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УПРАВЛЕНИЕ СТРУКТУРОЙ И МОРФОЛОГИЕЙ МЕТАЛЛОМАТРИЧНЫХ КОМПОЗИТОВ С ИСПОЛЬЗОВАНИЕМ ЧАСТИЦ СУБМИКРОННЫХ РАЗМЕРОВ С ИЗМЕНЯЕМОЙ РЕДОКС-АКТИВНОСТЬЮ

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Показано, что совместная поликонденсация смешанных ванадиевой и молибденовой оксокислот в сольвотермических условиях сопровождается образованием твердого раствора замещения V_2O_5 : MoO_3, изоструктурного ксерогелю V_2O_5, редокс-активность которого увеличивается с ростом концентрации MoO_3. Полученный таким образом смешанный оксид $0{,}5V_2O_5$: $0{,}5MoO_3$ обладает высокой редокс-активностью и при гальваническом соосаждении с никелем создает условия для многоцентрового зарождения металлической фазы, что обеспечивает образование компактного композитного покрытия с повышенной коррозионной стабильностью.

Ключевые слова: смешанный оксид ванадия – молибдена; сольвотермический синтез; металломатричный композит; коррозионная стабильность.

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FINE CONTROL OVER THE STRUCTURE AND MORPHOLOGY OF METAL-MATRIX COMPOSITES EMPLOYING SUBMICRON OXIDE PARTICLES WITH THE ADJUSTABLE REDOX-ACTIVITY

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It is shown that copolycondensation of mixed vanadic and molybdic acids under the solvothermal conditions yields substitutional solid solution V_2O_5 : MoO_3 (isostructural to V_2O_5 xerogel) the redox activity of which exhibits increase with the MoO_3 content. Thus obtained mixed oxide $0.5V_2O_5$: $0.5MoO_3$ with high redox activity, being codeposited with the galvanic nickel, ensure multicenter nucleation of metal phase, yields compact composite with the enhanced corrosion stability.

Keywords: mixed vanadium – molybdenum oxide; solvothermal synthesis; metal-matrix composite; corrosion stability.

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Introduction

Electrochemically-grown metal matrix composites consisting of a metal matrix film with the incorporated ultra-fine particles of oxides, carbides, borides and industrial diamonds have attracted much attention in recent years [1–4] due to their outstanding mechanical properties [1; 2; 4; 5–9] and enhanced corrosion stability [10–13]. The occlusion of the inert particles in the metal film occurs through their sorption by growing galvanic deposit [14–17] and, therefore, it is obvious to use rather concentrated suspension plating baths to attain high volumetric content of the incorporated particles [17; 18]. Dispersions of vanadium and molybdenum oxides represent a special class of particles for composite formation due to pronounced redox activity inherent in them that makes it possible very effective redox mechanism of metal-matrix composite deposition and facilitates overgrowing of the entrapped particles with matrix metal due to localization of metal electrocrystallization at the oxide surface [4; 19; 20].

In the present study we demonstrate that combination of vanadium and molybdenum oxides yields mixed oxides of the variable composition permiting one to regulate the redox properties of the incorporated particles and to exert an effective control over the morphology and compactness of electrochemically grown metal-matrix that, in its turn, affects the corrosion protection properties of the resultant composite film.

Material and methods

Bare and mixed vanadium and molybdenum oxides in the form of highly dispersed particles have been prepared *via* thermally-induced polycondensation of individual and mixed oxoacids obtained by acidification of corresponding metallates or their mixtures on a resin [21; 22]. For these purposes 0.2 mol/L solutions of oxoacids (molybdic or vanadic ones as well as their 1 : 1 mixture) were incubated at 100 °C for 240 min, with the reaction volume being maintained constant during the entire synthesis. The resultant particles were separated from the reaction solution by centrifugation.

Morphology of the oxide particles was examined by scanning electron microscopy (SEM) using Leo-1420 electron microscope (*Carl Zeiss*, Germany). The X-ray diffraction analysis of oxide samples was performed with the use of PANalytical Empyrean difractometer (the Netherlands) with CuK_α radiation.

The electrolyte used for deposition of nickel-matrix composites was so-called Watts-type bath [23] containing 200 g/L $NiSO_4$, 50 g/L $NiCl_2$, 35 g/L H_3BO_3. The mixed-oxide particles were added to the electrolyte under vigorous stirring immediately before the composite electrodeposition in the amount of 0.5 g/L. The temperature of electrolyte was kept at 20 °C. The steel substrate (2 cm in length and 1 cm in width) was mounted vertically in the cell and the nickel foil was used as the counter electrode (the interelectrode distance was 1 cm). Taking into account that as-prepared plating solution shows sufficient stability, the electrodeposition of composite films was performed without electrolyte stirring. The thickness of resultant electrochemically grown composite films was *ca*. 20 μm. To evaluate oxide content, the composite coating was dissolved in concentrated HCl in presence of H_2O_2 and resultant solution was investigated with the use of atomic emission spectroscopy (Spectroflame ICP-P spectrometer (*Spectro Analytical Instr.*, Germany)).

The investigations of the surface relief of composite films and microtribological tests were performed employing atomic force microscopy (AFM) using TT2 microscope (*AFMworkshop*, the USA). The corrosion resistance of nickel-matrix composite films was evaluated with the use of PGSTAT 209 (*Metrohm Autolab B. V.*, the Netherlands) by recording the electrochemical impedance spectra in 0.5 mol/L NaCl which play a role of the depassivating electrolyte. Preliminary examination of the data recorded in a broad frequency range has shown significant inconsistency below 0.1 Hz resulted from violation of stationary condition of the electrochemical system, so the infra-low frequencies were omitted in the further impedance analysis.

Results and discussion

A very slow polycondensation inherent into molybdic acid [21; 24] facilitates its copolymerization with vanadic acid yielding solid solution which retains structure of V_2O_5 xerogel [22] as evident by XRD analysis (fig. 1), it is also seen from fig. 1 that crystallization of MoO_3 as the separate phase appears to be completely suppressed under these synthetic conditions.

According to X-ray fluorescence spectroscopy data, the V : Mo atomic ratio in obtained $V_2O_5 : MoO_3$ mixed oxide is *ca*. 0.3 that can be attributed to the different rates of polycondensation typical to the vanadic and molybdic acids in aqueous solution. It is seen from SEM images given in fig. 2 that the resultant mixed oxide microparticles were needle-shaped.

By contrast, the tablet-shaped V_2O_5 particles with the average size of 1–5 μm and regular prism-like MoO_3 microcrystals with the average size of 0.1 × 0.5 μm were obtained *via* the solvothermal synthesis under the same synthetic conditions and used for comparison. The dispersions of these individual and mixed oxides are capable to coprecipitate with galvanic nickel *via* redox mechanism yielding nickel-matrix composites with the incorporation level of *ca*. 5 wt. %. However, in the case of substitutional V_2O_5 : MoO_3 solid solutions there exist especially favorable conditions for realization of redox mechanism of matrix metal growing due to formation of large amount of redox centers resulted from the non-compensated valences. The localization of metal electrocrystallization at the surface of V_2O_5 : MoO_3 particles during Ni-MoO_3 : V_2O_5 composite formation is illustrated by fig. 3, *a*, which provides an evidence of spherical growing of metal nuclei at V_2O_5 : MoO_3 needles and very effective overgrowing of the trapped particles of oxide phase with matrix metal. The MoO_3 content thus has a synergic effect on the redox activity of the resultant mixed-oxide phase which far exceeds redox activity of bare V_2O_5 and MoO_3. The fact that metal electrodeposition is governed by the redox mechanism also manifests itself in the decrease of nickel electrocrystallization in the presence of V_2O_5 : MoO_3 particles in the plating bath observed in the polarization dependencies given in fig. 4.

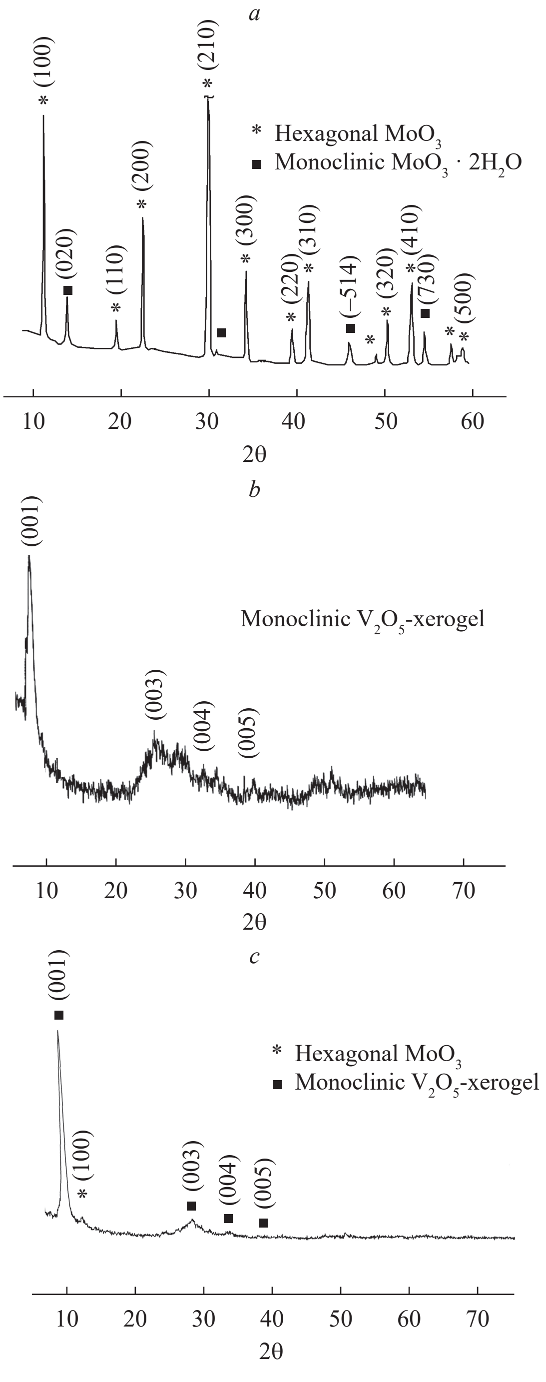

Fig. 1. XRD patterns of MoO_3 (*a*), V_2O_5 (*b*) and V_2O_5 : MoO_3 (*c*)

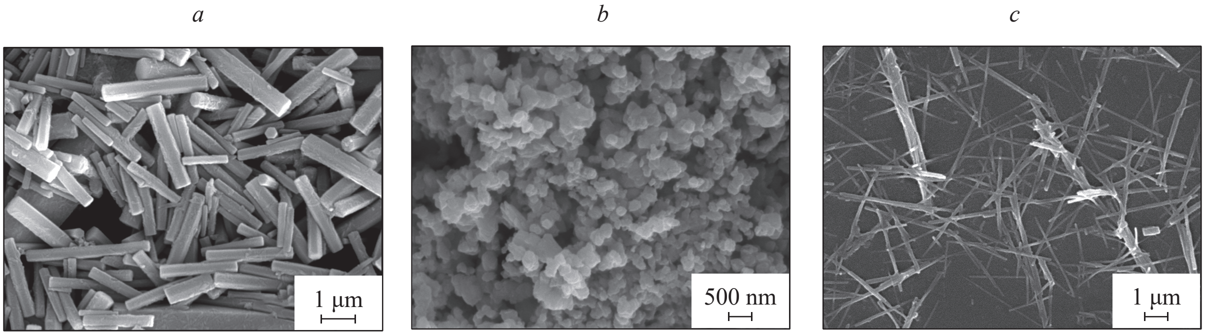

Fig. 2. The SEM images of MoO_3 (*a*), V_2O_5 (*b*) and $MoO_3 : V_2O_5$ (*c*) crystallites

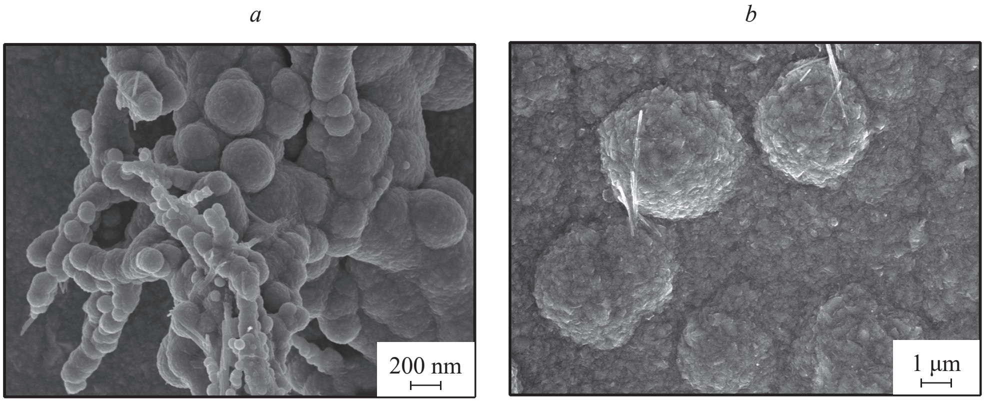

Fig. 3. The SEM image of Ni-$MoO_3 : V_2O_5$ composite film: the initial stage of composite growing (*a*), the terminal stage of the composite growing (*b*)

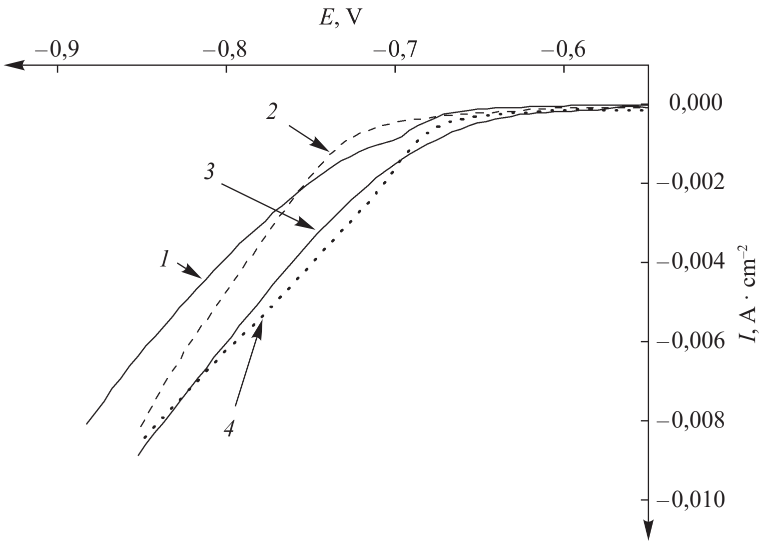

Fig. 4. Potential-current curves for electrochemical deposition of nickel (*1*) and Ni-MoO_3 (*2*), Ni-V_2O_5 (*3*), Ni-$MoO_3 : V_2O_5$ (*4*) composites

The redox mechanism of metal-matrix growing ensure multicenter nucleation of metal phase which occurs not only at the free surface of metal deposit but also on the oxide particles thus facilitating their encapsulation in the arising composite film (see fig. 3, *b*). As the result, a compactness of the resultant composite film exhibits considerable increase as evident by AFM investigations: it is seen from 3*D* AFM plots given in fig. 5 that the roughness of the surface of composite film decreases considerably when coming from V_2O_5- and MoO_3-containing composite films to the $V_2O_5 : MoO_3$-cotaining one.

Figure 6 shows the impedance spectra of nickel, Ni-MoO_3, Ni-V_2O_5 and Ni-$MoO_3 : V_2O_5$ electrodes obtained at open circuit potentials in the Cl^--containing electrolyte. Nickel gives slightly distorted semicircle in Nyquist coordinates which is fitted well with a simple equivalent circuit composed of capacitance and charge transfer resistance acting in parallel. Ni-MoO_3 and Ni-V_2O_5 composites give higher impedance (see fig. 6) evidencing that the embedment of particles of transition metal oxides reduces corrosion susceptibility of nickel deposit.

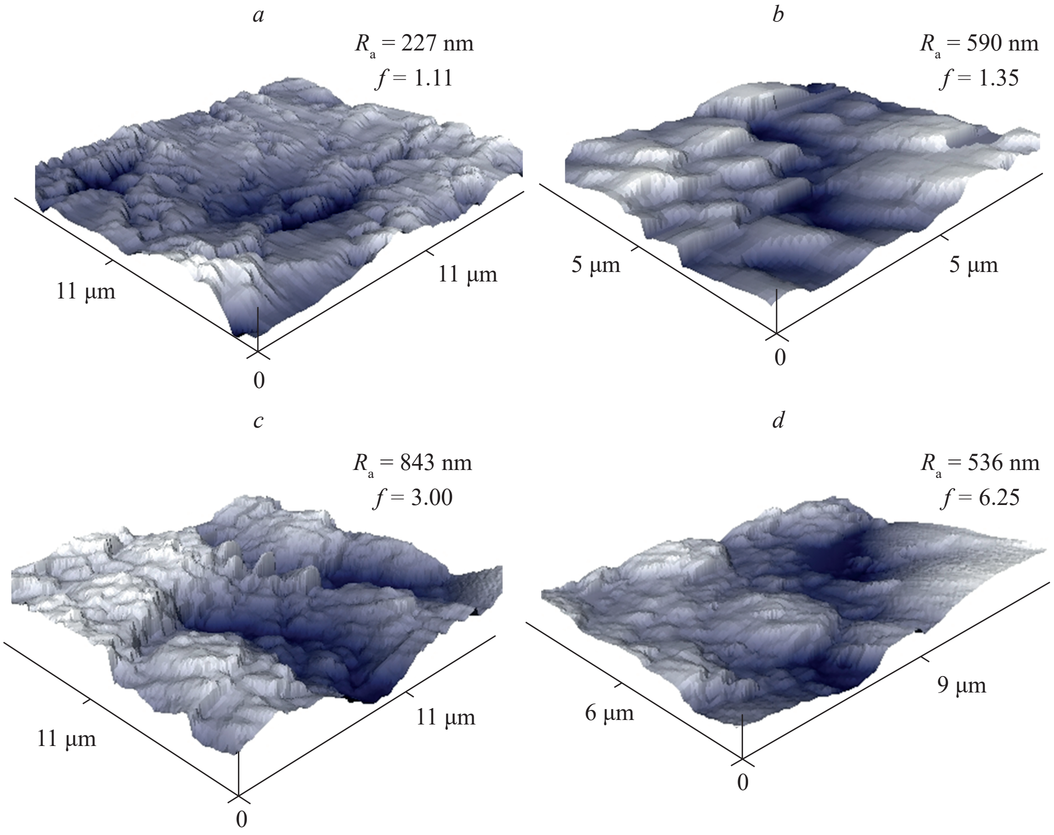

Fig. 5. AFM surface plots for bare nickel (*a*), and Ni-MoO_3 (*b*), Ni-V_2O_5 (*c*), Ni-MoO_3 : V_2O_5 (*d*) composite films. The values of the mean roughness (R_a) and the friction coefficient (f) are given at the plots

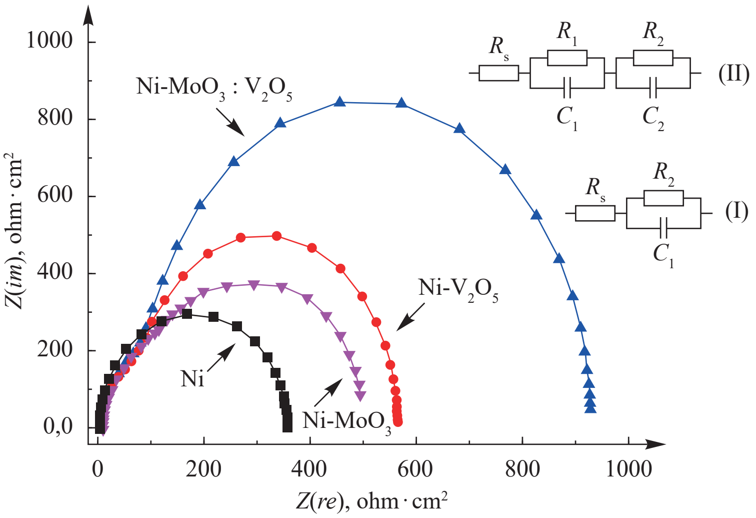

Fig. 6. Electrochemical impedance spectra of bare nickel, Ni-MoO_3 composite, Ni-V_2O_5 composite and Ni-MoO_3 : V_2O_5 composite in 0.5 mol/L NaCl. Measurements were done under the open circuit potentials. Solid lines show data fit to the circuits given in the insertion: (circuit I) is the equivalent circuit describing the electrochemical behavior of bare nickel and Ni-V_2O_5 composite; (circuit II) is the equivalent circuit describing the electrochemical behavior of Ni-MoO_3 composite and Ni-MoO_3 : V_2O_5 composite. The series resistance R_s is the electrolyte resistance

It is also seen from fig. 6 that Ni-MoO_3 composite gives more complex spectrum corresponding to a circuit composed of a series of two RC fragments pointing to the formation of adherent protective layer resulted from the adsorption of molybdate species released from the incorporated MoO_3 particles [20; 25]. On the other hand, the embedment of the V_2O_5 : MoO_3 particles leads to a considerable further increase of impedance (see fig. 6), the molybdate inhibition effect being also observed in the Nyquist plots as the impedance spectrum of a complex shape. The observed effects can be attributed to the enhanced compactness of the nickel matrix grown *via* the redox mechanism, the latter factor being the most pronounced in the case of the embedment of V_2O_5 : MoO_3 particles which demonstrate the highest redox activity and redox conductivity.

The results of this work provide clear evidence that the employment of mixed oxides of transition metals with high concentration of redox centers for electrodeposition of metal-matrix composites opens fresh possibilities of growing composite coatings with the enhanced corrosion resistance resulted from high compactness of the metal matrix.

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