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NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

Effect of the Structure of the Oxidized Titanium Surface on the Particle Size and Properties of the Deposited Copper–Molybdate Catalyst

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Abstract—The parameters of wetting of oxide coatings on titanium formed by the method of plasma electrolytic oxidation (PEO) in an aqueous silicate electrolyte with subsequent deposition of a layer of TiO_2 nanoparticles and ultrasonic treatment by a polymer–salt gel including copper and molybdenum compounds have been investigated. The effect of the oxidized surface microrelief, TiO_2 nanoparticle layer, and pore shape and size on impregnation solution spreading and the structure of the copper–molybdenum catalytic coating formed at further thermal treatment has been demonstrated. Complex oxide composites with ultradispersed catalyst particle sizes characterized with high activity in oxidation of carbon black particles have been obtained.

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INTRODUCTION

The development of oxide coatings with required levels of strength and functional properties on the surface of metals has been and remains a rather complicated and important task. Great attention has been paid to the development of methods of oxidation of the substrate surface [1–3] and to obtaining a homogeneous microstructure and chemical and phase composition of the deposited layer [4, 5]. A promising approach to formation of composites on the surface of constructions of complex shapes consists in combining solution technologies, producing a porous oxide sublayer on the metal by means of the method of plasma electrolytic oxidation with subsequent chemical deposition of the required coating components. In particular, earlier we showed the high efficiency of application of the extraction–pyrolysis (EP) method of deposition of the copper–molybdate catalyst on the surface of titanium pretreated using the method of plasma electrolytic oxidation (PEO) in the silicate electrolyte [6]. The maximum activity of catalytic coatings in oxidation of carbon black particles was achieved through formation of crystallites of the $CuMoO_4$ phase of sizes up to 200 nm on the surface of the $TiO_2 + SiO_2/Ti$ oxide film. As compared to the EP synthesis, which requires large amounts of volatile and rather toxic organic reagents, certain ecological advantages are associated with the method of pyrolysis of polymer–salt composites (PPSC) [7]. As was found in preliminary studies, the oxidation annealing of the polymer–salt gel on the oxidized titanium surface was accompanied by a growth of particles of the copper–molybdate phase attaining a size of 10–12 μm. A substantial decrease of the sizes of particles of the catalyst deposited using the PPSC method down to 150–350 nm was revealed upon creation of an extra sublayer of TiO_2 nanoparticles on the PEO coating surface [8]. The effect of the substrate nanostructure on the grain growth dynamics and the catalyst activity has been noted in a number of works [5, 9, 10]. However, the physical-chemical processes forming the basis of the above effect have been investigated to a significant extent only for catalysts containing platinum group metals [11] and have not been examined in works dealing with oxide catalytic systems.

Producing coatings by chemical solution methods includes different stages of treatment—preparation of the substrate surface and preparation, deposition, drying, and subsequent destruction of impregnation solutions—each of which can significantly affect the particle size and the catalyst properties. To obtain thin—film coatings with preset reproducible characteristics, it is necessary to study individual stages of their formation and the peculiarities of the related processes. The main factors determining the homogeneity and thickness of the liquid layer on the substrate surface include roughness and the presence of pores and bumps, as well as the viscosity and surface tension of the impregnation solution [12]. The objective of the present work consisted in studying the wetting of oxide surfaces ($TiO_2 + SiO_2/Ti$, $TiO_2/TiO_2 + SiO_2/Ti$) differing in microrelief in having a polymer–salt gel incorporating copper and molybdenum compounds and determination of the factors affecting the microstructure and properties of catalysts that form upon their subsequent oxidation pyrolysis.

MATERIALS AND METHODS

The formation of oxide layers of different morphologies on plates and wire made of technical grade titanium (VT1–0) was carried out through application of several approaches: PEO-treatment of samples, creation of a layer of TiO_2 nanoparticles on the surface of PEO coatings, and ultrasonic (US) treatment of the oxide layer. PEO coatings on titanium substrates were obtained in an aqueous electrolyte containing 0.05 mol/L Na_2SiO_3 + 0.05 mol/L NaOH in the galvanostatic mode at an average current density of 0.2 A/cm^2 for 10 min [13]. The final voltage on the electrode was about 280 V. The solution temperature during the process did not exceed 30°C. To create a nanostructured TiO_2 sublayer, a colloid suspension containing 22 wt % of anatase particles of a cubic shape of edge sizes 30–40 nm was prepared using the solvothermal synthesis [14]. The suspension was deposited on samples by immersion, after which they were consecutively heated 2 hours each at 120 and 220°C to remove solvents and, thereafter, at 350 and 550°C to decompose and oxidize organic precursors. The density and size of shrinkage cracks of the TiO_2 layer were adjusted by reduction of the nanoparticle concentration in the initial suspension as well as through changes in the sample heating conditions at the pyrolysis stage. The samples US treatment was carried out in water for 3 min; the irradiator power was 140 W.

Copper–molybdate coatings were obtained by deposition of the polymer–salt gel containing Cu and Mo compounds on the oxidized titanium surface modified with TiO_2 nanoparticles with subsequent thermal treatment in air up to 550°C. To prepare the polymer–salt gel, an aqueous solution of the polyvinyl alcohol of 16/1 grade was sequentially added with solutions of ammonium paramolybdate and copper nitrate at a quantitative ratio corresponding to the $CuMoO_4$ phase. The concentrations of metals and polyvinyl alcohol providing the gel stability were equal to 2 and 4 wt %, respectively. In the experiments, reagents of chemically pure and analytical grades were used.

The composition and structure of the produced composites were studied by the methods of X-ray diffraction analysis (XRD) using a DRON-7 diffractometer and scanning electron microscopy (SEM) using an EVO 40 microscope and a Hitachi S5500 high-resolution microscope. The topographic profile of the coating surface (R_a) was determined using a Surfcom 1800D Accretech profilometer. Specific surface area S_{spec} of wire samples was determined using a Sorbi 4.1 META device on the nitrogen thermal adsorption: the determination error did not exceed 4%. Wetting angle θ was determined at 25°C by photography within 5 min upon deposition of a solution drop, tangentially from the substrate surface to that of the drop. For each sample, at least 10 measurements were made, and the results were averaged. Surface tension σ_{lg} and the impregnation solution viscosity were measured using a capillary viscometer.

The carbon black catalytic burning was studied using a NETZSCH STA 449 F3 in air flow (50 mL/min) at a heating rate of 5°/min. Titanium wire samples were coated with carbon black in the burner flame at burning of a diesel fuel (*GOST* (State Standard) 305-82) until the sample weight increased by at least 0.2–0.4%. Temperature of the carbon black burning start t_0 was determined on thermogravimetric curves, and temperature of the process maximum rate t_m was found on extrema of differential calorimetry (DTA) curves with an accuracy of ±2°C.

RESULTS AND DISCUSSION

As can be seen from the SEM image (Fig. 1a), the PEO coating $TiO_2 + SiO_2/Ti$ obtained in the silicate electrolyte is characterized by high porosity of the outer part of the oxide layer. The thickness of the oxide layer homogeneously covering the titanium surface is equal to 10–12 μm. The size of oxide crystallites reaches 7–13 μm, and the pore diameter is 2–8 μm. According to the XRD data, coatings contain TiO_2 in rutile and anatase modifications and amorphous silica.

Upon deposition of a suspension of TiO_2 nanoparticles with subsequent thermal treatment, an additional layer with a thickness of up to ~2.5 μm separated into smooth parts with sizes of 10–20 μm by a network of surface cracks with widths of 2–4 μm (Fig. 1b) is formed. This layer has a homogeneous continuity and consists of particles of a size of 30–50 nm bound to each other at contact sites (Fig. 1b, insert). The X-ray image of the oxide coating contains diffraction peaks attributed to the anatase structure. Changes in the sample heating conditions at the stages of drying and pyrolysis of the deposited suspension demonstrated that the coating cracking resulted from its shrinkage at the removal of gaseous products of thermal decomposition of organic reagents. The most intensive cracks development and widening up to 7–14 μm occurs along the increase of the pyrolysis temperature from

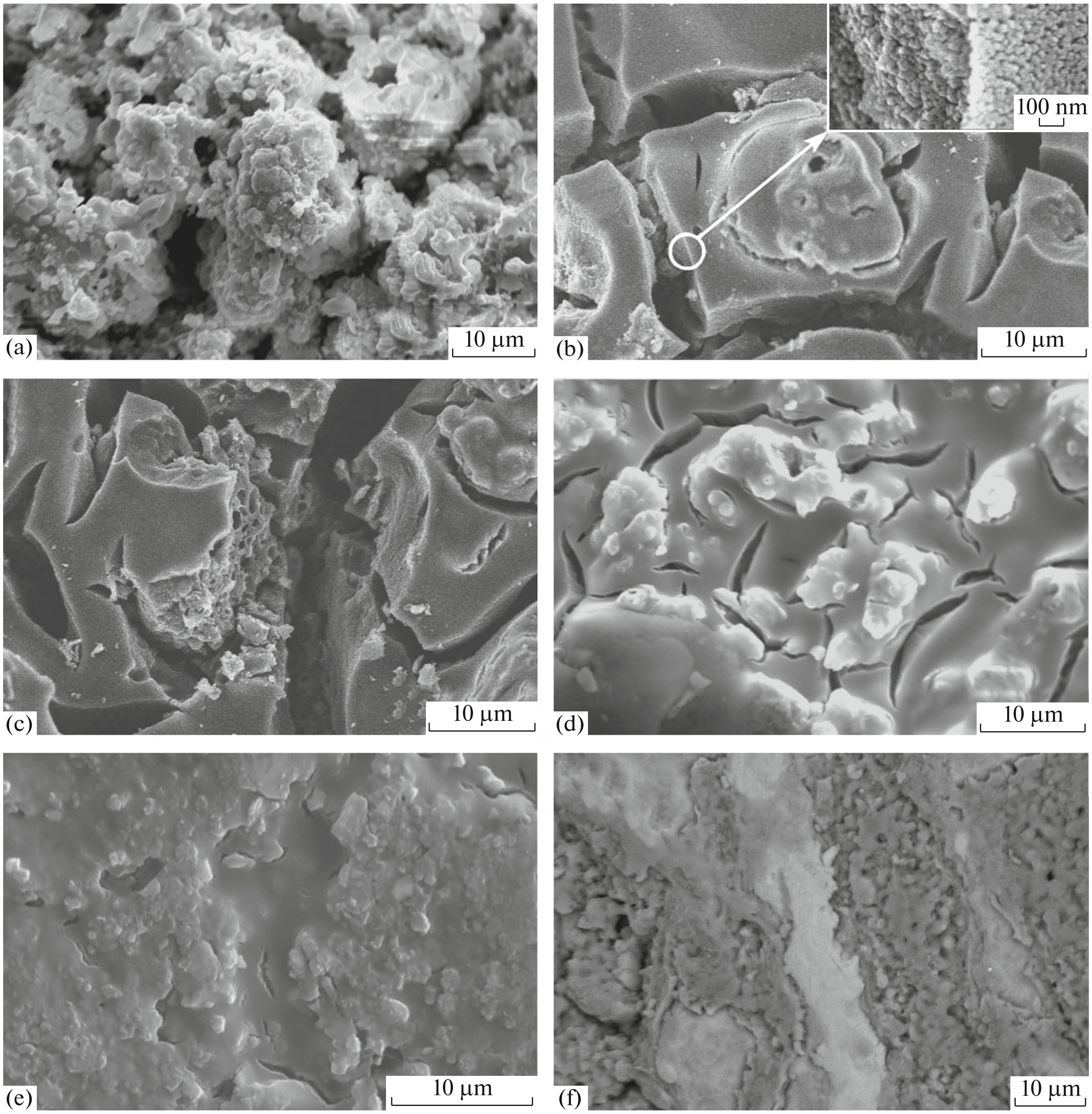

Fig. 1. (a) SEM images of the surface of the PEO coating; TiO_2 layer on the PEO coating: pyrolysis of the initial suspension of anatase nanoparticles at (b) 350 and (c) 550°C, (d) triply diluted suspension at 350°C, (e) fivefold diluted suspension at 350°C, and (f) the same sample upon US treatment.

350 to 550°C (Fig. 1c). An almost complete covering of roughnesses of the initial relief of the PEO coating by an extra TiO_2 layer yields a decrease of the roughness values (R_a), whereas the sample S_{spec} values (Table 1) increase along with the increase of the volume of microcracks, cleavages of which, unlike the layer smooth outer surface, are characterized with a developed mesoporous structure (Fig. 1b, insert). Conversely, using a suspension triply diluted by toluene, one observes the decrease of the cross-section size of cracks down to 0.5–2 μm (Fig. 1d) until their complete disappearance at a fivefold suspension dilution (Fig. 1e). The R_a value for these samples is larger than for those obtained from the initial suspension, since the thin and smooth layer of the deposited TiO_2 replicates the outer relief of the PEO coating. The specific surface area of such a layer is too low to be determined and does not exceed the device error limit. Upon the US treatment, the surface acquires roughnesses of sizes up to 1 μm (Fig. 1f): here, the weight losses of the TiO_2 layer did not exceed 10%. One should mention that the US treatment yields the cohesion destruction of more than 60% of the titanium

Table 1. Parameters of wetting of the surface of oxide coatings on titanium by the polymer–salt gel (W_c = 129.2 mJ/m^2)

Sample	TiO_2 suspension pyrolysis conditions	S_{spec}, m^2/g	R_a, μm	θ, deg	W_a, mJ/m^2	f, mJ/m^2
$TiO_2 + SiO_2/Ti$	–	0.02	3.5	42.2	112.5	–16.7
$TiO_2/TiO_2 + SiO_2/Ti$	350, 550°C	0.37	1.7	26.0	121.5	–6.5
$TiO_2/TiO_2 + SiO_2/Ti$	550°C	0.55	2.3	30.1	118.7	–8.7
$TiO_2/TiO_2 + SiO_2/Ti$*	350, 550°C	–	2.7	32.4	119.2	–10.1
$TiO_2/TiO_2 + SiO_2/Ti$**	350, 550°C	–	2.7	36.4	116.6	–12.6
$TiO_2/TiO_2 + SiO_2/Ti$***	350, 550°C	–	2.9	31.1	119.9	–9.3

* TiO_2 nanoparticle suspension triply diluted with toluene.
** TiO_2 nanoparticle suspension fivefold diluted with toluene.
*** TiO_2 nanoparticle suspension fivefold diluted with toluene + US treatment.

oxide layer produced from the initial suspension of TiO_2 nanoparticles. The increase of the strength of the deposited TiO_2 layer with a decrease of its thickness may be related to the summarized effect of several factors: layer defect level, internal stresses, and deformation processes. Thus, the oxide coatings formed on titanium differed in their surface relief, the presence of various microstructure defects, and their specific surface area.

Estimation of wetting parameters for the obtained oxide substrates was carried out using a polymer–salt gel, the surface and viscosity of which were equal to 64.6 mJ/m^2 and 2.35 mPa s, respectively. The values of limiting wetting angle θ, cohesion work $W_c = 2\sigma_{lg}$, adhesion work $W_a = \sigma_{lg}(1 + \cos\theta)$, and spreading coefficient $f = W_a - W_c$ are shown in Table 1. According to ten measurements, the error of θ determination did not exceed 5%.

For all the substrates under examination, the conditions of their wetting by the impregnation solution were valid ($\theta < 90°$). The polymer–salt gel is characterized by low f values, which is responsible for limitations related to impregnation and solution attachment to the substrate, its thickness and degree of homogeneity, and adhesion of the produced coatings. The largest value of the wetting angle was found for the PEO coating $TiO_2 + SiO_2/Ti$ formed by accumulations of particles agglomerated into large crystallites (Fig. 1a): one can see that the shape of pores in the layer is rather complex with narrowing and widening parts. At a small radius of the widening pore neck, the capillary pressure could block the liquid motion and its penetration into a pore [12]. Probably, this phenomenon is manifested in the case of the polymer–salt gel having sufficiently high values of surface tension and viscosity. Such a result is in compliance with the earlier-established formation of a heterogeneous layer of particles of copper–molybdate on a PEO coating by the PPSC method: pores remain unfilled, while large $CuMoO_4$ agglomerates of a size attaining 10–12 μm are located on the tops of the elevated sites of the coating relief [8].

The highest surface wettability is observed for a nanostructured titanium oxide layer of the composition $TiO_2/TiO_2 + SiO_2/Ti$ comprising a network of connected microcracks of a size of 2–4 μm. Under the effect of capillary forces, the liquid moves from the drop along the cracks resulting in the decrease of the wetting angle. Since the liquid flow along the microgrooves proceeds faster than over a smooth surface, one can suppose that the limiting wetting angle would decrease along with the surface roughness increase. However, according to the obtained data (Table 1), the wettability of the surface with lower R_a and S_{spec} parameters and smaller width of surface cracks (Fig. 1b) appeared to be better than that for coatings with more developed surface and the cracks widths in the range 7–14 μm (Fig. 1c). Such a result can be explained as being a result of the known effect of the increase of the liquid spreading rate upon narrowing of the lengthwise crack angle [12].

According to the Laplace equation [12], the equation below holds for wetting of the surface of an ellipse-type pore by liquid:

$$D = \frac{\left[4\sigma_{lg}\cos\theta\sqrt{1 + E^2/2}\right]}{EP},$$

where D is the ellipse minor axis, $E - D_l/D$ (D_l is the ellipse major axis), and P is the gas bubble pressure (under equilibrium conditions, $P = P_{atm}$). For all the samples under examination (Figs. 1b–1d), the range of cross-section and lengthwise crack sizes yields changes in the E value of from 2 to 20. Critical size D at which the condition of liquid penetration into an ellipse-type pore is valid calculated taking into account the above data corresponds to 1.4–1.7 μm. The obtained result demonstrates that the polymer–salt gel would fill all cracks of the layer prepared using the initial suspension of TiO_2 nanoparticles, whereas, in the case of diluted suspension, some layer cracks remain unfilled with liquid. Indeed, for the surface

Table 2. Characteristics of carbon black burning in the presence of complex oxide composites

Catalyst	TiO_2 suspension pyrolysis conditions	d_{av}, nm $CuMoO_4$	t_0, °C	t_{m1}, °C	t_{m2}, °C
$CuMoO_4/TiO_2/TiO_2 + SiO_2/Ti$	350, 550°C	226	280	362	397
$CuMoO_4/TiO_2/TiO_2 + SiO_2/Ti$	550°C	321	280	330	407
$CuMoO_4/TiO_2/TiO_2 + SiO_2/Ti$*	350, 550°C	–	280	342	403
$CuMoO_4/TiO_2/TiO_2 + SiO_2/Ti$**	350, 550°C	915	320	–	418
$CuMoO_4/TiO_2/TiO_2 + SiO_2/Ti$***	350, 550°C	–	290	–	403

* TiO_2 nanoparticle suspension triply diluted with toluene.
** TiO_2 nanoparticle suspension fivefold diluted with toluene.
*** TiO_2 nanoparticle suspension fivefold diluted with toluene + US treatment.

with narrow cracks or without them, the limiting wetting angle value increases (Table 1). A positive effect on the wettability of such coatings is provided by the sample US treatment, which must be caused by the formation of a rougher surface (Fig. 1f). Juxtaposition of the obtained data (Table 1) demonstrates that the presence of lengthwise surface pores of the TiO_2 layer and its nanosized structure have comparable effects on the wetting ability of the polymer–salt gel. High chemical stability of nanoparticles is known [15] to provide the increase of the quantity of the adsorbed molecules at the interface, which, in this case, may result in the decrease of surface tension of the impregnation solution.

Upon deposition and subsequent pyrolysis of the polymer–salt gel containing Cu and Mo compounds, a homogeneous layer of $CuMoO_4$ particles is formed on the nanostructured TiO_2 coating. Here, one observes a certain correlation between the values of the impregnation solution spreading coefficient (Table 1) and copper–molybdate phase particles' average diameter d_{av} calculated through processing of at least five SEM–images (Table 2). For instance, d_{av} decreased sequentially from 915 to 226 nm at an f value increase from –12.6 up to –6.5 (Fig. 2). One can suppose that the formation of a thinner layer of the impregnation solution on the substrate surface results in a decrease in the size of particles of the deposited catalyst.

Results of studies of the process of catalytic burning of diesel carbon black in the presence of the obtained complex oxide composites are shown in Table 2. For the samples distinguished by the presence of microcracks in the nanostructured TiO_2 layer, one observes a two-stage shape of kinetic curves (Fig. 3a) with superposition of exothermic effects, the extrema of which (t_{m1} and t_{m2}) were manifested in the temperature ranges of 330–362 and 397–407°C, respectively. The contribution of the first stage of the carbon black burning into total process heat emission determined through separation of peaks of DTA curves and calculation of their areas (Peak Separation program, NETZSCH) is directly proportional to the volume of sublayer cracks calculated from measurements of their areas and the average arithmetic deviation of the coating surface profile (Fig. 3b). This effect is probably caused by the quantity of carbon black present in the crack bulk, whereas the significant increase of the process rate may be a result of local temperature increase in their space due to the high exothermic character of the carbon oxidation reaction. This result also indicates filling of the layer cracks by the catalyst and corroborates calculations of the critical pore size at which the condition of impregnation solution penetration into them occurs. The temperatures of the start and the second stage of the catalytic process in the presence of the $CuMoO_4/TiO_2/TiO_2 + SiO_2/Ti$ composite (d_{av} = 226 nm) are comparable with results obtained earlier using the EP method [6], which is evidently caused, in both cases, by the formation of an ultradispersed structure of the catalytic layer. Moreover, one can note a sequential decrease of t_{m2} along with the increase of the $CuMoO_4$ particle size (Table 2). Thus, the obtained results enable one to suppose that the targeted modification of the structure of the titanium oxide sublayer is able to affect both the deposited catalyst particle size and characteristics of the process of carbon black burning in the presence of the formed catalytic composites.

CONCLUSIONS

Using a combination of methods of treatment of titanium samples (PEO in aqueous silicate electrolyte, deposition of a layer of TiO_2 nanoparticles, and US treatment), oxide coatings ($TiO_2 + SiO_2/Ti$, $TiO_2/TiO_2 + SiO_2/Ti$) differing in surface microrelief, roughness, and pore size and shape have been obtained. The polymer–salt gel containing Cu and Mo compounds (σ_{lg} = 64.6 mJ/m^2, viscosity of 2.35 mPa s) is characterized by low parameters of wetting of the PEO coating formed by large oxide crystals with pores of complex shape between them. A significant decrease of the limiting wetting angle is achieved through creation of an extra nanostructured TiO_2 layer (anatase

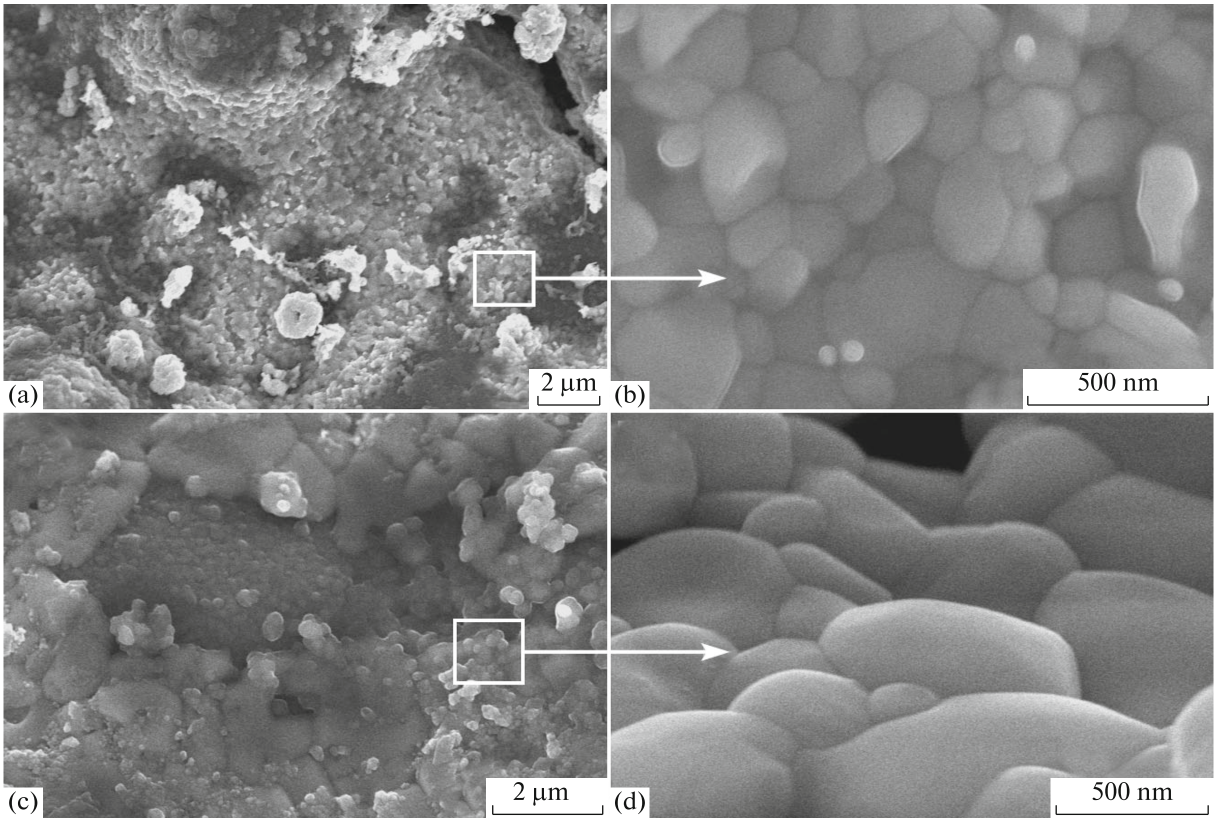

Fig. 2. SEM images (different magnifications) of the copper–molybdate coating on the TiO_2 layer (pyrolysis at 350°C): (a, b) initial suspension of anatase nanoparticles; (c, d) fivefold diluted suspension.

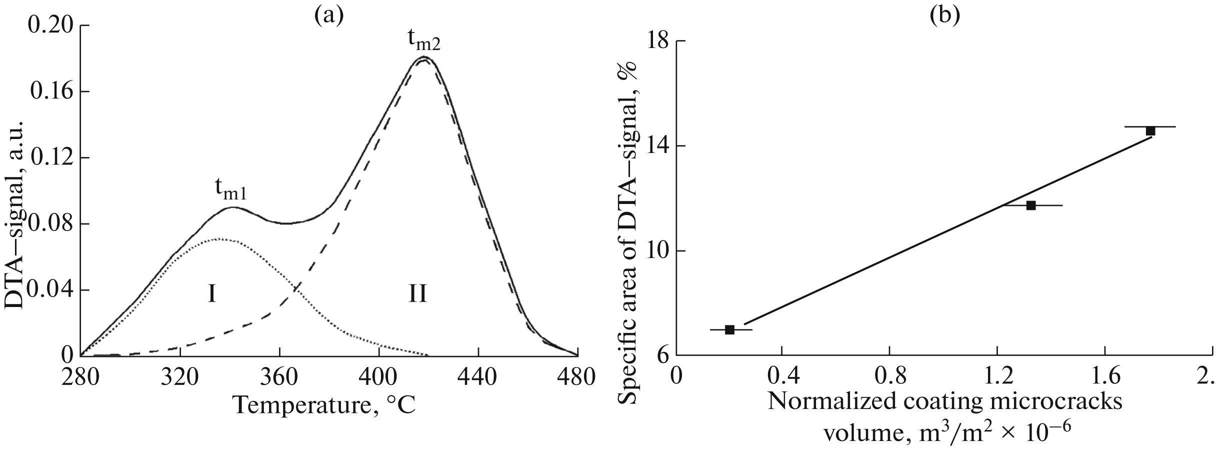

Fig. 3. (a) Example of the DTA curve of carbon black burning in the presence of $CuMoO_4$ catalyst formed on TiO_2 with microcracks (pyrolysis at 550°C); (b) dependence of the exoeffect value of the process first stage (I) on the volume of microcracks of the TiO_2 layer.

particles with a size of 30–50 nm) separated into individual smooth parts by a network of connected shrinkage microcracks, the widths of which can be changed upon variation of the layer deposition conditions, on the PEO coating. Here, cracks in the TiO_2 layer and its nanosized structure have comparable effects on the wetting ability of the polymer–salt gel. It has been demonstrated that the critical cross-section size of cracks, at which the used impregnation solution penetrates into them, corresponds to 1.4–1.7 μm, whereas their widening up to 7–14 μm decreases the solution spreading rate. A positive effect of the US treatment on the wettability of smooth parts of the TiO_2 layer caused by microrough surface formation has been registered. The revealed correlation between the gel spreading coefficient and the particle size of the copper–molybdate catalyst deposited using the PPSC method enables one to suppose that the formation of a thinner layer of the impregnation solution on the substrate surface results in the decrease of the catalyst particles size. It has been demonstrated that the $CuMoO_4/TiO_2/TiO_2 + SiO_2/Ti$ composite formed on the TiO_2 layer having the highest wettability is characterized by an ultradispersed structure of the copper–molybdate layer ($d_{av} = 226$ nm), which ensures its high activity upon oxidation of carbon black particles.

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