

Application of pulse current for producing a strengthening composite nickel coating

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Carbon-containing nickel coatings deposited with use of pulse current from aqueous electrolyte solution comprising ultradispersed diamond particles were studied. Effect of pulse current on concentration and distribution of co-deposited nanodiamond particles through a metal substrate matrix, structure, mechanical and resistance properties of composite electrolytic coatings was analyzed. It was demonstrated that application of new generation additives, more specifically nanocarbon ones, provides opportunity for improving physicochemical properties of coatings. During pulse mode of deposition fine-grained coatings are formed with microlayer growth structure in cross section that enhance their microhardness, wear strength and corrosion resistance.

Kohlenstoffhaltige Nickelbeschichtungen, die unter Verwendung von Impulsstrom aus wässrigen Elektrolytlösungen, die ultradisperse Diamantpartikel enthalten, abgeschieden wurden, wurden untersucht. Der Einfluss des Pulsstroms auf die Konzentration und Verteilung der mit abgeschiedenen Nanodiamantteilchen durch eine Metallsubstratmatrix, die Struktur, die mechanischen Eigenschaften und die Beständigkeit von elektrolytischen Verbundbeschichtungen wurde analysiert. Es wurde nachgewiesen, dass die Anwendung von Additiven der neuen Generation, insbesondere von Nanokohlenstoffen, die Möglichkeit bietet, die physikalisch-chemischen Eigenschaften von Beschichtungen zu verbessern. Im Pulsmodus der Abscheidung werden feinkörnige Schichten mit Mikroschichtwachstumsstruktur im Querschnitt gebildet, die ihre Mikrohärtigkeit, Verschleißfestigkeit und Korrosionsbeständigkeit verbessern.

1 Introduction

Development of modern science and technology makes increased demands to intended use materials. Significant progress in this area was achieved owing to development of metal-based composite materials (CM) [1, 2]. Carbon nanostructures (CNS) such as fullerenes C60, single- and multi-wall nanotubes, onions (OLC), nanodiamonds and graphenes occupy special place among potential reinforcing materials. These products are distinguished for their high heat conductivity and electrical conduction, superelasticity and strength being close to a theoretical strength value that gives an opportunity for obtaining CM possessing unique package of physicochemical properties [2–4].

Production of CM by electrolytic method and reinforced with various CNS is governed by solution of fundamental scientific and technical challenges connected with uniformity of carbon nanomaterial distribution through electrolytic coating volume, for-

mation of strong links between CNS and matrix of substrate and coating.

Application of electrolysis in its non-steady mode represents one of the methods for improvement of composite electrolytic coatings (CEC) functional properties [5–7]. With continuous growth of interest to nanocomposite electrolytic materials reinforced with CNS not too many research and consequent technical applications are conducted and realized in this field. So, development of CNS-reinforced CEC production methods and integrated analysis of their structure and properties represent topical issues of both scientific and practical interest.

2 Materials and Methods

Electrodeposition of composite coatings on a low-carbon steel substrate was performed from sulphate nickel-plating electrolyte with the following composition: $\text{Ni}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ – 300 g/l, H_3BO_3 – 30 g/l, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ – 50 g/l at pH 5 and temperature

293...298 K. Concentration of ultradispersed diamond (UDD) in aqueous electrolyte solution made 2 g/l. Deposition was carried out with 50 Hz (f) rectangular current pulses, at interpulse period 50 (Q), pulse duration 0.4 ms and average current density 100 A/m² (j_{av}). To make comparative analysis coatings were deposited from the same electrolyte water solution with use of 100 A/m² direct current. Microstructure of nickel films was analyzed using an optical microscope „Neophot-21“. Microhardness tester PMT-3 was used to determine coatings microhardness subject to 0.196 N load application to penetrator. Samples wear was checked using a reciprocating friction test machine at frequency 0,5 s⁻¹ in conditions of dry friction against Steel 45 subject to 1.7 N load application. Friction way run in parallel to the substrate and made 0.15 m. Wear resistance was evaluated by loss of coating mass per area unit ($\Delta m/S$). Coating structure was analyzed by diffractometer DRON-2.0 with use of X-rays scintillation recording. Electron microprobe analysis of coatings was performed using a scanning electron microscope JSM-64901LV (Japan) with energy-dispersive spectrometer INCA PENTAx3 (OXFORD Instruments). UDD concentration and distribution through the coating

was evaluated via carbon (C) lines of characteristic X-ray radiation. Corrosion rate was defined by gravimetric method (through loss of metal coating mass). Samples were analyzed visually daily until display of the first indications of corrosion evaluated according to a ten-point scale.

3 Results and their discussion

Results of electron microprobe analysis and micro-level-based calculation of effective parameters for

Tab. 1: Deposition modes effect on UDD deposited particles concentration and distribution in a nickel coating

Deposition mode						
	j A/m^2	f Hz	Q	C_{UDD} mass %	S_d/S %	\bar{l} μm
DC	100	-	-	2.24	10.8	8.04
Pulse current		50	2	2.38	11.3	6.64
			25	2.66	11.9	5.89
			50	4.45	12.4	4.69

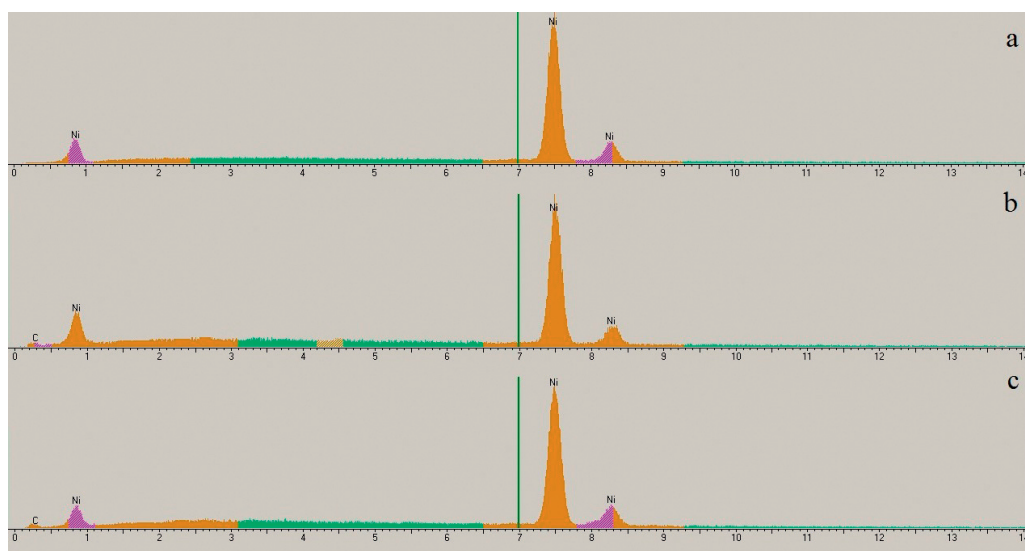


Fig. 1: Electron microprobe analysis: a: nickel coating (DC, $j = 100 \text{ A/m}^2$), b: composite nickel coating (DC, $j = 100 \text{ A/m}^2$), c: composite nickel coating (PC, $j_{av} = 100 \text{ A/m}^2$, $f = 50 \text{ Hz}$, $Q = 50$)

CEC evaluation (concentration of dispersed phase in a coating (CUDD), average distance between dispersed phase particles in the coating (\bar{l}), degree of surface fill with dispersed phase particles (ratio between

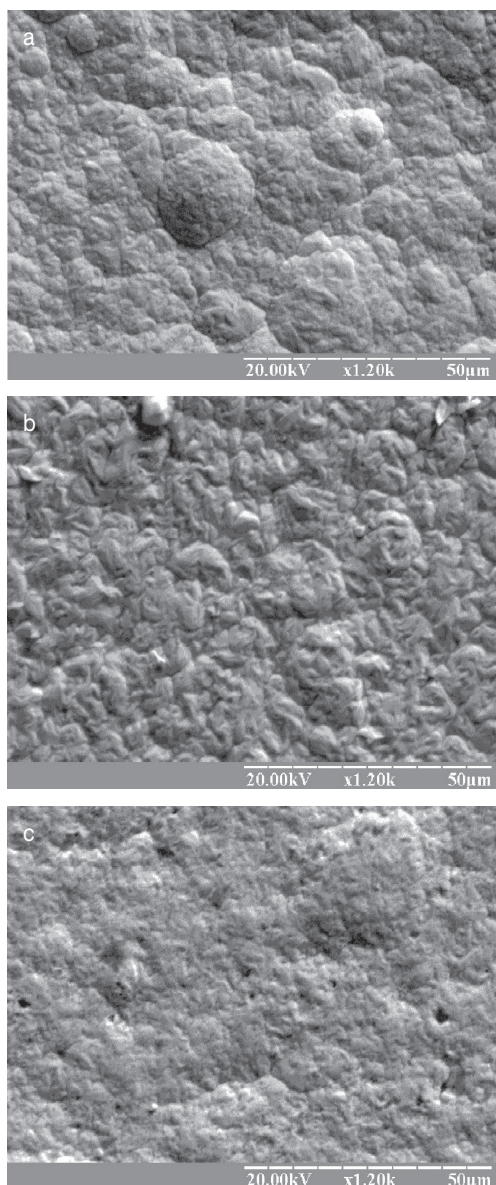


Fig. 2: SEM microphotographs of the surface: a: nickel coating (DC, $j = 100 \text{ A/m}^2$), b: composite nickel coating (DC, $j = 100 \text{ A/m}^2$), c: composite nickel coating (PC, $j_{av} = 100 \text{ A/m}^2$, $f = 50 \text{ Hz}$, $Q = 50$)

surface occupied with a dispersed phase (S_d) and surface across which particles are distributed (S) are shown in Figure 1 and presented in Table 1.

It was found out that composite nickel coatings deposited with use of pulse current were characterized with the more uniform and higher UDD particles distribution density across a coating; degree of surface filling with UDD particles was two times higher than for DC-deposited composite nickel coatings.

Analysis of nickel coatings microphotographs (Fig. 2) made with use of scanning electron microscope (SEM) discovered that dimensions of coating grains vary depending on deposition conditions. Examination of the coating fine structure showed decrease of size of DC-deposited pure nickel crystalline grains from 100 nm (Fig. 2a) to 65 nm for pulse current-deposited composite nickel coatings (Fig. 2b) [8, 9].

Corrosion test results are shown in Figure 3. It is necessary to note that corrosion rate of tested samples was uniform. However, mass variation of PC-deposited carbon-containing nickel coatings within 144 hours runs more slowly as compared to DC-deposited coatings. When 144-hour period elapsed corrosion reached very low steady-state rate, and along with this mass of PC-deposited coatings was not reduced within 96-hour period as compared to DC-deposited coatings owing to increase of interlamellar boundaries in which UDD particles are located. Results of corrosion resistance analysis enable to rate DC-deposited nickel coatings as “Stable” with 4 score points, whereas application of pulse deposition mode provides obtaining of composite nickel

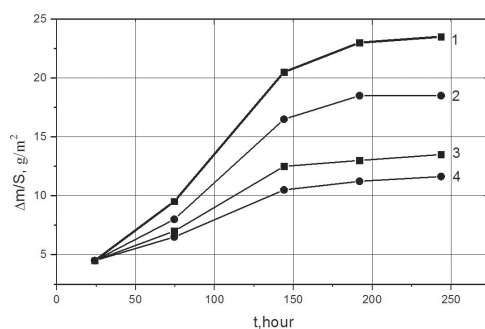


Fig. 3: Mass variation of nickel electrolytic coatings: 1: without nanodiamonds, DC; 2: without nanodiamonds, PC; 3: with nanodiamonds, DC; 4: with nanodiamonds, PC

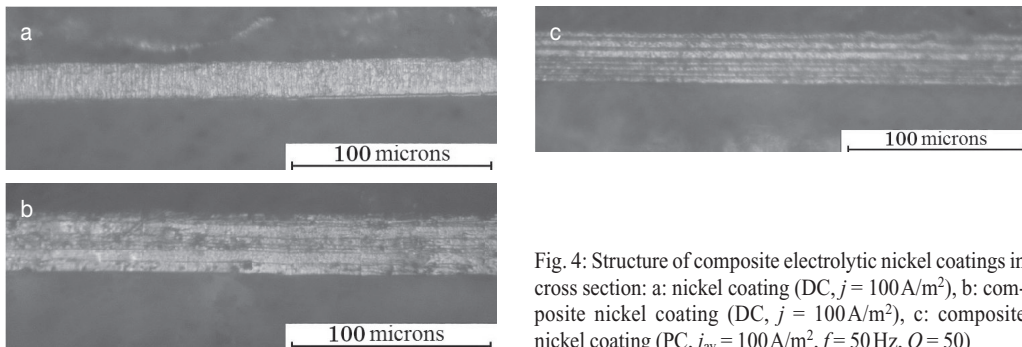


Fig. 4: Structure of composite electrolytic nickel coatings in cross section: a: nickel coating (DC, $j = 100 \text{ A/m}^2$), b: composite nickel coating (DC, $j = 100 \text{ A/m}^2$), c: composite nickel coating (PC, $j_{\text{av}} = 100 \text{ A/m}^2$, $f = 50 \text{ Hz}$, $Q = 50$)

Tab. 2: Deposition modes effect on mechanical and resistance properties of nickel and carbon-containing nickel coatings

Deposition mode		j	f	Q	$H\mu$	Average wear,	Average corrosion penetration,	Number of pores per
		A/m^2	Hz		MPa	mg/hour	mm/year	1 cm^2
DC			-	-	1,800	1.8	0.011 ... 0.014	24
Pulse current	100		50	50	3,200	0.6	0.005 ... 0.010	10

coatings which can be rated as “Very Stable” with 3 score points. First of all, it is caused by UDD particles passivating effect on cathodic surface that results in changing a coating growth structure in a cross section (Fig. 4a) from columnar structure to microlayer structure (Fig. 4b); and in the second it is specified by high instantaneous current density in pulses that promotes more intensive UDD particles penetration into a deposited coating.

Formation of more fine-crystalline CEC and change of growth structure in cross section from columnar structure to microlayer structure in conditions of pulse deposition mode governed increase of mechanical and resistance properties of carbon-containing nickel coatings (coating microhardness increase by 75–77%, wearing and porosity decrease in 3 and 2.4 times respectively) (Tab. 2).

4 Conclusions

1. Application of pulse deposition mode promotes increase of UDD particles concentration in composite nickel coatings from 2.24 to 4.45 mass percentage that results in formation of higher dispersed structure: crystalline grains size goes down from 104 nm to 65 nm.

2. UDD particles introduction into a nickel coating results in changing the growth structure in cross section from columnar structure to microlayer structure which is caused by passivating effect of dispersed phase particles on emerging surface. Decrease of microlayers thickness from $4 \mu\text{m}$ to $2 \mu\text{m}$ indicates increase of UDD particles speed of approach to surface and more uniform distribution of particles in cross section of pulse-deposited coatings.

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