

Properties of Ni–TiO₂ composites electrodeposited from methanesulfonate electrolyte

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The effect of conditions of preliminary preparation of methanesulfonate suspension electrolyte used in electrodeposition of Ni–TiO₂ composites, on the aggregate stability of the dispersed phase is studied. It has been found that increase in the electrolyte exposition time prior to the dispersion analysis allows obtaining the equilibrium sizes of TiO₂ particles, whose radius is close to 1 μm. It is shown that composition of the composites varies with the coating thickness and reaches the constant value at thicknesses above 6 μm. The titanium dioxide content of the composite coatings increases with increasing the concentration of TiO₂ in the suspension and decreasing the current density. Introduction of the dispersed phase into nickel matrix enhances the internal stresses and microhardness of the deposits, which is related with structural changes in the nickel matrix. X-ray studies shows that crystallite size of the composite is slightly less than that of pure nickel. A small refinement of the composite matrix grains and presence of the dispersed phase of TiO₂ on their surface are recorded while. It has been revealed that photocatalytic activity of the coatings correlates with the titanium dioxide content of the deposits.

Keywords: methanesulfonate electrolyte, Ni–TiO₂ composite, electrodeposition, photocatalytic activity, dispersed phase.

Проаналізовано вплив умов підготовки суспензійного метансульфонатного електроліта для електроосадження композитів Ni–TiO₂ на агрегативну стійкість дисперсної фази. Установлено, що збільшення часу витримки електроліта перед проведенням дисперсійного аналізу сприяє досягненню рівноважних розмірів частинок TiO₂, радіус яких близький до 1 мкм. Показано, що склад композитів змінюється за товщиною покриття і досягає постійних значень при товщинах, перевищуючих 6 мкм. Вміст діоксида титану в композиційних покриттях зростає з підвищенням концентрації TiO₂ в суспензії і при зниженні щільності струму. Введення дисперсної фази в нікелеву матрицю приводить до збільшення внутрішніх напружень і мікротвердості осаду, що пов'язано з структурними змінами нікелевої матриці. Рентгеноструктурні дослідження показали, що розмір кристалітів композита невеличкий порівняно з чистим нікелем. Обнаружено незначне дрібнення зерен матриці композита і наявність на їх поверхні дисперсної фази TiO₂. Установлено, що фотокаталітична активність покриттів корелює з вмістом діоксида титану в осадах.

Електроосадження композитів Ni–TiO₂ із метилсульфонатного електроліту.
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Проаналізовано вплив умов попередньої підготовки суспензійного метилсульфонатного електроліту для електроосадження композитів Ni–TiO₂ на агрегативну стійкість дисперсної фази. Установлено, що збільшення часу витримки електроліту перед проведенням дисперсійного аналізу сприяє досягненню рівноважних розмірів частинок TiO₂, радіус яких близький до 1 мкм. Показано, що склад композитів змінюється за товщиною покриття і

досягає постійних значень при товщині, яка перевищує 6 мкм. Вміст диоксиду титану у композиційних покриттях зростає з підвищенням концентрації TiO₂ у суспензії та зниженні густини струму електроосадження. Інкorporація дисперсної фази у нікелеву матрицю призводить до збільшення внутрішніх напружень і мікротвердості осадів, що пов'язано зі структурними змінами нікелевої матриці. Рентгеноструктурні дослідження показали, що розмір кристалітів композиту дещо менший, ніж чистого нікелю. Встановлено невелике подібнення зерен матриці композиту і наявність на їх поверхні дисперсної фази TiO₂. Встановлено, що фотокаталітична активність покриттів корелює з вмістом диоксиду титану в осадах.

1. Introduction

Electrodeposited composite Ni-TiO₂ coatings are of practical interest due to their useful operational properties, such as enhanced hardness, corrosion resistance, and photocatalytic activity. Incorporation of TiO₂ nanoparticles into nickel matrix increases microhardness of the composites [1], which is accompanied by changes in the deposit texture. Effect of concentration of titanium dioxide nanoparticles and electrolysis conditions on the composition of Ni-TiO₂ composites, their structural changes and preferential orientation were also investigated in [2] in deposition of coatings from the Watts electrolyte. In [3], Ni-TiO₂ nanocomposites were obtained from the Watts electrolyte by depositing of nickel on TiO₂ nanotubes. Similar electrolyte was used in [4] for deposition of Ni-TiO₂ coatings to provide high corrosion and abrasion resistance to NdFeB magnet. Ni-TiO₂ composites exhibit photocatalytic properties, which are due to the electronic structure of titanium dioxide. The latter exhibits semiconducting properties and absorbs electromagnetic radiation in UV region, which leads to formation of electron-hole pairs. Thus, separate reduction and oxidation centers are formed. On the surface of titanium dioxide particles, the electron and the hole are spatially separated. In the aerated aqueous medium, reduction of oxygen and oxidation of water occur to form hydroxide and oxygen radicals [5] having the high reactivity. This may be used for decomposition of chemical contaminants [6, 7] and water disinfection [8].

In selection of the coating deposition conditions, the composition of the electrolyte used is played an important role. In this regard, new electrolytes based on methanesulfonic acid should be brought to a focus; their application give encouraging results in deposition of the composite nickel-based coatings [9, 10]. Therefore, it is relevant to study the process of electrodeposition of Ni-TiO₂ composites from the methanesulfonate-based electrolyte and the properties of the coatings obtained.

2. Experimental

Composite coatings were obtained from methanesulfonate electrolyte (Table). Nickel methanesulfonate was obtained from nickel carbonate and methane sulfonic acid. As dispersed phase, the titanium dioxide nanopowder P 25 was used, which is a mixture of anatase and rutile (80:20), with an average particle diameter of 30 nm [11]. Electrodeposition was carried out at $T = 333$ K; a magnetic stirrer was used for the electrolyte agitation. A copper plate with surface area of 6 cm² was used as a cathode. Anodes were nickel NPAN. The deposition current densities in the galvanostatic mode were: 2, 3, 5, and 7 A/dm².

Prior to the experiments, the suspension electrolyte was prepared by stirring for 30 min.

Dispersion analysis of the suspension solutions was carried out by gravity sedimentation. The rate of the dispersed phase particle sedimentation was measured and used to calculate the particle sizes.

Sedimentation curve was produced using a device based on digital analytical balance Vibra HT (Shinko denshi, Japan). The balance was used to measure the time variations of masses of TiO₂ particles deposited onto a horizontal glass disc. The disc was placed in a glass cylinder filled with a suspension electrolyte and suspended by balance on a rod coaxial with the cylinder. The experimental data were processed by the analytical method suggested by N.N.Tsyurupa [12] for calculating and plotting the particle size distribution curves $F = f(r)$.

The titanium dioxide content in the composite Ni-TiO₂ coating was calculated from the difference in mass between the composite and its nickel content. The nickel mass was calculated from the analytical concentration of nickel (II) ions in the mixture of sulfuric and nitric acids after dissolution of the composite coating in it. The analysis was performed by direct complexometric titration using Trilon B and Murexide. The mass of nickel was determined by the formula:

Table. The composition of the deposition electrolyte

Bath component	Content
Ni(CH ₃ SO ₃)	21.0 mol/dm ³
H ₃ BO	30.7 mol/dm ³
NaCl	0.3 mol/dm ³
TiO ₂	2 g/dm ³ , 4 g/dm ³ , 7 g/dm ³ , 10 g/dm ³
pH	3

$$m_{\text{Ni}} = \frac{C \cdot V \cdot M}{2 \cdot 1000} \cdot \frac{V_1}{V_2}, \quad (1)$$

where m_{Ni} is the mass of nickel in the composite coating; C is the Trilon B concentration; V is the volume of Trilon B solution spent in titration (ml); M is the molar mass of nickel (g/mol); V_1 is the volume of sulfuric acid solution (ml); V_2 is the volume of aliquot (ml).

The volume of TiO₂ incorporated into the coating was evaluated by the formula:

$$V_{\text{TiO}_2} = \frac{(m - m_{\text{Ni}})}{\rho_{\text{TiO}_2}}, \quad (2)$$

where m is the mass of the composite coating; $\rho_{\text{TiO}_2} = 4.5 \text{ g/cm}^3$ [13] is the density of titanium dioxide.

The volume of nickel in the composite coating:

$$V_{\text{Ni}} = \frac{m_{\text{Ni}}}{\rho_{\text{Ni}}}, \quad (3)$$

where $\rho_{\text{Ni}} = 8.9 \text{ g/cm}^3$ [13] is nickel density.

The volume fraction of titanium dioxide in the coating:

$$Y = \frac{V_{\text{TiO}_2}}{V_{\text{TiO}_2} + V_{\text{Ni}}}. \quad (4)$$

Surface morphology of Ni-TiO₂ coatings was examined using scanning electron microscope REM-106I.

Structure of the electrodeposited coatings was studied by X-ray diffraction using DRON-3 diffractometer in monochromatized CoK α -radiation. The crystallite sizes were calculated by the Scherrer formula:

$$L = \frac{k \cdot \lambda}{(\beta \cdot \cos \theta)}, \quad (5)$$

where λ is the wavelength of X-ray radiation; β is the broadening of the sample line due to

refined crystallite dimensions; k is a constant close to unity; θ is the diffraction angle.

The Vickers microhardness was measured with PMT-3 device at a load $P = 100 \text{ g}$. The microhardness was determined by the formula:

$$H = \frac{1854 \cdot P}{l^2}, \quad (6)$$

where l is the diagonal length of the diamond pyramid impression, mm.

Internal stresses of the composite coatings were assessed by flexible cathode method. The upper end of a copper plate isolated on one side was fixed, while the lower end was free. During electrolysis, the cathode was bent under effect of the internal stresses arising in the deposit. The internal stresses σ (MPa) were calculated by the equation [14]:

$$\sigma = \frac{zE_c d_c (d_c + d_d)}{3l^2 d_d}, \quad (7)$$

where E_c is the modulus of elasticity of the cathode plate (MPa); d_c is the cathode thickness (m); d_d is the deposit thickness (m); l is the length of the cathode working part (m); z is the cathode end deviation from the initial position (m).

2.5 Photocatalytic studies

Photocatalytic activity of Ni-TiO₂ coatings was evaluated by photodegradation of methyl orange dye in aqueous solution subject to UV radiation. The composite coatings of 3 cm² area were placed in 20 ml of methyl orange solution and irradiated with an EXO TERRA Repti Glo10 lamp. The range of the lamp radiation was 280 to 315 nm. The initial concentration of methyl orange was 6 $\mu\text{mol/dm}^3$, pH7. The change in the concentration of the dye was assessed by photocolometric method using KFK-2-UHL 4.2 and a color filter corresponding to wavelength of 490 nm.

The efficiency of the photocatalyst action was evaluated by degree of the methyl orange degradation X , calculated by the equation:

$$X = \frac{C_0 - C}{C_0}, \quad (8)$$

where C_0 is the initial concentration of methyl orange; C is the concentration of methyl orange at time θ of the experiment.

3. Results and discussion

In electrodeposition of the composite coatings from suspension electrolytes, one of

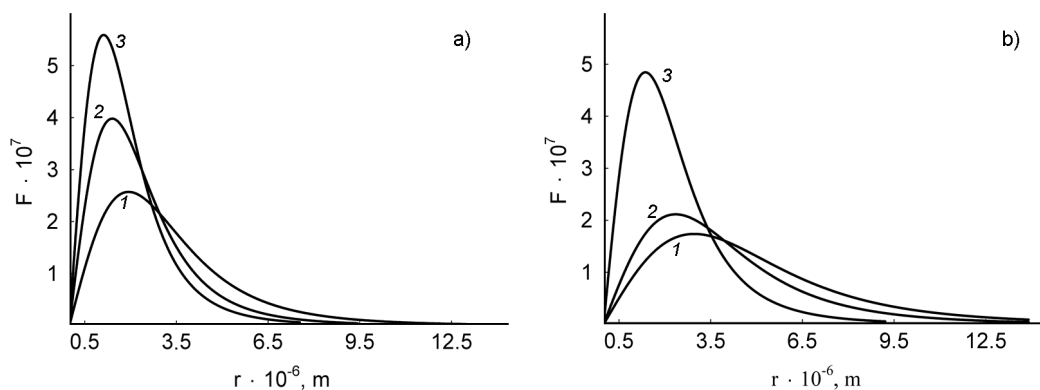


Fig. 1. Differential curves for the size distribution of TiO₂ particles in a freshly prepared solution (1), after 1 day (2), after 7 days (3). Content of TiO₂ in electrolyte, g/dm³: a — 2; b — 10. Temperature is 298 K, pH — 3.

the factors that affect the dispersed phase content of metal matrix is the concentration and size of the particles to be incorporated. Fig. 1 shows that differential dependences of the particle size distribution, which were obtained immediately after introduction of the titanium dioxide powder into the methanesulfonate nickel electrolyte and further stirring it for 30 min, are curves with a rather vague maximum. This indicates that freshly prepared suspension electrolyte contains approximately the same amounts of different fractions of the dispersed phase in a wide range of the particle sizes. In this case it is difficult to distinguish the prevailing fraction. Significant changes in the distribution of the dispersed phase particles in size were revealed by increasing the time of the electrolyte exposition with no operations of any kind (Fig. 1a). With increase in concentration of the dispersed phase in the electrolyte, the wider range of particle sizes is observed (Fig. 1b). The range of the particle sizes also decreases with increasing the time of the electrolyte exposition prior to the experiments. It should be noted that the primary particles of titanium dioxide with radius of 30 nm have an excess of surface energy and interact with each other inside the volume of the powder to form agglomerates. Under certain conditions, the agglomerates may decay into smaller particles. In the aqueous solution, these agglomerates are unstable, which causes their disintegration. The ions present in the electrolyte participate in formation of a double electric layer at the interface between the surfaces of the dispersed phase particles and the electrolyte, thereby decreasing the thickness of the double electric layer, which causes the particle coagulation.

Thus, adding into the electrolyte a powder of titanium dioxide P 25 in the form of polydispersed agglomerates of primary TiO₂ particles evokes two opposite processes: destruction of the agglomerates and coarsening of the fine particles due to coagulation. Since 2 h 0 time of registration of the sedimentation dependence is negligible when compared with the time intervals between the experiments, it may be assumed that the differential curves of TiO₂ particle size distribution correspond to some stationary states of the dispersed system. Increase in the electrolyte exposition time decreases the range of the particle radius so that TiO₂ particles attain equilibrium in sizes close to 1 μm. This process may apparently be accelerated by forced crushing of the agglomerates using ultrasound technique or intensive stirring of the suspension.

Based on the above studies, to receive reproducible data on the composition and properties of the composite Ni-TiO₂ coatings, it was decided to use the suspension electrolyte subject to 7-day exposition after its preparation, and to apply 30-min stirring prior to the composites deposition.

The dispersed phase content in the composite coatings increases with increasing the powder concentration in the electrolyte (Fig. 2a). In the region of low titanium dioxide concentrations in the electrolyte, a rapid increase in the particles content is observed in the composite. Increase in the TiO₂ concentration above 7 g/dm³ in the suspension will not significantly change the coating composition. We showed in [15] that this form of the dependence $Y = f(c)$ results from the fact that the incorporated particles occupy a certain portion of the cathode surface θ , which is proportional to volume fraction of the particles in the coating Y . The rate of coverage of

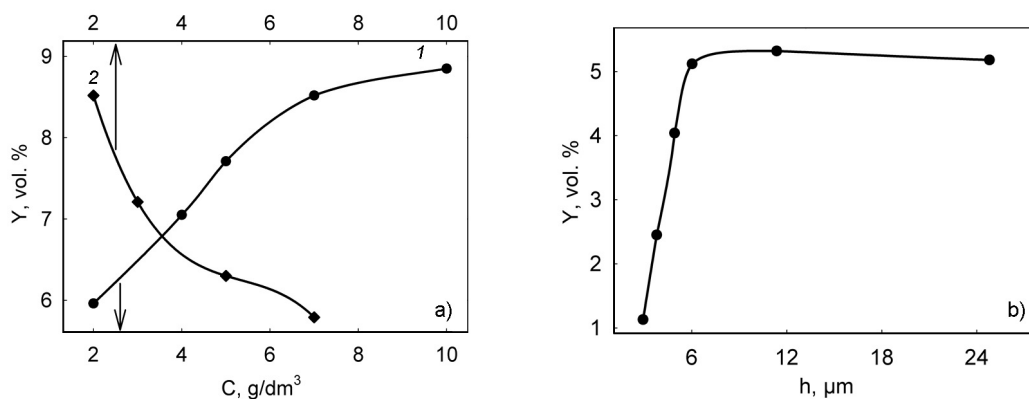


Fig. 2. Dependences of TiO₂ content of composites on: a — concentration of dispersed phase in electrolyte ($i = 2 \text{ A/dm}^2$) and density of the deposition current ($C_{\text{TiO}_2} = 7 \text{ g/dm}^3$), b — thickness of composites produced from methanesulfonate electrolyte containing 4 g/dm^3 TiO₂ at a current density of 7 A/dm^2 .

the free surface is proportional to $(1 - \theta)$ and to the dispersed phase concentration in the volume of the electrolyte (c). In formation of the composite coating, the particles are incorporated and the matrix surface is renewed. The matrix surface again becomes accessible for interaction with the dispersed phase particles. This process is similar to desorption of molecules adsorbed on the surface, and its rate is proportional to θ .

Under steady-state conditions of the composite coating deposition process the rate of particles transfer from the solution volume to the surface and the rate of their incorporation into the metallic phase are:

$$k_1 c(1 - \theta) = k_2 \theta, \quad (9)$$

where k_1 is the rate constant for coverage of the electrode surface with particles, k_2 is the rate constant for incorporation of particles into the composite coating.

After conversion, we obtain an expression for degree of the surface coverage with dispersed particles, which is similar to the Langmuir isotherm:

$$\theta = \frac{Bc}{1 + Bc}, \quad (10)$$

where $B = k_1/k_2$.

Since θ is proportional to Y , the observed similarity of the experimental dependence $Y = f(c)$ to the Langmuir isotherm can serve as confirmation of the reliability of the model for the electrochemical composite coating formation proposed in [15]. Under galvanostatic conditions, the composite coating is formed by electrodeposition of metal onto the electrode surface that is either free or conventionally occupied by the dispersed phase particles. Uneven distribution of

the lines of force causes the differences in the current density in these areas of the cathode $i_1 \neq i_2$. Increasing the overall current density may change $i_1:i_2$ ratio, which will affect the composite composition. Indeed, change in the current density from 2 to 7 A/dm^2 reduces TiO₂ content of the coating (Fig. 2a).

Since the composite coating is formed through overgrowing the dispersed phase by metal, situation may arise in which thickness of the metal matrix is insufficient for incorporating all the particles that are present on the electrode surface for the period of time sufficient for this process. Data presented in Fig. 2b show that the composite coating composition will keep changing until a certain coating thickness δ_{min} is reached. The content of titanium dioxide of the composites remains constant at the thickness values above $6 \mu\text{m}$. Obviously, this value is determined by the size of the incorporated particles. The larger the particle size and the dispersed phase concentration, the greater is the value of δ_{min} .

Incorporation of titanium dioxide into the nickel matrix should obviously affect structure of the coatings. The Ni-TiO₂ composites exhibit a fine-grained surface morphology with grain sizes slightly smaller in comparison with the pure nickel (Fig. 3). Furthermore, inclusions of titanium dioxide are clearly seen on the surfaces of dihedral nickel grains; the TiO₂ inclusions are present as formless clusters of the smaller particles. X-ray phase analyses showed that the obtained composites exhibit weak lines corresponding to TiO₂ in their spectra (Fig. 4). The size of nickel crystallites is 104 nm , which is somewhat less than for the pure nickel deposited from methanesulfonate electrolyte (120 nm). Probably, the crystal-

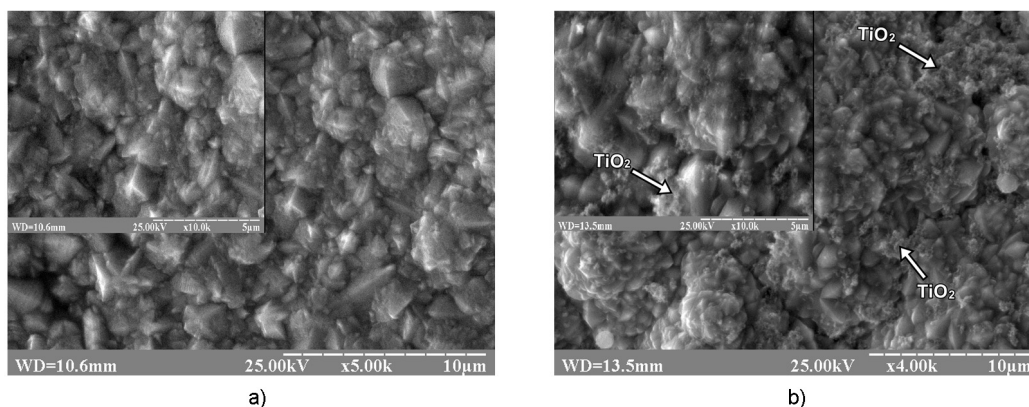


Fig. 3. Surface morphologies of nickel (a) and Ni-TiO₂ (b) composite, obtained at $i = 2 \text{ A/dm}^2$ and $C_{\text{TiO}_2} = 7 \text{ g/dm}^3$.

lite growths are inhibited in the electrocrystallization of nickel under the conditions of adsorption of the dispersed phase of titanium dioxide on the electrode surface, which causes decrease in their sizes.

Changes in the crystalline structure of the deposits, caused by inclusion of the titanium dioxide particles in the nickel matrix, affect the structurally dependent properties of the coatings. Increase in titanium dioxide content in the composites increases the internal tensile stresses in the deposits (Fig. 5a). However, these changes are insignificant, and do not exceed 20 %, which is in complete agreement with the slight distortion of the crystal lattice revealed by X-ray studies.

The incorporation of TiO₂ particles enhances the coatings microhardness (Fig. 5a). Increase in the content of the dispersed phase also increases the deposits microhardness. This effect can be described by the well-known Hall-Petch equation [16]:

$$H = 3\sigma_y, \quad (11)$$

$$\sigma_y = \sigma_0 + kd^{(-0.5)}, \quad (12)$$

where σ_y is the yield point, σ_0 is the macroelasticity limit, k is the grain boundary hardening coefficient that characterizes the contribution of grain boundaries to hardening, and d is the crystallite size.

Equations (11) and (12) show that the microhardness of the metallic deposits depends on the crystallite sizes. The decrease in d , exhibited by the Ni-TiO₂ composites, should enhance the coatings microhardness, which is observed in the experiment.

UV irradiation of methyl orange solution, which contacts with the Ni-TiO₂ composites, leads to decrease in the dye concentration to a greater extent than in the ab-

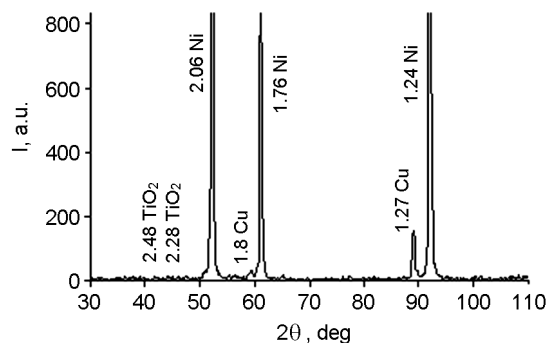
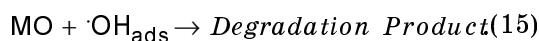
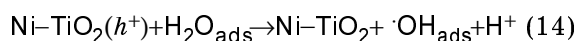
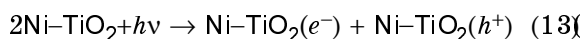


Fig. 4. X-ray diffraction pattern of Ni-TiO₂ deposit obtained from methanesulfonate electrolyte containing 7 g/dm^3 TiO₂ at $i = 2 \text{ A/dm}^2$.

sence of the photocatalyst (Fig. 5b). The decomposition of the methyl orange (MO) is explained by the following processes occurring on the surface of the Ni-TiO₂ composite [17]:



Under effect of the ultraviolet radiation, electrons on the Ni-TiO₂ surface pass from the valence band to the conduction band, which leads to formation of electron-hole pairs. The hole migrates to the surface of TiO₂ and decomposes the adsorbed water to form hydroxyl radical. The latter, because of its high reactivity, reacts with the dye adsorbed on the surface of the composite.

Deposits having a high content of photocatalytically active TiO₂ provide the more complete destruction of methyl orange in comparison with the coatings that are poor in the dispersed phase. Similar form of the dependences presented in Fig. 5b and Fig.

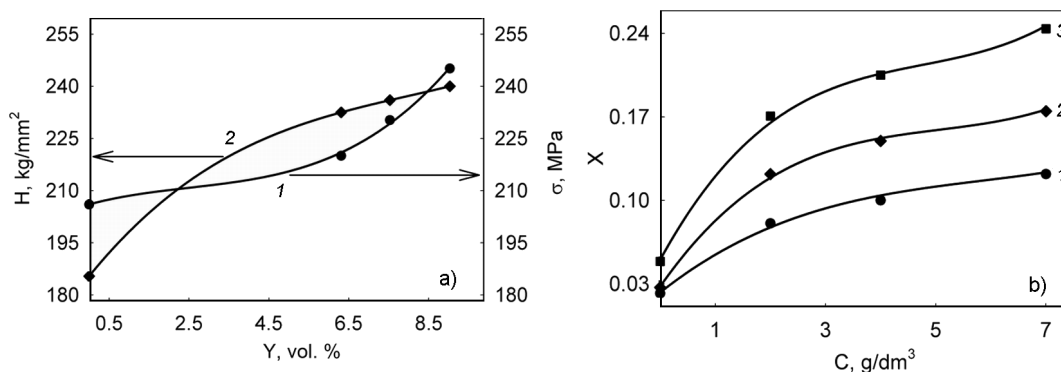


Fig. 5. Dependences of the internal tensile stresses and microhardness of composites on TiO₂ content of coatings obtained at $i = 2$ A/dm² (a). Dependence of the degree of photodestruction of methyl orange upon contact with Ni-TiO₂ on concentration of TiO₂ in the electrolyte of deposition of composites (b). Time of photodestruction, min: 1 — 80; 2 — 160; 3 — 280.

2a may indicate the direct dependence of the photocatalytic effect on the surface area of TiO₂ particles, which is accessible to the ultraviolet radiation. It is proportional to the degree of coverage of the composite surface with titanium dioxide.

Increase in the time of the composite surface exposure to the UV radiation naturally leads to increase in the degree of conversion of the methyl orange into the products of its destruction. As the concentration of the reagent in the solution decreases and the photocatalyst operating time increases, the intensity of the conversion decreases.

4. Conclusions

The dispersion analysis of the suspension solutions was carried out by the method of sedimentation in gravitational field. It showed that increase in the electrolyte exposition time up to 7 days allows the achievement of equilibrium sizes of TiO₂ particles, whose radius is close to 1 μ m. The study revealed the dependences of the dispersed phase content of Ni-TiO₂ composites on the concentration of TiO₂ particles in the electrolyte and on the deposition current density. It was shown that incorporation of TiO₂ particles into the nickel matrix enhances internal stresses and microhardness of the coatings. Increase in the titanium dioxide content in the deposits increases the photocatalytic activity of the coatings in model solutions of methyl orange. It was also shown that the photocatalytic activity of Ni-TiO₂ composites is directly related to the degree of coverage of their surface with titanium dioxide particles. In this regard, it seems promising to develop techniques for

increasing the TiO₂ content in the coatings. The obtained experimental data may be used in the development of the technology of depositing the wear-resistant photocatalytic Ni-TiO₂ coatings from methanesulfonate electrolyte for the decontamination of waste waters of the textile industry.

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