Название: Electrochemical Synthesis of Nickel-Based Composite Materials Modified with Nanosized Aluminum Oxide

Другие названия: Электрохимический синтез композиционных материалов на основе никеля, модифицированных наноразмерным оксидом алюминия

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композиционные покрытия, электролитические фольги, наноразмерный оксид, гидрозоль оксида алюминия, дисперсная фаза, микротвердость, предел прочности, предел текучести

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Реферат: Electrochemical synthesis of nickel-based composite coatings and foil reinforced with nanosized aluminum oxide is reported. $Ni\text{-}Al_2O_3$ composites with different content of the modifying phase were prepared by chemical dispersion of aluminum oxide using the “from above down” principle. The influence of the aluminum oxide concentration in the electrolyte on the physicomechanical properties of the reinforced foil was determined. Incorporation of reinforcing phase particles into the metal matrix leads to a decrease in the grain size and enhances by a factor of 2–6 the strength characteristics of the coatings and foil. The topography of the surface and the cross section profile of the composites were examined, and the influence of these characteristics on the properties of the materials was determined.

Представлены результаты электрохимического формирования композиционных покрытий и фольг на основе никеля, армированных наноразмерным оксидом алюминия. Для получения композитов Ni – Al_2O_3 с различным содержанием модифицирующей фазы использован метод химического диспергирования оксида алюминия по принципу сверху–вниз. Установлено влияние концентрации оксида алюминия в электролите на физико-механические свойства армированных фольг. Включение в основную матрицу металла частиц армирующей фазы приводит к уменьшению размеров

зерен и повышает в 2–6 раз прочностные характеристики покрытий и фольг. Изучена топография поверхности и профиль сечения композитов и установлено их влияние на свойства материалов.

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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrochemical Synthesis of Nickel-Based Composite Materials Modified with Nanosized Aluminum Oxide

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Abstract—Electrochemical synthesis of nickel-based composite coatings and foil reinforced with nanosized aluminum oxide is reported. $Ni–Al_2O_3$ composites with different content of the modifying phase were prepared by chemical dispersion of aluminum oxide using the "from above down" principle. The influence of the aluminum oxide concentration in the electrolyte on the physicomechanical properties of the reinforced foil was determined. Incorporation of reinforcing phase particles into the metal matrix leads to a decrease in the grain size and enhances by a factor of 2–6 the strength characteristics of the coatings and foil. The topography of the surface and the cross section profile of the composites were examined, and the influence of these characteristics on the properties of the materials was determined.

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The development of novel technologies and of equipment for their implementation requires materials with unique operation characteristics. Composite coatings and foils based on metal matrices with incorporation of particles of a secondary phase show promise in this respect. Oxides, carbides, silicides, borides, nitrides, and other substances are usually used as materials of the secondary phase. The resulting composites combine the properties of the metal and dispersed phase and exhibit higher levels of corrosion resistance, microhardness, and wear and heat resistance. The practically important properties of composite coatings and foils are determined by the nature of the dispersed phase. Because improvement of operation characteristics of composite materials is associated with combination of two essentially different materials, it is necessary to use materials whose interaction with the metal matrix is sufficiently strong. That is the reason for the interest in metal (aluminum, zirconium, etc.) oxides as material for the secondary phase. The chose of aluminum oxide is dictated by the fact that this material exhibits the required physicomechanical properties: high levels of hardness, compression strength, and resistance to corrosion and wear. Furthermore, aluminum oxide is cheap, and its use does not lead to a considerable increase in the production cost of the composites [1, 2].

It is particularly important to synthesize composite materials with improved physicomechanical properties without altering the crystal lattice of the metal, so as to preserve the plasticity and other properties of the metal matrix. This result can be reached by incorporating into the matrix as small amount of the reinforcing phase as possible; however, in so doing, the reinforcing effect will be low. A new class of composite materials meeting these requirements appeared relatively recently. It is based on the use of a secondary phase (corundum, zirconium dioxide, etc.) with the particle size varying in the interval 1–100 nm [3, 4].

Wide use of nickel plating is due to valuable physicochemical properties of nickel, namely, to its resistance to atmospheric corrosion and to corrosion in solutions of alkalis and some acids. Therefore, nickel plating is used for enhancement of the chemical resistance of steel in aggressive media, in particular, under load or under erosion action, and also for protection from fretting corrosion and for decorative finishing of items. On the

other hand, these coatings are relatively strained and brittle, which makes it topical do develop nickel-based composite electrochemical coatings and foil reinforced with nanosized aluminum oxide [5].

EXPERIMENTAL

Electrochemical deposition of the nickel-based foil reinforced with the nanosized phase of aluminum oxide was performed onto a support of polished stainless steel Cr18Ni10Ti (AISI 304). Adhesed composite coatings of similar composition were deposited onto steel of grade 20 from electrolytes with variable content of the dispersed phase [6].

Synthesis of nickel foil and coatings was performed from sulfamate nickel-plating electrolytes [7] of the following compositon (g dm^{-3}): nickel sulfamate 80–320, nickel chloride 7–20, and boric acid 25–40, with variable content of the dispersed phase. Electrolyte solutions were prepared from certified chemically pure grade chemicals in distilled water. Electrolysis was performed with a stabilized dc source of B5-47 series; the current density was maintained in the range 2–3 A dm^{-2}. Electrolysis was performed at 20–25°C for 30–40 min. The thickness of the composites obtained was 30–50 μm.

In electrosynthesis of $Ni–Al_2O_3$ composites, the sulfamate nickel-plating electrolyte was chosen for the following reasons. Because the properties of coatings largely depend on the composition of the electrolytes used and on the plating conditions and the main component of the electrolyte, nickel sulfamate, exhibits high solubility at relatively low temperatures, it can be taken in high concentration, so as to ensure high working current density. However, the main advantage of nickel deposits obtained from sulfamate electrolyte is the lower level of internal stresses, compared to coatings deposited from other electrolytes [8, 9]; therefore, even at large thickness they remain plastic.

Solutions for the deposition of the foil with reinforcing phase particles in the metal matrix were prepared by adding to the base electrolyte 0.2–0.8 volume part of aluminum oxide sol containing 4–4.6 g dm^{-3} dispersed phase of nanosized aluminum oxide. Thus, the content of the secondary phase in the electrolyte solution was varied from 1 to 2.5 g dm^{-3}. The aluminum oxide hydrosol, as previously [10], was prepared by dispersing the high-temperature form γ-Al_2O_3 in an aqueous solution at pH ≥ 13 for 10–30 min and subsequently decanting the colloidal solution. The aluminum oxide particles were dispersed owing to partial chemical dissolution of the amphoteric oxide at pH ≥ 13 with the formation of hydroxo complexes $[Al(OH)_4]^-$, which are adsorbed on the Al_2O_3 surface, thus determining the charge of the colloidal particle. The particles delivered to the cathode initiate the nucleation in sites of contact with the cathode surface, which stimulates their overgrowth with the metal [11, 12].

Physicomechanical tests of the $Ni–Al_2O_3$ foil (to determine the microhardness, yield point σ_y, ultimate strength σ_u) were performed at room temperature with a TIRAtest-2300 mechanical testing machine at a scanning velocity of 0.36 mm min^{-1}.

The state of the surface of nickel-based composite coatings and foil modified with nanosized aluminum oxide were studied by atomic force probe microscopy. Measurements were performed under standard conditions with an NT-206 scanning probe microscope (CSC-37 probe, cantilever B, probe curvature radius 10 nm) at the minimal scanning step of 0.3 nm and scanning velocity of up to 10 μm s^{-1}.

RESULTS AND DISCUSSION

Analysis of the concentration dependences of the strength characteristics of the synthesized composite foil specimens shows that, as the content of nanosized aluminum oxide in the electrolyte is increased from 0.25 to 1.5 g dm^{-3}, the microhardness increases from 1800 to 2900 MPa; the yield point, from 150 to 980 MPa; and the ultimate strength, from 550 to 1200 MPa, with the plasticity decreasing insignificantly (Fig. 1). This behavior of the composites is caused by incorporation of Al_2O_3 particles into the matrix. These particles reliably prevent the movement of dislocations, which is typical of the disperse mechanism of strengthening according to Orowan (dislocation bowing around the particles of the second phase).

The measurement results have shown that introduction of even a small amount (up to 1 g dm^{-3}) of aluminum oxide nanoparticles into the electrolyte solution significantly influences the strength of the foil specimens obtained. Reinforcement of the composites with the dispersed phase is due to formation of fine secondary phase inclusions in the metal matrix. These inclusions can have one or another