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Mechanical Properties of Zn–Ni–SiO_2 Coating Deposited under X-ray Irradiation

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Using X-ray microanalysis and scanning electron microscopy Zn-Ni-SiO_2 plating containing SiO_2 nanoparticles were studied. It was found that X-ray irradiation of the electrolyte leads to the increased Ni concentration in Zn-Ni-SiO_2(X) films and the grain size is also increasing (the grain size is twice that in the unirradiated case). A thickness of Zn-Ni-SiO_2(X) plating is 20 μm and a thickness of the Zn-Ni-SiO_2 plating is about 15 μm. The surface morphology was studied using AFM method. Increasing Ni concentration and Ni_5Zn_{21} phase due to X-Ray irradiation of the electrolyte leading to the improved mechanical properties of the coating.

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1. Introduction

In the last few years the introduction of nanoparticles (SiO_2, Al_2O_3, TiO_2, and the like) into electrochemical coatings contributing to their better mechanical and protective properties [1–7] has attracted a great interest. This method for modification of the properties becomes more and more involved into the industrial technologies (e.g., Zn–Ni–SiO_2 coatings are used in aerospace branches).

As shown by analysis of the relevant works [1–6], a mechanism of the coprecipitation of Zn, Zn–Ni + SiO_2 coatings is still inadequately understood. The differences in the chemical composition of the electrolyte solution, deposition conditions and parameters suggest that particles of SiO_2 are incorporated into matrices in different ways giving rise to great variations in the coating properties. The coprecipitation process is associated with hydrophilic, negatively charged particles of SiO_2 which always interact with electrolyte. Adsorption of the electrolyte ions into particles and the initial surface composition of the particles are responsible for the change inducing the formation of a double layer of the electrolyte ions around the particle. This double layer in the electrolyte is of particular importance for interactions between the particles and also between the particles and the electrode. Zn^{2+} and Ni^{2+} ions should surround the particles of SiO_2 to give them the net positive charge resulting in coprecipitation on the negatively charged cathode.

The structure and properties of Zn–Ni coatings deposited under the effect of X-ray radiation on electrolytes of different acidity have been studied in our previous work [8]. It has been demonstrated that, as compared to the nonirradiated coatings, this effect leads to better microhardness of the coatings deposited from a neutral electrolyte (pH = 7) and to lower microhardness in the case of an acid electrolyte (pH = 3), whereas with the use of a slightly acid electrolyte (pH = 4) no changes in microhardness have been observed.

The principal objective of this work is to study the effect of X-rays on the properties of Zn–Ni coatings deposited from a slightly acid electrolyte containing the nanodimensional particles of SiO_2 (sample Zn–Ni–SiO_2(X)). The coatings (Zn–Ni–SiO_2) formed without X-ray irradiation of the electrolyte represent the reference samples.

2. Experimental method

The coatings were formed from the electrolyte (pH = 4) onto the substrates of 08 structural carbon steel at the current density 2 A/dm^2. The source was an X-ray tube with a molybdenum anode ($\lambda = 0.708$ Å). Powdered SiO_2 (1 g/l) with a particle size of about 10 nm was introduced into the electrolyte of the following composition: $H_3BO_3(25) + ZnSO_4(125) + NiSO_4(75)$ (g/l).

The surface morphology of the coatings was studied using a LEO1455VP scanning electron microscope with an energy dispersive SiLi — semiconductor detector produced by Rőntec (Germany).

Diffraction patterns for the samples under study were recorded by diffractometer under Cu K irradiation using the Bragg–Brentano focusing procedure.

The Berkovich hardness H_μ was measured by means of a SHIMADZU DUH 202 dynamic ultra microhardness meter. To exclude the scale-adjusting factor, measurements of microhardness were performed at different indentation loads ($P = 0.05$; 0.10 and 0.20 H). The mean values of microhardness were obtained by 10 indentations for every load. A relative error of the measurements performed was below 6–13%. The Young modulus was estimated by the Oliver–Farr method [9].

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Tribological tests of the coatings were carried out using an apparatus in conditions of dry friction on back-and-forth motion of the tested surface under the spherical indenter made of WC8 alloy and having the curvature radius 0.5 mm ($P = 0.10$ N). The surface topography of the coatings was studied in the contact mode with the help of an NT-206 atomic-force microscope.

3. Experimental results

Photomicrographs of the coating surfaces are shown in Fig. 1. Zn–Ni–SiO_2 features a granular structure with the characteristics particle size 0.2–0.5 μm. The coatings formed when the electrolyte was subjected to X-ray irradiation exhibited a significant modification of their surface morphology: particles increased in their size coming to 0.5–1.0 μm, larger particles being formed due to coalescence of the smaller ones. The surface layer composition for Zn–Ni–SiO_2(X) coatings is distinguished by a greater content of nickel (and reduced content of oxygen) as compared with Zn–Ni–SiO_2 (Table II). As demonstrated by a qualitative X-ray phase analysis, both coatings contain Zn and Ni_5Zn_{21} (γ-phase) (Fig. 2).

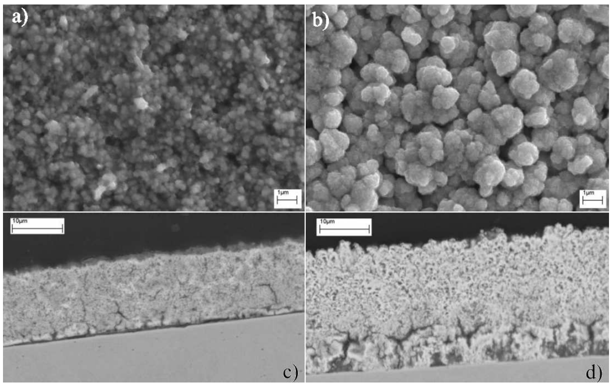

Fig. 1. Surface morphology and cross-section of Zn–Ni–SiO_2 (a, c), Zn–Ni–SiO_2(X) (b, d) coatings.

TABLE I

Physical and mechanical properties of the coatings based on Zn–Ni: microhardness (H_μ), Young modulus (E), elastic recovery (R), plasticity index (E/H), friction factor (μ), roughness R_a.

Sample	H_μ [GPa]	E [GPa]	R [%]	E/H	μ	R_a
Zn–Ni–SiO_2	0.9 ± 0.1	29 ± 6	40	32	0.3	0.2
Zn–Ni–SiO_2(X)	1.4 ± 0.1	144 ± 29	22	103	0.4	0.3

For the identical precipitation times, a thickness of Zn–Ni–SiO_2(X) coatings comes to 20 μm and that of Zn–Ni–SiO_2 is smaller by 30% (Fig. 1). The structure of the coatings is homogeneous; the cracks are observed close to the substrate to a greater extent for Zn–Ni–SiO_2(X).

It has been found (Fig. 3a) that microhardness was markedly increased ($\frac{\Delta H_\mu}{H_{\mu 0}} = 55\%$) for Zn–Ni–$SiO_2$(X) coatings. Based on the loading-unloading curves (Fig. 3b), the Young modulus E and the elastic recov-

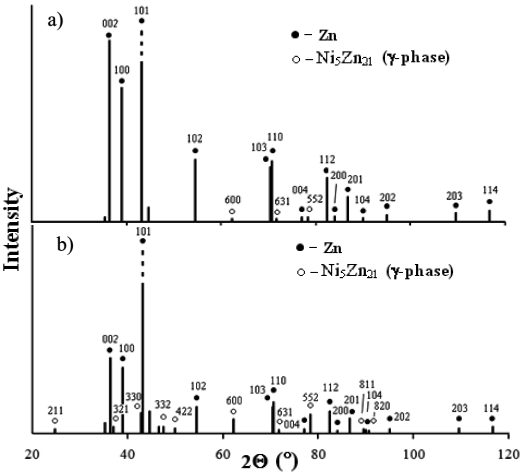

Fig. 2. Diffraction patterns of Zn–Ni–SiO_2 (a) and Zn–Ni–SiO_2(X) (b) coatings.

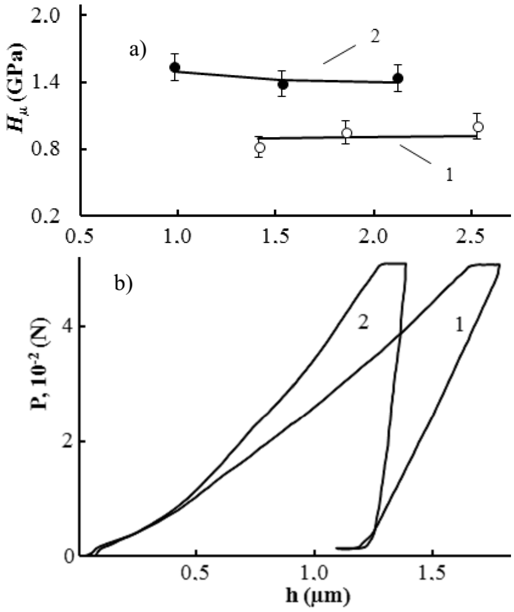

Fig. 3. Microhardness as a function of the indentation depth and loading-unloading curves for Zn–Ni–SiO_2 (1) and Zn–Ni–SiO_2(X) (2) coatings.

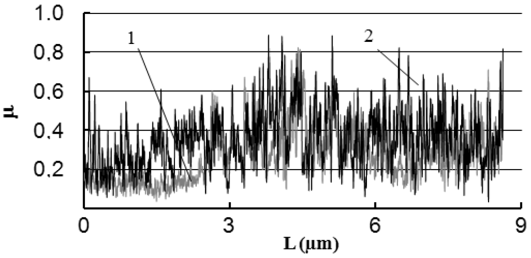

Fig. 4. Friction factor of Zn–Ni–SiO_2 (1) and Zn–Ni–SiO_2(X) (2) coatings as a function of the indenter path length.

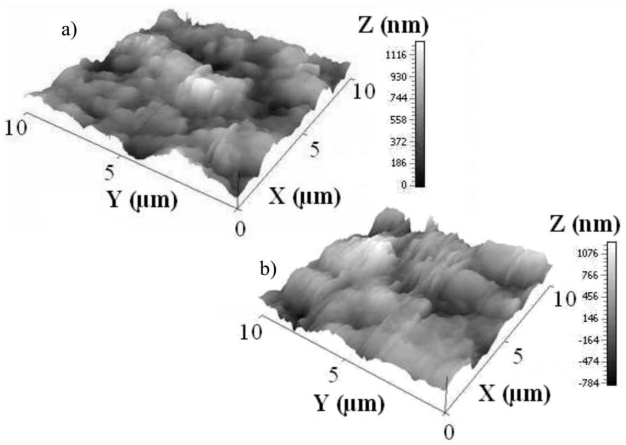

Fig. 5. AFM-images of the surface of Zn–Ni–SiO_2 (a) and Zn–Ni–SiO_2(X) (b) coatings.

ery $R = \frac{h_\mathrm{m} - h_0}{h_\mathrm{m}}$ (h_m — maximal indentation depth, h_0 — depth of the permanent indentation) were determined. The coatings Zn–Ni–SiO_2(X), as compared to Zn–Ni–SiO_2, revealed the decreased elastic recovery factor and the increased plasticity index (Table I), precisely which, along with the surface roughness, govern the wear processes. As seen from Fig. 4, in the case of Zn–Ni–SiO_2 the friction factor μ is practically invariable at the initial stage, coming to 0.1, then its value is growing over the range 0.2–0.6, and finally it becomes constant $\mu \approx 0.3$. In the case of Zn–Ni–SiO_2(X) one can observe a similar behavior $\mu = f(L)$. However, initially μ is higher and the steady-state factor is about 0.4. With the use of atomic-force microscopy, it has been found that Zn–Ni–SiO_2(X) is characterized by a more developed relief and hence by a greater roughness of the surface (Fig. 5, Table I).

4. Discussion

The observed morphological features of the coating surfaces may be associated with the fact that SiO_2 particles introduced into the electrolyte suppress stratification and precipitation of its components. In the electrolyte, silanole groups (SiOH) at the surface of particles may interact by means of hydrogen bridge compounds, creating the skeleton structure that is responsible for greater viscosity of the electrolyte [10]. As quanta of X-rays influence the electrolyte, growth of the centers may be enhanced due to radiolysis that may result in the formation of the particles intricate in their shape and having greater sizes. In other words, the effect exerted by X-rays on the electrolyte in the process of electrodeposition is similar to the increased current density.

The diffraction pattern of the coating formed in a field of X-ray radiation exhibits the intensity redistribution of diffraction lines for the phases: an intensity of Zn lines is lowered and that of γ-phase is enhanced, indicating an increase of its volume fraction due to a greater content of Ni (Table II) and contributing to the coating microhardness (Fig. 3).

It is believed that cracks in Zn–Ni–SiO_2(X) coating are caused by stresses at the interface "substrate–coating". Since such an empirical parameter as elastic recovery characterizes the coating yield point, its decreasing indicates that the coating becomes less elastic to increase the possibility of cracking [11].

The observed growth of μ for Zn–Ni–SiO_2(X) coatings, compared to Zn–Ni–SiO_2, is due to a greater surface roughness (Fig. 5). Both coating types reveal a complex character of variations in the values of μ bearing witness to adherence with subsequent peeling of the coating material in the process of indentation, the wear products falling between the rubbing surfaces and interfering with the process of friction.

TABLE II

Chemical composition of the studied coatings and powder (at.%).

Sample	Zn	Ni	O	Fe	Si
Zn–Ni–SiO_2	72.7	1.9	25.1	0.3	–
Zn–Ni–SiO_2(X)	81.7	6.3	12.0	–	–
powder	–	–	68.5	–	31.5

5. Conclusions

Under X-ray irradiation of the electrolyte containing SiO_2 particles, the deposited Zn–Ni coatings have a great content of nickel and hence a greater volume fraction of the phase Ni_5Zn_{21}, featuring the improved microhardness, Young modulus, and significant plasticity as compared to the coatings formed without X-ray irradiation of the electrolyte. The friction factor of these coatings is higher possibly due to greater surface roughness and abrasive wear.

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