resemble droplets (or "hedgehogs") with a developed structure in the form of leaf formations, as in the case of coatings obtained in electrolyte. According to elemental analysis data, the regions containing nanostructures include at.%, 11.2 Mn, 18.5 Ti, 56.2 O, 14.1 C, neighboring regions are depleted of manganese and contain at. %, 6.3 Mn, 26.3 Ti, 58.6 O, 7.8 C, 1.1 Na.

Evidently, in the electrolyte with tetraborate and manganese acetate, acetonitrile changes the mechanism of incorporation of manganese into the coatings as a result of interaction with dispersed particles of manganese hydroxide, changing their charge and mobility.

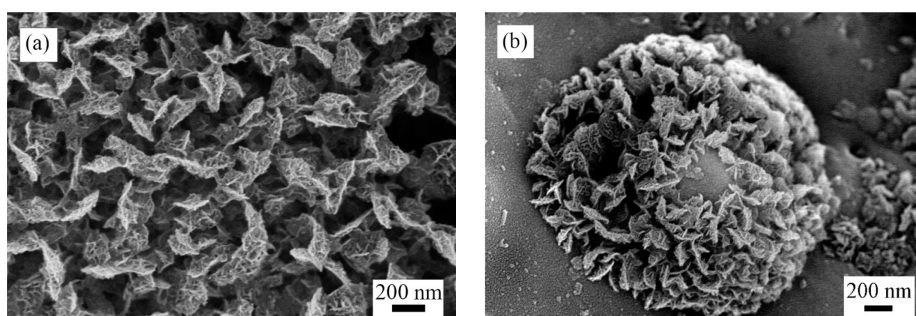


Fig. 1. SEM images of Mn-containing oxide coatings, fabricated in the Electrolyte I (a) and Electrolyte II (b).

The results of the investigation of the catalytic activity of formed manganese-containing oxide layers in the oxidation of CO in CO₂ are shown in Fig. 2. The degree of conversion of CO to CO₂ at 400 °C in the presence of samples formed in the Electrolyte I is 98.8% (Fig. 2, curve 1), whereas coatings formed in the Electrolyte II are not active in the investigated reaction (Fig. 2, curve 2).

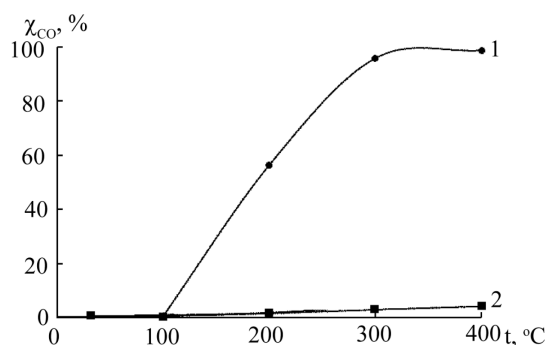


Fig. 2. Temperature dependence of the CO conversion degree for manganese-containing layers on titanium formed in Electrolyte I (curve 1) and Electrolyte II (curve 2).

It was established that, under UV radiation, all the formed coatings displayed photocatalytic activity in the reaction of MB degradation. However, as in the case of CO oxidation, the oxide layers formed in the Electrolyte I exhibited the higher photocatalytic activity compare with oxide layers formed in the Electrolyte II. The decomposition degree of MB reaches 49 % and 16 % in the presence of coatings formed in the Electrolyte I and in the Electrolyte II accordingly.

Summary

Manganese-containing oxide coatings on titanium were formed by plasma electrolytic oxidation in the tetraborate electrolyte containing manganese acetate with and without the additions of acetonitrile. The ordered "leaf-like" mesh nanostructures were found on the surface of coatings

formed in the electrolyte without acetonitrile addition. These nanostructured manganese-containing have a high catalytic activity in the oxidation of CO into CO₂ and in the photodegradation of methylene blue. The addition of acetonitrile to the electrolyte leads to a change in the morphology of the coating surface, a significant reduction in the manganese content and, as a consequence, practical loss of activity in the oxidation of CO and a reduction in the photocatalytic activity in the decomposition of methylene blue.

Acknowledgements

The work was partially supported by grants of the Russian Foundation for Basic Research RFBR (project no. 18-03-00418).

References

- [1] Q. Zhang, X. Cheng, C. Zheng, X. Feng, G. Qiu, W. Tan and F. Liu, Roles of manganese oxides in degradation of phenol under UV-Vis irradiation: adsorption, oxidation, and photocatalysis, *J. Environ. Sci.* 23 (2011) 1904-1910.
- [2] H. Einaga and A. Ogata, Benzene oxidation with ozone over supported manganese oxide catalysts: effect of catalyst support and reaction conditions, *J. Hazard. Mater.* 164 (2009) 1236-1241.
- [3] A. Izgorodin, R. Hocking, O. Winther-Jensen, M. Hilder, B. Winther-Jensen and D. R. MacFarlane, Phosphorylated manganese oxide electrodeposited from ionic liquid as a stable, high efficiency water oxidation catalyst, *Catal. Today* 200 (2013) 36-40.
- [4] F. Patcas and W. Krysmann, Efficient catalyst with controlled porous structure obtained by anodic oxidation, *Appl. Catal. A: Gen.* 316 (2007) 240-249.
- [5] V.S. Rudnev, I.V. Lukiyanichuk, M.S. Vasilyeva, M.A. Medkov, M.V. Adigamova and V.I. Sergienko, Aluminum- and titanium-supported plasma electrolytic multicomponent coatings with magnetic, catalytic, biocide or biocompatible properties, *Surf. Coat. Technol.* 307 (2016) 1219-1235.
- [6] H. Guo and M. An, Effect of surfactants on surface morphology of ceramic coatings fabricated on magnesium alloys by micro-arc oxidation, *Thin Solid Films* 500 (2006) 186-189.
- [7] V.S. Rudnev, M.S. Vasilyeva, N.B. Kondrikov and L.M. Tyrina. Plasma-electrolytic formation, composition and catalytic activity of manganese oxide containing structures on titanium, *Appl. Surf. Sci.* 252 (2005) 1211-1220.
- [8] S.-C. Yeh, D.-S. Tsai, S.-Y. Guana and C.-C. Chou, Influences of urea and sodium nitrite on surface coating of plasma electrolytic oxidation, *Appl. Surf. Sci.* 356 (2015) 135-141.
- [9] H. Yongyi, C. Li, Y. Zongcheng and Z. Yalei, Effects of CH₃OH addition on plasma electrolytic oxidation of AZ31 magnesium alloys, *Plasma Sci. Technol.* 17 (2015) 761-766.
- [10] J. Cassidy, B.S. Khoo, S. J. Pons and M. Fleischmann, Electrochemistry at very high potentials: the use of ultramicroelectrodes in the anodic oxidation of short-chain alkanes, *J. Phys. Chem.* 89 (1985) 3933-3935.
- [11] I.V. Dumayeva, Sh. F. Rekuta and N.A. Egorov, Synthesis and calculations of aminonitriles and their complexes with salts of metals of transitive valency, *Bashkir chemical journal* 16 (2009) 178-180 [in Russian].