Surface Modification of Composites with Metal Nanoparticles

N. V. Sotskaya\textsuperscript{a}, S. V. Makarov\textsuperscript{b}, O. V. Dolgikh\textsuperscript{a}, V. M. Kashkarov\textsuperscript{a}, A. S. Lenshin\textsuperscript{a}, and E. A. Kotlyarova\textsuperscript{a}

\textsuperscript{a} Voronezh State University, Universitetskaya pl. 1, Voronezh, 394006 Russia
\textsuperscript{b} Ivanovo State University of Chemistry and Technology, pr. Engel’sa 7, Ivanovo, 153460 Russia
e-mail: nvs@chem.vsu.ru

Received May 25, 2009; in final form, January 14, 2010

Abstract—This work examines the possibility of using copper, nickel, and cobalt nanoparticles in the electrodeposition of nickel coatings and for surface modification of porous silicon, and also colloidal silver particles for surface modification of silver-containing polymer-matrix composites. It is shown that the deposition of metal nanoparticles may influence the morphology, electronic structure, and phase composition of the surface and the catalytic, electrical, and optical properties of the material.

DOI: 10.1134/S0020168510110063

INTRODUCTION

One priority area of modern science and technology is the development of nanomaterials possessing unique physical, electrochemical, and catalytic properties [1, 2], which might open up great possibilities for creating novel, effective catalysts, sensor systems, and bioactive materials. Of particular interest are metal nanoparticles, which possess specific properties, differing from those of both isolated atoms and bulk metals. Owing to their high stability, such particles can be used as additives to various solutions and effective surface modifiers [3, 4].

This work examines the possibility of using metal (Ni, Co, Cu, and Ag) nanoparticles for surface modification of electrodeposited nickel coatings, silver-containing polymer-matrix composites, and porous silicon.

EXPERIMENTAL

Preparation of colloidal particles. Colloidal metal suspensions were prepared by chemical condensation [4]. Metal ions were reduced with thiourea dioxide (TDO) in a mixture of water and isopropanol (10 vol %) at 70°C. The copper sulfate, nickel chloride, and cobalt chloride concentrations were \(2 \times 10^{-3}\) M, and the TDO concentration was 0.1 M. The suspensions were stabilized by gelatin additions (up to 3 vol %). The particle size of the dispersant was determined on an EMV-100L electron microscope (SEM) on a JEOL JSM-6380LV. Their morphology, electronic structure, and phase composition were determined using X-ray diffraction (XRD) on a DRON-3 diffractometer [3].

Deposition of nickel coatings. Electrodeposition was performed in galvanostatic mode \((i = 5\) mA/cm\(^2\), \(\tau = 20\) min) in a standard three-electrode cell using a Pl-50-1.1 potentiostat. The solution contained 0.08 M NiCl\(_2\) \(\cdot\) 6H\(_2\)O, 0.20 M NH\(_2\)CH\(_2\)COOH, and 0.66 M Na\(_2\)SO\(_4\) (pH 5.5). Doping was performed by adding suspensions of Ni, Cu, and Co nanoparticles to this electrolyte in the volume ratio 1 : 50 or 1 : 100.

Preparation of silver-containing composites. Silver-containing polymer-matrix composites were prepared using the macroporous sulfonated cation exchange resin KU-23 15/100. The process involved ion exchange in a 6% AgNO\(_3\) solution followed by complete reduction with hydrazine [5]. The resultant samples were immersed in colloidal metal suspensions and left standing for 24 h. Next, the samples were washed with deoxygenated water and stored in it until tests.

Preparation of porous silicon. Porous silicon samples were prepared from (100)-oriented single-crystal KEF 0.2 (phosphorus-doped) silicon wafers as described by Kashkarov et al. [6]. The porosity of the samples was on the order of 70%. After etching, the porous silicon samples were washed with distilled water and then with isopropanol in order to remove the residual electrolyte from the pores. The samples thus prepared were immersed in colloidal metal suspensions for seven days. Next, the samples were washed with water and dried.

Characterization of the materials. The surface of the modified materials was examined by scanning electron microscopy (SEM) on a JEOL JSM-6380LV. Their composition was determined using an INCA-250 energy dispersive X-ray analysis system. The structure of the nickel coatings was determined by X-ray diffraction (XRD) on a DRON-3 diffractometer (CuK\(_\alpha\) radiation, 35 kV, 20 mA). The electronic structure and phase composition of the as-prepared and surface-modified porous silicon layers were assessed by ultrasoft X-ray emission spectroscopy on an RSM-500 X-ray spectrometer/monochromator under electron-beam excitation (1.5 keV, 2 mA, vacuum of \((2–4) \times 10^{-4}\) Pa). The sampling depth was 25 nm [7].

Evaluation of the catalytic properties of the Ni(M) coatings and silver-containing polymer-matrix compos-
Surface modification of composites with metal nanoparticles. We evaluated the catalytic activity of the materials for the anodic oxidation of the hypophosphite ion. The samples were anodically polarized in a 0.25 M NaH₂PO₂ solution at a zero-current potential of +1.2 V in potentiodynamic mode at a sweep rate \( v = 5 \times 10^{-2} \text{V/s} \). In the case of the silver-containing polymer-matrix composites, we used a graphite paste electrode with one grain of the composite [8].

**RESULTS AND DISCUSSION**

**Nickel coatings.** When codeposited with nickel, metal nanoparticles may influence the deposit composition and structure. We examined the effect of Ni, Co, and Cu nanoparticles on the characteristics of electrodeposited nickel coatings. Energy dispersive X-ray analysis detected no significant incorporation of any foreign metals into the coatings, but the presence of nanoparticles in solution was found to influence the structure and morphology of the deposit. XRD patterns of the coatings studied are presented in Fig. 1. Analysis of the XRD data indicates that the electrodeposited nickel has a (200) texture. The coatings modified with nanoparticles are also textured, but the relative texture coefficient \( \text{RTC}_{200} \) decreases in the order Ni > Ni(Ni) > Ni(Co) > Ni(Cu) from 96 to 72%.

The catalytic properties of the modified nickel coatings were quantified by the rate of the anodic oxidation of the hypophosphite ion on the coatings. The nanoparticles primarily influence the zero-current potential \( E_{\text{Ni(M)}} \), causing it to shift to more negative values compared to the unmodified nickel coating. The effect is strongest for the Ni(Ni) coatings (Table 1). We also observe changes in the parameters of the peak (potential \( E_p \) and peak current density \( i_p \)) in the anodic voltammograms obtained for the coatings in NaH₂PO₂ solutions (Fig. 3), which corresponds to the oxidation of the hypophosphite ion [10]. The peak shifts to higher potentials by 30–200 mV relative to the unmodified nickel coating. The peak current

---

**Fig. 1.** XRD patterns of electrodeposited coatings in the angular ranges \( 2\theta = (a) \ 40^\circ–55^\circ \) and \( (b) \ 40^\circ–50^\circ \): (1) Ni, (2) Ni(Ni), (3) Ni(Co), (4) Ni(Cu).