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Copper (nickel) based composite coatings reinforced with nanosized oxides

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The work reports the method for copper and nickel based coatings reinforced by ultrafine particles of alumina or zirconia deposition. The electrolytes' compositions as well as electrosynthesis modes are grounded. Considerable enhance in the both physical-mechanical properties and corrosion resistance of synthesized composite systems over traditional monolayer coatings by copper and nickel is shown.
Keywords: composite electrochemical coatings, physico-mechanical characteristics, nanosized oxide, dispersion phase, current density, the hydrosol of alumina.

Предложен метод получения покрытий на основе меди и никеля, армированных ультрадисперсными частицами оксида алюминия или циркония. Приведены составы электролитов и режимы электросинтеза. Показано значительное повышение физико-механических свойств и коррозионной стойкости синтезированных композиционных систем по сравнению с традиционными однослойными покрытиями меди и никеля.

Армовані наноструктурними оксидами композиційні покриття на основі міді (нікелю). *М.Сахненко, О.Овчаренко, М.Ведь.*
Запропоновано метод отримання покриттів на основі міді і нікелю, армованих ультрадисперсними частинками оксиду алюмінію або цирконію. Приведено склади електролітів, і режими електросинтезу. Показано значне підвищення фізико-механічних властивостей і корозійної стійкості синтезованих композиційних систем у порівнянні з традиційними одношаровими покриттями міді і нікелю.

1. Introduction

Development of key sectors of the modern industry is based on the new materials and high technologies using. Application of thin-film coatings obtained by electrodeposition can significantly improve the performance of the products, such as wear-, heat- and corrosion resistance, as well as give specific technological characteristics of the working surfaces of the machine parts and tools. Priority in the electroplating development is to create a new type of the coating metals and alloys, in particular, composite electrochemical (CEC). Nano-sized particles are used as the second phase of such coatings. Such heterogenous system as compared to their monometallic analogs have specific , and in some cases, unique physical-chemical and physical-mechanical, including tribological characteristics [1, 2].

In this connection it is of interest to obtain the coatings and foils based on metal copper and nickel matrix reinforced by nanostructured alumina or zirconia. Necessary size of the adding particles is provided by chemical dispersion.

2. Experimental

The copper and nickel foil reinforced with nanoscale aluminum or zirconia was prepared by electroforming on substrates made of polished stainless steel X18H10T (AISI 304). The adherent CEC of similar

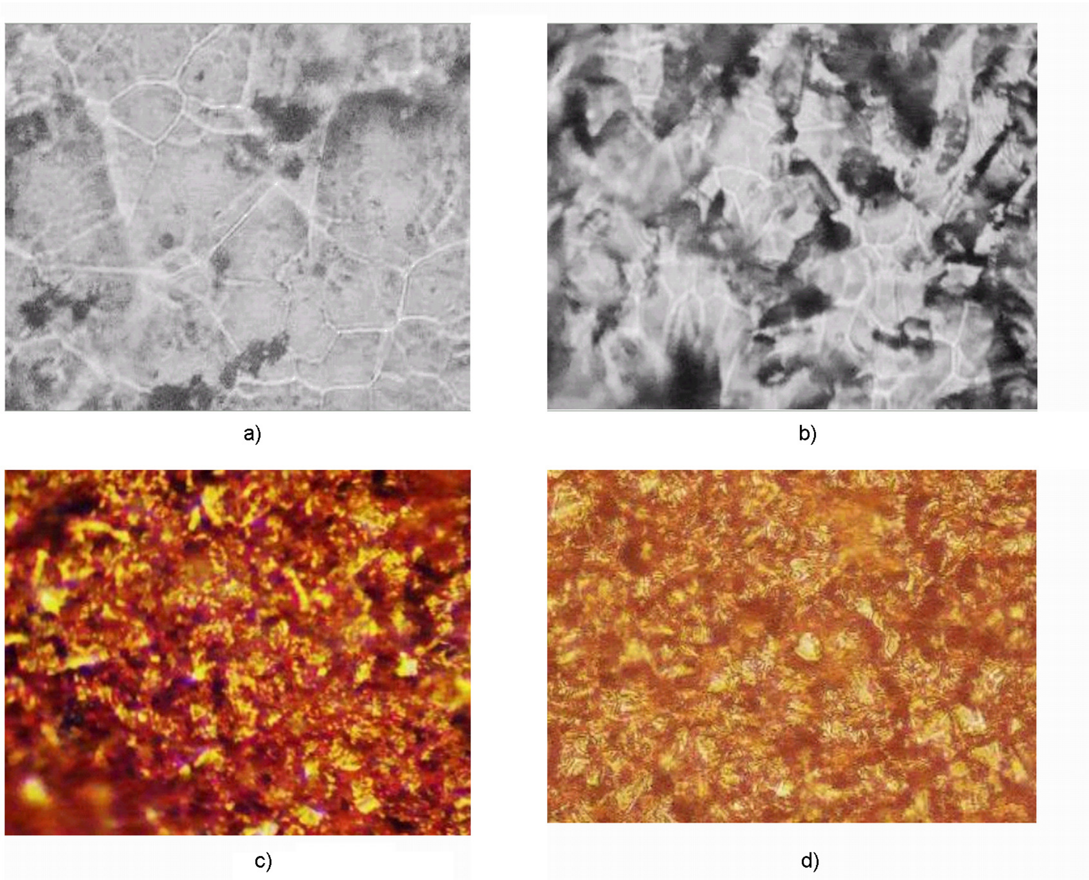

Fig. 1. Structure of the electro-consisting composite coatings: $Ni–ZrO_2$ (a), $Ni–Al_2O_3$ (b), $Cu–ZrO_2$ (c) and $Cu–Al_2O_3$ (d). Concentration of the dispersoid in electrolyte is 25 g/dm^3.

composition was deposited on mild steel [3] from the electrolyte with a varying content of the disperse phase [4, 5].

Both the copper foil with the thickness of 10–30 μm and the CEC based on copper were obtained by electrolysis in electrolyte solution with following ingredients (g/dm^3): potassium pyrophosphate 330–380; copper sulfate 70–90; citric acid 15–25, at the current density of 1–3 A/dm^2 and temperature of 20–25°C for 30–40 min. As an auxiliary electrode a copper plate was used. For reinforcement of the foil we added 10–40 cm^3 of sol containing 10–50 g/dm^3 nanosized alumina dispersed phase to 50 cm^3 of the basic electrolyte.

Foil and CEC based on nickel were formed at the current density of 2–3 A/dm^2, the temperature of 20–25°C for 30–40 min from the Watts sulfate electrolyte containing, g/dm^3: nickel sulfate 80–320; nickel chloride 7–20; boron hydroxide 25–40. The dispersed phase was added in a proportion as for the copper foil [6, 7]. As an auxiliary electrode a nickel plate was used.

Alumina hydrosol was prepared by dispersing a high-temperature form $\gamma–Al_2O_3$ in aqueous alkali solution at pH≥13 for 10–30 min and followed by decantation of the colloidal solution. Dispersion of the alumina particles occurs due to the partial chemical dissolution of amphoteric oxide under above pH value to form the hydroxylic complexes $[Al(OH)_4]^-$. As a result the size of the dispersed phase particles is reduced and stability of the sol increases as $[Al(OH)_4]^-$ are more efficient and stable charge-forming ions with substantial stability constant $K_s \sim 3.2 \cdot 10^{32}$. Thus, colloidal particles of the following composition are forming in the solution:

$$\left\{m(Al_2O_3) \cdot n[Al(OH_4)]^- \cdot (n-x)Na^+ \cdot yH_2O\right\}^{x-} \cdot$$
$$\cdot\, xNa^+ \cdot zH_2O.$$

Additionally the sol stability is ensured by presence in the composition of charge-forming ions simultaneously the two elements of which are similar in nature to the nucleus — oxygen and aluminum. Shredding of the high-temperature form $\gamma–Al_2O_3$

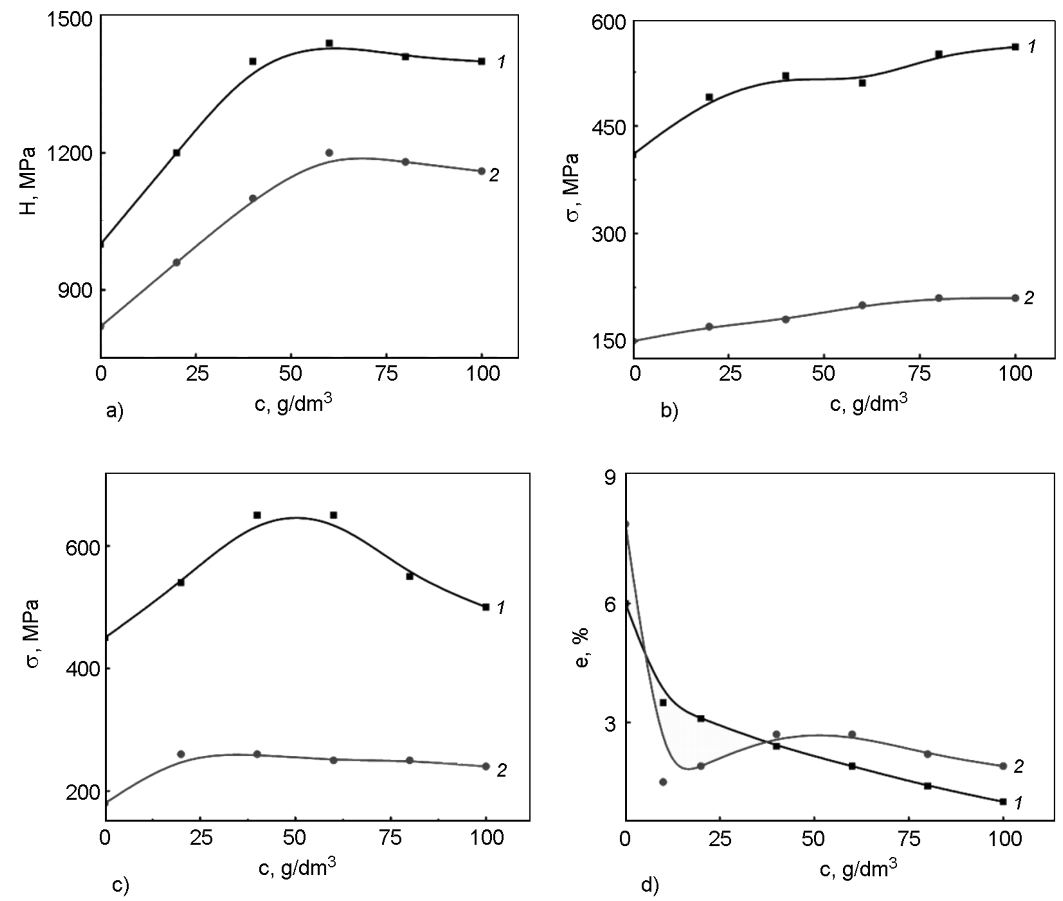

Fig. 2. Dependences of microhardness (a), tensile strength (b), the fluidity limit (c) and plasticity (d) of Nickel (*1*) and Copper (*2*) composites on Al_2O_3 percentage in electrolyte.

is going by top-down mode, and peptization is provided by that for the nanoscale particles the Brownian motion is competing with sedimentation. In such way we can control the composition and structure of the intermediates during dispersion of the reinforcing phase. The resulting material is promising for synthesis of the CEC with improved functional properties [8].

We synthesized CEC reinforced with nanoscale particles of zirconia stabilized with yttria (according to the tech specification the size of the particles was 1 nm). The phase of ZrO_2 was added to the basic electrolyte in amount of 10–50 g/dm^3. The electrolysis was conducted at the current density 0.5–3.5 A/dm^2 and temperature 20–55°C for 40–60 min.

Physical and mechanical properties (ductility, tensile strength and yield point) of the foils and coatings of $Ni–Al_2O_3$, $Ni–ZrO_2$, $Cu–ZrO_2$ and $Cu–Al_2O_3$ were determined on TIRAtest-2300 machine, the microhardness was measured using PMT-3 apparatus, the grain size and surface morphology were analyzed by MIM-7 microscope at magnification of 1,200 times. Corrosion tests were carried out in the neutral (0.5 M NaCl) environment, the corrosion rate was determined using the polarization resistance technique. Polarization measurements were performed in a thermostated glass cell using potentiostat IPC-Pro, with automated system of data registration. As an auxiliary electrode a stainless steel plate was used. Examination of chemical composition and surface morphology of the coatings was performed with a scanning electron microscope (SEM) ZESS EVO 40 XVP. The image of surfaces of the samples was obtained by detecting secondary electrons (BSE), by scanning the surface with the electron beam, allowing to investigate morphology of the surface with the high resolution and contrast.

3. Results and discussion

The SEM results analysis shows that the composite structure of copper and nickel (Fig. 1) can be isolated polyhedral particles

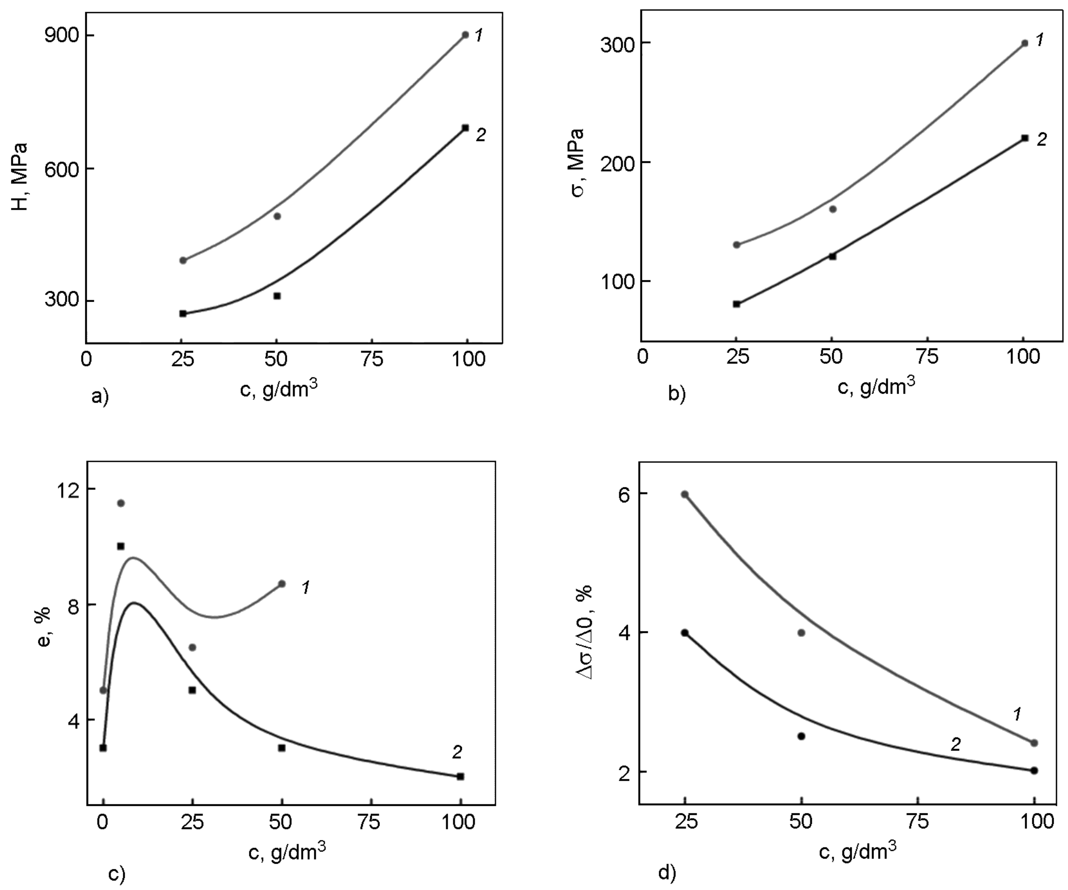

Fig. 3. Dependences of microhardness (a), the fluidity limit (b), plasticity (c) and specific depth of relaxation (d) in Nickel (*1*) and Copper (*2*) composites on ZrO_2 percentage in electrolyte.

with the grain phase of ZrO_2 or Al_2O_3. Average size of the inclusions is less than 1 μm for ZrO_2 and it is in the range of 1–5 μm for Al_2O_3, while the size of the copper grain is 5–7 μm. The second-phase particles are located the both as in the grains as on their boundaries and grain size of copper in the obtained composites with Al_2O_3 is reduced to 3 μm. There is a tendency to aggregation and formation of conglomerates of the particles with increasing dopant concentration in the solution. Therefore, we need to set the optimum content of the hardening phase for forming the composites with the high strength properties [9].

It should be noted that the concentration dependences of physical and mechanical characteristics of the CEC, reinforced with alumina (Fig. 2) have both monotonous and extreme characters. Thus, when increasing the content of Al_2O_3 in the slurry phase from 10 to 50 g/dm^3 microhardness of the CEC based on copper increases from 850 to 1100 MPa, a tensile strength — from 150 to 250 MPa, yield point — from 100 to 200 MPa. For nickel-based composites with increasing content of Al_2O_3 in the slurry from 10 to 50 g/dm^3 the microhardness increases from 1000 to 1400 MPa, a tensile strength — from 400 to 500 MPa and yield point — from 450 to 650 MPa.

Quite predictable is antibate variation of ductility of composites with increasing of the dispersed phase concentration in the solution [10]. The reason for this behavior is due to the inclusion of composite particles of Al_2O_3, which act as obstacles to dislocation motion reliably, which is typical for particulate hardening mechanism for the Orowan (rounding of the second phase particles by dislocations). The nickel coatings exhibit higher mechanical properties in comparison to the composites based on copper [11].

The concentration dependences of physical and mechanical properties for the foils reinforced with ZrO_2 are similar. Indeed, a microhardness of the composite coatings based on copper was increased from 270 to 310 MPa and the yield point — from 80 to 120 MPa when increasing the content of ZrO_2 in the slurry phase of 25 to 50 g/dm^3.

For the nickel-based composites with increasing content of Al_2O_3 in the slurry phase from 10 to 50 g/dm^3 the microhardness increases from 390 to 490 Mpa and yield strength — from 130 to 160 MPa. Relaxation resistance increases with increasing content of the disperse phase as for the composites based on nickel and copper. Similar trends are observed for coatings which reinforced by alumina particles.

Corrosion testing of the CEC in neutral (pH 6–7) chloride containing solutions showed that the inclusion of nanosized Al_2O_3 particles in the metal-based matrix contributes to reduction of the corrosion rate of 0.02–0.07 mm/year.

4. Conclusion

The composite compact grained nonporous coating and foil of variable thickness based on nickel and copper matrix reinforced with nanoscale alumina and zirconia were fabricated by electrochemical method. It is shown that the application of chemical dissolution of amphoteric alumina allows the flexibility to manage the size of the dispersed phase and stabilize the colloidal solution. The synthesized materials have the high barrier and physical-mechanical properties, in particular, the microhardness and yield point of the coatings were increased substantially while a slight decrease in ductility was observed.

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