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Copper Metal Matrix Composite Cu-TiO_2 Electrodeposited in Aqueous Suspensions of the Nanometric Size Particles of Anatase and Rutile[*]

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The electrolytic codeposition of nanometric size TiO_2 particles with copper from an aqueous electrolyte has been investigated. Two crystalline modifications of TiO_2 – anatase and rutile were used to prepare a nanodispersed suspension. Qualitative dispersion-hardened Cu-TiO_2 composite coatings were obtained with the reproducible results only from a freshly prepared concentrated electrolyte-suspension. It has been revealed that nanodispersed materials can be obtained electrochemically with an anatase sort of titania. Rutile powder is not as suitable as anatase for this purpose.

Key words: copper composite, nanometer-dispersed aqueous suspension of TiO_2

The primary attention of researchers in obtaining the composite coatings was devoted to the inert ceramic particles of micrometer size by electrodeposition with metals and alloys. The materials, obtained from the structured micrometer-dispersed suspensions, possess high strength due to the connection-contacts of coagulation type, which are formed as a result of cohering of the particles through the layer of the liquid medium of electrolyte with a force of 10^{-8}–10^{-12} N. The coatings formed have a dispersion-hardened metallic matrix with an evenly distributed solid phase of particles. For example, nickel composite coatings containing micrometric size particles such as SiC, Al_2O_3 are widely used in the automotive industry and in the aeronautics as wear, corrosion and oxidation resistance coatings [1–8].

Relatively little information is available on the formation of metal matrix composite coatings in aqueous electrolyte-suspensions with particles of submicrometric size [9–12]. The development of composite plating with submicrometric size particles is, however, hampered by the following problems. In aqueous plating electrolytes, particles easily agglomerate due to the compression of the diffusive double layer surrounding the particles with the high ionic strength. As a consequence, the codeposition of agglomerated particles takes place and the anticipated mechanical, chemical and/or physical properties of the composite coatings are not reached. Sec-

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ondly, the codeposition of particles from aqueous electrolytes increases due to decrease in the hydrophilicity of particles by using surfactants with the hydrophobic effect [4–6]. In an attempt to overcome the problems of agglomeration of submicrometric/or nanometric size particles and their low degree of codeposition linked to the surface hydrophilic-hydrophobic balance, the other way is the electrolytic codeposition of particles from a non-aqueous, for example, aluminium electrolyte [13].

The interest in metallic coatings containing particles has also led to research in the structuring of thin films with the help of nano-sized powders. Nanophase ceramics have generated considerable scientific interest recently because of the improvements in a variety of properties that are expected to result from grain-size reduction to the nanometer scale. These materials have several technical applications like catalysts lowering the sintering temperature, increasing the sintering rate, controlling the microstructure in high performance ceramic materials, and electronic and magnetic applications, micro-electromechanical components. The desirability of small and uniform particle size for obtaining quality ceramics has been documented in general [14] and for TiO_2 specifically [15,16].

Titania powders, widely used in industrial application as pigments, opacifiers, photocatalysts, and fillers, have been obtained either directly from titanium-bearing minerals or by precipitation from solutions of titanium salts. Titania particles have also been made by reaction in aerosols. The most common procedure for the preparation of TiO_2 particles reported in literature is based on the hydrolysis of acidic solutions of Ti (IV) salts and hydrolysis reactions of titanium alkoxides have been employed to generate finely divided, high purity TiO_2 powders [17–24].

Titanium(IV) oxide (TiO_2) is nontoxic, opaque and brilliant white. It is commonly known that these properties make it suitable as a pigment in white paint. Titania exists in two tetragonal forms, a metastable phase, anatase, and a stable form, rutile and a orthorhombic form as brukite. Brukite is non stable and not used in practice. The volume free energy of the rutile phase is always lower than that of anatase. Therefore, on heat treatment, the anatase phase transforms into the stable rutile form. The transformation is a nonreversible metastable-to-stable transformation; the transition temperature reported in literature ranges from 450 to 1200°C. The majority of chemical methods of preparation yield the metastable anatase phase, which on further heat treatment gives the rutile phase. Rutile phase, for example, in pigments has a smaller photochemical activity than that of anatase form, and, consequently, higher atmospheric stability [22,25].

Attempts to obtain the composite coatings on the basis of copper with the particles of titania were undertaken [4,26]. The absence of experience in this field and look on the problem as on conventional electrodeposition process did not lead researchers to the desirable results.

The goal of this work was to investigate the aqueous suspension preparation with nanometric size TiO$_2$ powder, or more precisely, with its crystalline modifications as anatase and rutile in a nanopowder form in order to obtain new materials by electrodeposition with copper.

EXPERIMENTAL

Materials: The coatings studied were electrodeposited on the copper substrate (1 cm^2) for morphology, elemental composition by XPS, crystalline state investigations and for microhardness measurements, on titanium (for morphology studies) in an acidic 0.5 M copper electrolyte and in electrolyte-suspensions with TiO$_2$ particles (with its crystalline modifications form as rutile or anatase) at a cathodic current density (i_c) of 2 A/dm^2 and at 18 ± 1 °C. A magnetic stirrer was used to agitate electrolyte-suspension. Electrolytic copper was used as an anode.

The preparation of suspension: To prepare the suspension the average size of TiO$_2$ particles was (nm): in the case of anatase – 100÷ 1000 and rutile –100÷2000. The concentration of TiO$_2$ particles in electrolyte-suspensions was 100 and 200 $g\cdot dm^{-3}$. 100 ml volume electrolyte-suspensions were freshly prepared to obtain stable hydrosols of TiO$_2$. The hydrosols of TiO$_2$ were stabilized in aqueous suspension with the same constant 0.5 M concentration of ions of H^+; SO_4^{2-}; Cu^{2+}/Cu^+ at pH = 0.8 for two types and concentrations of suspensions. Analytical grade chemicals and bidistilled water were used to prepare solutions.

X-ray microprobe spectral analysis of titanium: The titanium (Ti) distribution in copper coatings was studied using a JXA-50A electron scanning microscope (Japan) by X-ray microprobe spectral analysis. The X-ray attack was applied to the whole surface using 25 to 100 discharges in different surface places of the materials under investigation. The duration of electron beam attack was 10–20 sec. The average X-ray intensity values on electron emission of Ti were obtained after computer data treatment. The amount of TiO$_2$ was calculated multiplying the quantity of the distributed Ti in copper composite coating on the ratio between the atomic mass of TiO$_2$ and Ti – 79.88 and 47.88, respectively.

X-ray photoelectron spectroscopy (XPS) analysis: The elemental composition of Cu-TiO$_2$ coatings deposited from freshly prepared electrolyte-suspension was investigated by XPS. The spectra were recorded with an ESCALAB MK-11 spectrometer (VG Scientific, UK) using characteristic MgK$_\alpha$ radiation (the energy of 1253.6 eV, pass energy of 20 eV). The spectrometer had a base pressure of 5×10^{-5} Torr in a spectrometer chamber where Ar$^+$ ion bombardment was performed. The argon gas pressure in preparation chamber was maintained at 6×10^{-5} Torr and the ion gun was operated at 2 kV and 20 mA at normal incidence. Under these conditions the titanium phase can be etched at a rate of 2–3 $nm\cdot min^{-1}$. The XPS spectrum lines were recorded at the surface and at the various depths of coating. When investigating the reference samples by XPS, the spectra of the following elements were recorded: Cu 2p$_{3/2}$; Ti 2p$_{3/2}$; O$_{1s}$; C$_{1s}$. The empirical sensitivity factors of the elements were taken. The measured binding energies (E_b) of elements were calibrated with respect to the C 1s electron peak at 284.6 eV due to residual pump-oil on the sample surface [27,28]. The maximum accuracy of the method was 0.1 at.%.

X-ray diffraction method: The crystalline state of TiO$_2$ particles both in copper coatings and in the powder form used were identified by the X-ray diffraction method using an X-ray diffractometer D8 (Bruker AXS) and applying CuK$_\alpha$ radiation at λ_{Cu} = 1.5418 Å. X-ray diffraction peaks of Cu and TiO$_2$ were recorded with a constant rate of $0.5°\cdot min^{-1}$ of detector [29].

The morphology study: The morphology of matrix surface of Cu-TiO$_2$ coatings was investigated by using a transmission electron microscope PEM-100 (Ukraine) and shadowed with Pd used carbon replics. A replicating C-Pd film (with adhered particles) was torn off from the surface with gelatin which was dissolved after that in hot water. The morphology of Cu and Cu-TiO$_2$ and that of particles incorporated in the copper matrix was studied and micrographed with a JXA-50A field-emission (SEI) type scanning electron microscope at an acceleration voltage of 25 kV and an electron current (ec) of $5\cdot10^{-12}$ A.

The measurement of microhardness: Vickers microhardness (HV_{50} in kgf · mm^{-2}) was measured using an indenter PMT-3 on a 50 μm thick surface by a 50 g indentation of load and was calculated by the formula:

$$HV_{50} = \frac{1857.4 \cdot P}{d^2} \tag{1}$$

where P is the load, g, and d is a diagonal of diamond prism, mm. The microhardness was measured under normal conditions for coatings from freshly prepared electrolyte-suspensions and after their ageing for 45 days.

RESULTS AND DISCUSSION

Both in the anatase and rutile case the amount of TiO_2 particles in Cu-TiO_2 coatings codeposited with copper in acidic copper electrolyte-suspension depends on the concentration of particles in electrolyte-suspension and on the suspension preparation time (Table 1). Qualitative dispersion-hardened Cu-TiO_2 composite coatings are obtained with the reproducible results only from freshly prepared concentrated electrolyte-suspensions (Table 2). One can see from the data on the microhardness of composite coatings obtained by prolonged electrolysis of electrolyte-suspension and presented in Table 2 that the hardening effect on copper matrix decreased in this case. A longer exposure time and ageing of electrolyte-suspension also had a negative effect on the microhardness of coatings (Table 2, column 5). The HV value of Cu-anatase coating decreased from 244 ± 25 to 179 ± 19 kgf · mm^{-2} at a concentration of TiO_2 equal to 100 and 200 g · dm^{-3}, respectively.

Table 1. The amount of titanium (Ti) in Cu-TiO_2 composite coating *versus* on concentration (c) of nanometric TiO2 particles-hydrosols in electrolyte-suspension. The thickness of coating in Tabs. 1, 2 – 50 μm.

Coatings from freshly prepared suspension	Concentration of suspension/g · dm^{-3}	Amount of Ti in coating/mass%	Calculated amount of TiO_2/mass%
1. Cu-TiO_2 (Anatase)	100	3.935	*6.53*
2. Cu-TiO_2 (Anatase)	200	6.275	*10.46*
3. Cu-TiO_2 (Rutile)	100	3.804	*6.338*
4. Cu-TiO_2 (Rutile)*	100	3.0	*4.99*
5. Cu-TiO_2 (Rutile)	200	6.174	*10.298*

**from 64 days-aged suspension.*

On the coating surface anatase particles have major advantages in adhesion to the electrode surface – this clearly was seen on the optical image of surface after the samples were carefully washed and centrifuged. It is worthy to note that the carbon replic method enables to observe stronger adhesion of anatase (Fig. 1 a, b). The study of elemental composition of coatings at depth has shown greater quantities (at. %) of titanium and oxygen in the anatase case as well (Table 3). Stronger adhesion in this case predominated and the amount of anatase particles on the surface was greater than that of rutile and due to this more incorporated into the Cu-TiO$_2$ coating (Table 3). The behaviour of rutile when electrodeposited with copper may be explained by weak adhesion of lesser quantity of particles in suspension – 100 g·dm^{-3}. The increase in concentration of rutile particles up to 200 g·dm^{-3} in suspension the dispersion hardenning effect of Cu-TiO$_2$ coatings is possible (Table 2). Strong adhesion with growing metal layer is essential for the incorporation of particles into the matrix.

Table 2. Microhardness (HV$_{50}$) ± its dispersion of Cu-TiO$_2$ coatings at 20 ± 1°C *versus* on concentration of TiO$_2$ in electrolyte-suspension (c) and on electrical charge quantity passed through the used suspensions (Q).

Coatings	c/g·dm^{-3}	HV$_{50}$/kgf·mm^{-2} ($Q_{1,2}$ = 206 C)	HV$_{50}$/kgf·mm^{-2} (Q_3 = 340 C)	HV$_{50}$/kgf·mm^{-2} (After 45 days + Q_4 = 880 C)
1	*2*	*3*	*4*	*5*
1. Cu	0	168±14	169±17	–
2. Cu-TiO$_2$ (Anatase)	100	244±25	229±33	179±19
3. Cu-TiO$_2$ (Anatase)	200	262±19	266±26	187±17
4. Cu-TiO$_2$ (Rutile)	100	190±25	190±12	219±12
5. Cu-TiO$_2$ (Rutile)	200	254±18	208±14	190±16

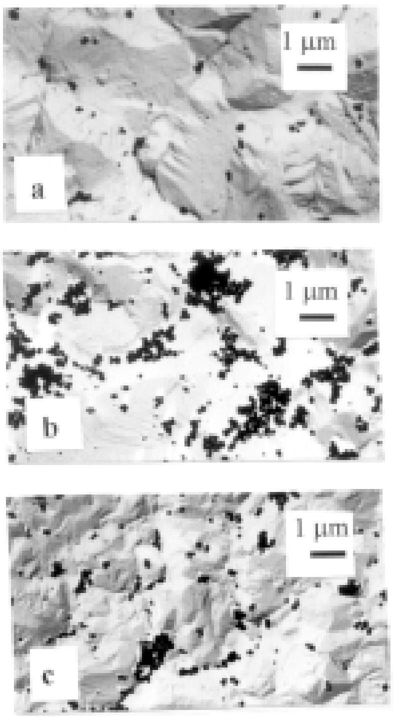


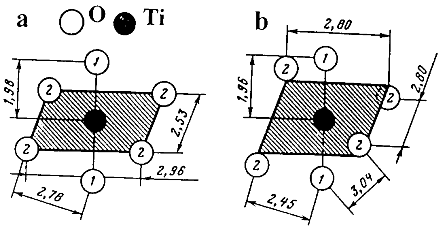
Figure 1. Morphology of Cu-TiO$_2$ coating surface with rutile (a) and anatase (b, c) particles codeposited in a freshly prepared (a, b) and 64 days-aged suspension (c). The concentration of suspension – 100 g·dm^{-3}. The thickness of coatings – 50 µm.

Table 3. Elemental composition (in at.%) of composite Cu-TiO_2 coatings on the surface and in the depth of matrix analysed by XPS method. Thickness of coating in Tables 3, 4 – 25 μm.

Etching depth/nm	Elements	TiO_2 amount $g \cdot dm^{-3}$ in suspension/			
		Anatase		Rutile	
		100	200	100	200
0 (on the surface)	Cu	10.71	14.63	16.89	16.09
	O	85.61	79.68	78.39	79.82
	Ti	3.68	5.69	4.72	4.1
	Ti:O	**1:23.28**	**1:14.01**	**1:16.6**	**1:16.4**
1.5	Cu	75.72	65.25	81.99996	75.82
	O	19.62	27.42	14.43	19.32
	Ti	4.66	7.33	3.61	4.86
	Ti:O	**1:4.20**	**1:3.74**	**1:3.99**	**1:3.97**
6.0	Cu	82.39	73.15	86.08	78.82
	O	14.86	22.43	11.26	16.82
	Ti	2.76	4.42	2.66	4.35
	Ti:O	**1:5.38**	**1:5.07**	***1:4.23***	**1:3.87**
66	*Cu*	*84.00*	*70.37*	*86.53*	*77.59*
	O	*14.03*	*27.66*	*11.45*	*20.31*
	Ti	*1.97*	*1.97*	*2.02*	*2.10*
	Ti:O	***1:7.12***	***1:14.07***	***1:5.68***	***1:9.67***
126	Cu	81.52	66.16	85.04	75.45
	O	15.32	28.24	11.85	20.30
	Ti	3.16	5.60	3.11	4.25
	Ti:O	**1:4.84**	**1:5.04**	**1:3.8**	**1:4.78**

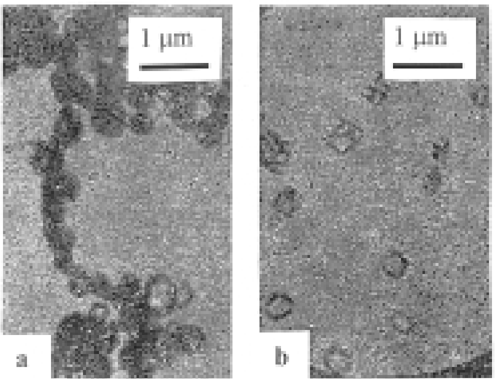
It should be emphasized that the oxide TiO_2 due to its special features and extraordinary casual state in solutions has been an object of studies for decades [30–33]. According to [30–32], the chemical-physical transformations in aqueous suspension with the futher colloidal stage affected the suspension state of superhydrophilic TiO_2 powder of anatase and rutile.

The structurization of suspension with the superhydrophilic TiO_2 particles due to chemical transformations, the first of them, hydrolysis of hydrated oxides $TiO_2 \cdot nH_2O$ to complex ions $[Ti(OH)_6]^{2-}$ in an aqueous solutions occurs. In addition, fourvalent transition-metal titanium due its oxophilic properties exibited in its strong binding to hydroxide to form simple octahedral complex. In accordance with [30–33], the subsequent polymerization of the existing aquacomplex as $[Ti(OH)_2(OH)_4]^{2+}$ takes place. The experimental data in Table 3 testify that the stechiometric elemental proportion of titanium to oxygen is greater than that in the formula of TiO_2. In Scheme 1 the coordination number (6) of titanium atom is related to the octahedral structure with oxygen atoms (or hydroxyl ions in aqua solutions) both in the anatase and rutile case.



Scheme 1. Interatomic spacings in crystalline structure of anatase (a) and of rutile (b).

According to [17,30], during a complicated multi-step structurization process in suspension the further colloidal stage that is formation of micelles and granules after the equilibrium processes of coagulation and peptization of the hydrosols of TiO_2 in strongly acidic solutions occurs. The formed in freshly prepared suspension hydrosols of TiO2 are stabilized with the ions of H^+; OH^-; SO_4^{2-} ; Cu^{2+}/Cu^+ present in solutions at pH = 0.8. Amorphous hydrosols are formed from a freshly prepared aqueous suspension of TiO_2. Nanocrystalline (≥ 100 nm) TiO_2 are formed after 1–2 h of suspension preparation with titania (Scheme 2) [30].



Scheme 2. SEM of TiO_2 hydrosols: a – amorphous particles formed from freshly prepared suspension; b – nanometric sized crystalline (≥ 100nm) particles of TiO_2 formed after 1–2 h of suspension preparation.

One can see in the SEM pictures of the surface morphology of Cu-TiO_2 coatings codeposited from an aged suspension (Figs. 2–4), that the shape of incorporated particles is perfect when compared to that from a freshly prepared suspension – most of observable codeposited into matrix particles had an amorphous shape (Scheme 2 and Figs. 2, 3). The formation of structurized suspension in co-deposition of sub/or nanocomposites is based on the crystalline or amorphous TiO_2 hydrosols formation in a freshly prepared suspension. In aged suspension their peptization occurred and particles were round and identical (Fig. 4). In this case the optimal structurization of suspension in order to obtain heterogenic dispersion-hardened coatings did not occur. The aged during peptization TiO_2 particles were incorporated into the matrix, probably, in a mechanical way and had not any hardening effect on it (Table 2, column 5).

On the other hand, it is known, that non-metallic inclusions in the metal can change its thin structure and break up the crystal lattice, resulting in changes in the physical and mechanical properties of the electrodeposits. The inclusions of inert particles affect fine structure parameters: the concentration of packing defects of both deformation and twinning types can increase, as well as the dislocations density and their movement [7,8,29,34].

The crystalline structure can be evaluated on the basis of the XRD peak broadening β, which is calculated from the formula:

$$\beta = B_{FWHM}^{Sp} - B_{FWHM}^{St} \qquad (2)$$

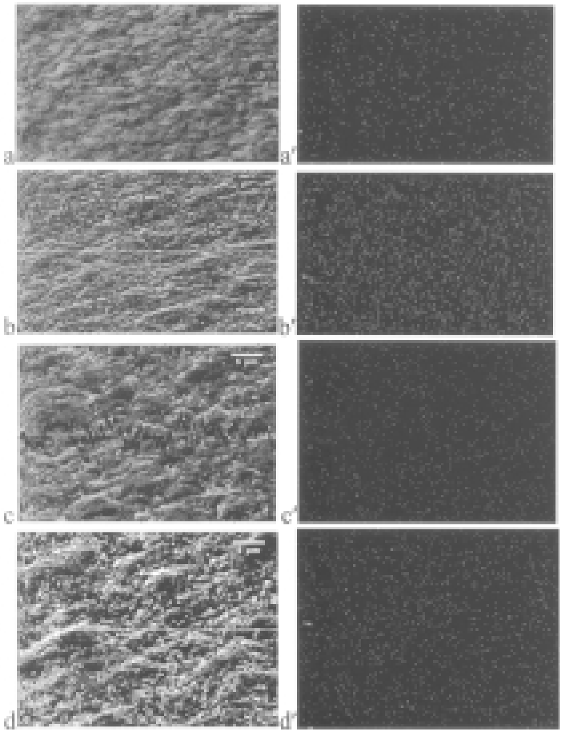


Figure 2. Secondary electron image of Cu-TiO_2 composite at a depth of coating of 5 μm as a function of concentration of nanometric size particles of anatase (a, b) and rutile (c, d). The distribution of Ti in Cu-TiO_2 coating: a′, b′ – with anatase and c′, d′ – with rutile. The concentration of TiO_2 particles in suspension ($g \cdot dm^{-3}$): (a, a′, c, c′) – 100 and (b, b′, d, d′) – 200.

Superscript *Sp* means the XRD peak's full width at the half maximum for specimen and superscript *St* that for the standard. The parameters of crystalline structure are crystallite size (*D)* and crystallite microdeformation (ε). The crystallite size (*D)* can be calculated from the Scherrer formula [29]:

$$D = \frac{0.9\lambda}{\beta\cos\Theta} \tag{3}$$

where λ is a wavelength of X-ray radiation used. Crystallite microdeformation level can be evaluated from the formula:

$$\varepsilon = \frac{\beta}{4tg\Theta} \tag{4}$$

The dependence of tg, $csec$ and β of Cu-TiO_2 coatings on the X-ray diffraction angle θ shows that β is closer to tg dependence and this indicates that broadening of diffraction peak is determined by microdeformation but not by crystallites (blocks) size (Fig. 5). The studies of crystalline structure of copper coatings have shown that the penetration of TiO_2 particles into the matrix has insignificant influence on the fine

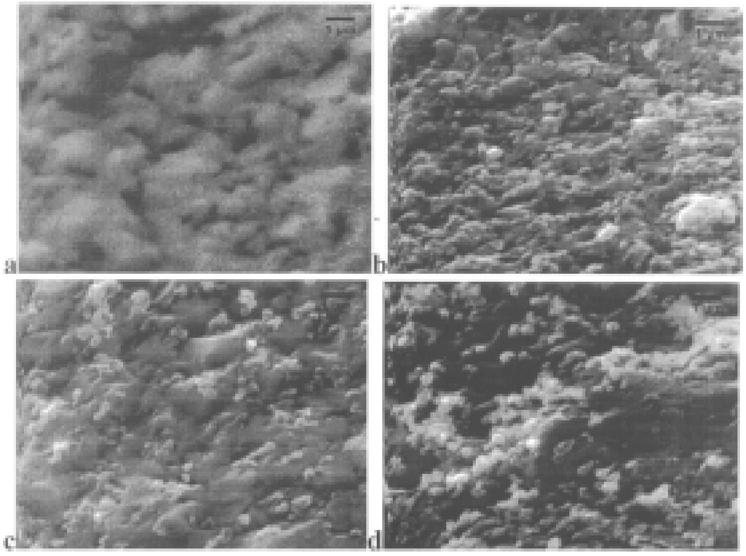


Figure 3. The morphology of Cu-TiO$_2$ coatings and particles themselves of anatase (a, b) and rutile (c, d). The concentration of particles in electrolyte-suspension (g·dm^{-3}): a, c – 100, b, d – 200.

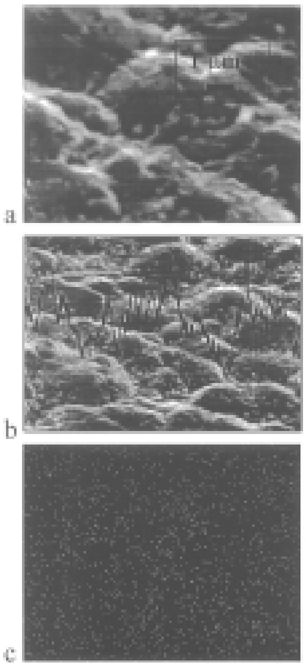


Figure 4. The morphology image of Cu-rutile coating and TiO$_2$ particles themselves from ageing suspension with concentration of nanometric size particles of rutile – 100 g·dm^{-3} (a). Secondary electron image of Cu-rutile composite at a depth of coating of 5 μm (b). The distribution of Ti in Cu-rutile coating (c).

crystalline structure of copper (Fig. 6; Compare B_{FWHM} values for copper standard with that for copper in composite coatings in Table 4).

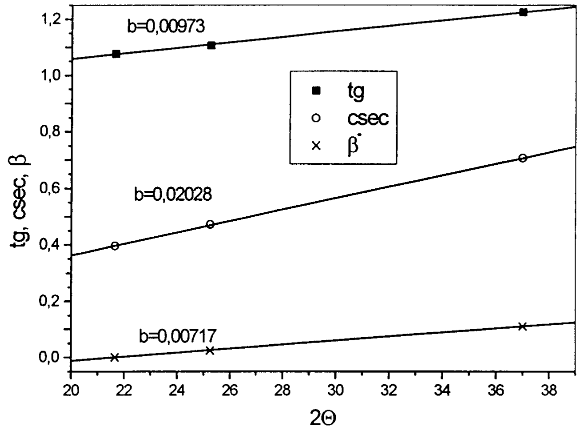


Figure 5. Dependence of tg, csec and β *versus* X-ray diffraction angle of obtained from aged suspension Cu-anatase coating (analogous to Nr 2 position in Table 4).

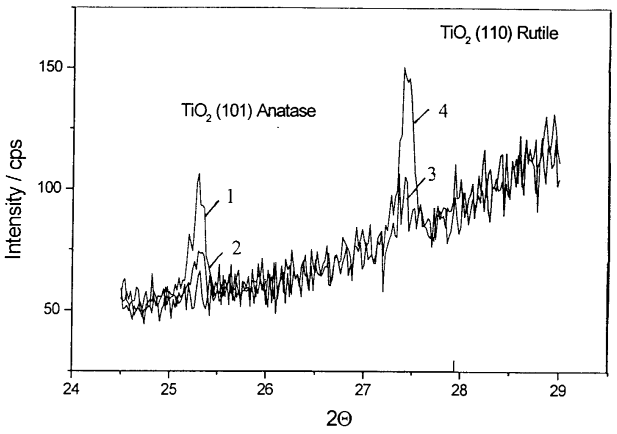


Figure 6. Diffractogram of Cu-TiO_2 coating with incorporated crystalline nanometric size particles of anatase and rutile. The coatings obtained from freshly prepared (curves 1, 3) and from aged suspensions (curves 2, 4). The thickness of coating in Figs. 5–7 – 25 μm.

An X-ray phase analysis of dry powders shows that the rutile powder used has ~ 2.0% of anatase phase (Fig. 7). Anatase powder has the same amount of unidentified crystalline phase. According to the Scherrer's formula the average size of TiO_2 crystallites in Cu-TiO_2 coatings may be as large as ≥ 250 nm.

At the same time it seems that the anatase suspension has higher stability. As can be seen from the appearance of the TiO_2 peaks on the XRD patterns and from the data in Table 4, columns 4 and 6, the crystalline state of anatase particles incorporated into matrix does not depend on suspension preparation time and on electrical charge quantity passed through the used suspensions (Q = 67.2 C) (Fig. 6, curves 1 and 2). Only after longer electrolysis (Q = 134 C) rutile particles has been detected in coating. The suspension with rutile powder structurized more complicated than that with anatase.

Table 4. Dependence of parameters of X-ray diffraction peaks on XRD patterns of Cu-TiO_2 coatings on suspension preparation time. Column 1: numbers 1, 3a–3c – coatings electrodeposited in freshly prepared suspension; 2,4 – in ageing suspension.

Sample	XRD peak	d/nm	B_{FWHM}/deg	I_{max}/cps	$I_{int}/(I/I_{max})\times 100$
1	2	3	4	5	6
1. *Cu-*TiO_2	Cu (111)	0.20877	0.190	12252	2327.8/100
	Cu (200)	0.18080	0.232	2875	669.9/28.8
	Cu (220)	0.12783	0.237	3610	973.6/41.8
	Anatase (101)	0.3518	0.153	47.4	7.56
2. *Cu-*TiO_2	Cu (111)	0.20878	0.188	39173	7235.0/100
	Cu (200)	0.18079	0.240	2345	590.6/8.2
	Cu (220)	0.12782	0.341	1732	552.2/7.6
	Anatase (101)	0.3514	0.143	18.6	2.66
3 a. *Cu-*TiO_2	Cu (111)	0.20877	0.193	15248	2951.8/100
	Cu (200)	0.18080	0.239	3042	757.7/25.7
	Cu (220)	0.12783	0.240	2944	826.0/28.0
	Rutile (110)	–	–	–	–
3 b. *Cu-*TiO_2	Cu (111)	0.20876	0.192	7531	1453.6
	Cu (200)	0.18080	0.232	2980	695.2
	Cu (220)	0.12784	0.232	4144	1054.0
	Rutile (110)	–	–	–	–
3 c. *Cu-*TiO_2	Cu (111)	0.20876	0.190	9078	1732.4/100
	Cu (200)	0.18079	0.235	3148	747.3/43.2
	Cu (220)	0.12783	0.240	2986	810.3/46.8
	Rutile (110)	–	–	–	–
4. *Cu-*TiO_2	Cu (111)	0.20876	0.191	21003	4050.6/100
	Cu (200)	0.18075	0.247	2506	662.3/16.4
	Cu (220)	0.12782	0.345	1807	594.4/14.7
	Rutile (110)	0.32484	0.153	68.5	12.1
5. *Cu standard*	Cu (111)	0.20881	0.191	8219	1526.9/100
	Cu (200)	0.18085	0.216	4069	839.9/55.0
	Cu (220)	0.12784	0.221	2353	488.4/32.0

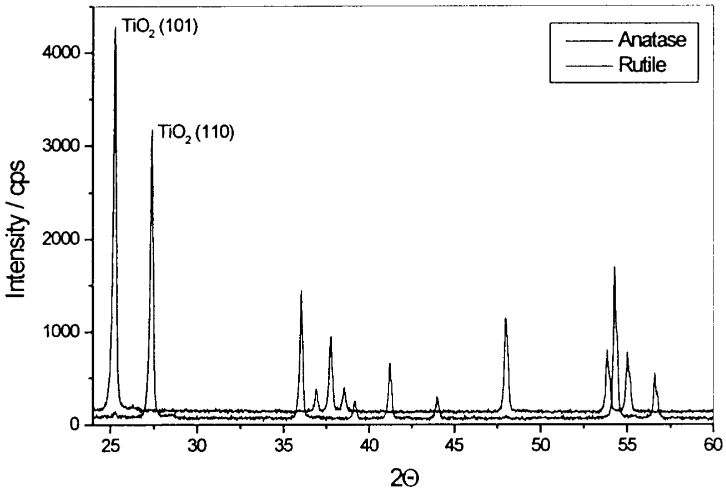


Figure 7. Diffractograms of dry powder of anatase and rutile used to obtain copper composite coatings.

Thus, submicro/ or nanodispersed materials can be obtained electrochemically with an anatase phase of titania (Tables 1–4). Rutile is not as suitable as anatase under the same conditions.

CONCLUSIONS

Qualitative dispersion-hardened Cu-TiO_2 composite coatings can be obtained with the reproducible results only in a freshly prepared concentrated electrolyte-suspension. Submicro/ or nanodispersed materials can be obtained electrochemically with an anatase sort of titania. Rutile powder is not as suitable for this purpose as anatase. The average size of TiO_2 phase in Cu-TiO_2 coating may be as great as ≥ 250 nm.

The main condition of formation of the nanodispersed system is the structurization of freshly prepared concentrated suspension with the superhydrophilic particles of TiO_2 due to formation of equilibrium hydrosols of TiO_2. Avoiding their ageing and prolonged electrolysis is the guarantee of obtaining the composite coatings in aqueous suspension by the electro-codeposition of TiO_2 particles with copper.

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