Codeposition of ultrafine WC particles in Ni matrix composite electrocoatings

M. Stroumbouli, P. Gyftou, E.A. Pavlatou*, N. Spyrellis

Laboratory of General Chemistry, School of Chemical Engineering, National Technical University of Athens, 9, Heroon Polytechniou Str., Zografos Campus, Athens GR-15780, Greece

Abstract

The electrolytic codeposition of ultrafine WC particles (mean diameter of 0.2 μm) from an additive-free nickel Watts' solution by applying both direct (DC) and pulse (PC) electroplating, has been investigated. Electrodeposition of Ni/WC composites was carried out on a rotating disk electrode (RDE) at various rotation velocities. The effect of type current and hydrodynamic conditions of the plating bath on the codeposition of WC particles with Ni matrix has been reported. The crystallographic orientation of nickel matrix, the distribution and the percentage of the embedded particles, were examined as well as the structure and the surface morphology of the produced composite coatings. It was found that electrodeposits prepared at DC conditions and low rotation velocities are highly porous. On the contrary, when applying PC conditions and high rotation velocities, compact deposits with high concentration of embedded WC particles and uniform distribution were produced. It has been observed that the presence of WC particles in the metal matrix imposes an almost random orientation of Ni crystallites along with a reinforcement of [210] orientation. Taking into consideration a surface complexation model and the experimental data, a mechanism of nickel electrocrystallization in the presence of WC particles has been proposed.
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1. Introduction

Composite electroplating is a method of codepositing micron- or submicron-sized particles of metallic, non-metallic compounds or polymers with a metal or alloy matrix. During the last decades, the main work carried out in this field is aimed almost entirely to the production of wear- and corrosion-resistant coatings, self-lubricating systems and dispersion-strengthened coatings [1–4]. In particular for nickel matrix electrodeposits, a great variety of particles have been used such as hard oxides SiO_2 [5,6], Al_2O_3 [7,8], ZrO_2 [5], TiO_2 [8], particles of SiC [5,6,9–11], liquid containing polymeric microcapsules [12,13], carbon nanotubes [14], etc. With the increasing availability of submicron

particles, the interest of the low-cost and low-temperature composite electroplating is continuously growing, with major challenge in the achievement of a high level of codeposition of the particles.

Although electrodeposited composites containing WC particles are frequently mentioned in literature reviews, only limited studies are available concerning the production of Ni/WC composites [15–18], the oxidation resistance of Ni/WC composites [16], and the tribological performance of CoNi/WC and CoNiP/WC coatings [19]. In general, it has been observed that the produced WC composite coatings from additive-free electrolytic baths are full of defects, giving rise to porous deposits [15,19]. On the contrary, nickel-based WC composites have been produced by other techniques, like high velocity oxygen fuel (HVOF) [20], thermal spraying [21], plasma spraying [22], hot isostatic pressing [23] and combination of physical and chemical vapor deposition [24].

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* Corresponding author. Tel.: +30 210 7723110; fax: +30 210 7723088.
  E-mail address: pavlatou@chemeng.ntua.gr (E.A. Pavlatou).

Fundamentally, the electrocodeposition process and hence the structure, the morphology and the properties of the composite coatings is affected by the electrodepostion parameters like the electrolysis conditions (composition and agitation of the electrolytic bath, presence of additives, temperature, pH), the current conditions (values of current density and type of current) and the reinforcement properties (type, size, shape, concentration and dispersion in the bath) [3,9,11,13,25–27]. Several studies have proved that the application of pulse current (PC) technique in nickel electroplating results to the production of composite deposits with enhanced mechanical properties, higher percentages of incorporation and more uniform distribution of the particles in the metallic matrix than those attained by direct current (DC) technique [10–13,28–30].

In the present study, the electrolytic codeposition of submicron-sized WC particles and Ni from an organic free nickel Watts' solution by applying both direct and pulse electroplating, was investigated. The effects of type current and hydrodynamic conditions of the plating bath on the codeposition mechanism of WC particles with Ni matrix have been reported. The distribution and the percentage of the embedded particles in the metal matrix were examined as well as the microstructure of the produced composite coatings. Based on the experimental findings, a possible electrocrystalization mechanism of nickel in the presence of WC has been discussed.

2. Experimental

Ni/WC composites were electrodeposited from an organic free Watts' nickel electrolyte with suspended ultrafine WC particles. The composition of the plating solution, as well as the plating parameters, is given in Table 1. WC particles purchased from OMG Americas were used without any pretreatment and maintained in the electrolytic bath in

suspension by continuous magnetic stirring with a rate of 250 rpm for at least 24 h before deposition. The concentration of the WC particles was 20 g/l. The electrolyte temperature was maintained by water circulation at a thermostated value of 50 °C, and the pH of the solution was adjusted to a constant value of 4.4 by appropriate additions of H_2SO_4 or NH_3 solutions. The same rate of magnetic stirring was also employed during electrodeposition at the cell bottom in order to maintain a uniform concentration of particles in the bulk solution. Nickel cylindrical plate of 99.9% purity was used as an anode and a standard calomel electrode served as a reference electrode.

Electrodeposition of the Ni/WC composites was carried out on a rotating disk electrode (RDE) with various rotation velocities (ω) in the range of 200–1200 rpm, under direct and pulse current conditions. Both types of current electrodeposition were performed with a current density of 7 A/dm^2 using a Wenking ST 88 potentiostat and a Wenking DPC 72 pulse generator. In the present study, the two additional parameters introduced in pulse plating, the frequency (v) and the duty cycle (d.c.) of the imposed pulses [i.e., d.c.=$T_{on}/(T_{on}+T_{off})$, where T_{on} is the time period the pulses are imposed and T_{off} is the relaxation time], were set at the values of 0.1 Hz and 50%, respectively. The substrates were brass discs with a total surface area of 0.05 dm^2, which were mechanically polished and chemically cleaned before deposition. In order to remove the loose adsorbed WC particles from the surface, ultrasonic cleaning of each composite deposit took place for 5 min, after the electrodeposition. The thickness of the produced electrodeposits was in the range of 60–150 μm.

Scanning electron microscopy (SEM) was applied in order to study the structure, morphology and composition of the surface and the cross-sectional profile of the Ni/WC composites. The concentration of WC particles on the surface as well as on the cross-section of the deposits was evaluated by using energy dispersive X-ray spectroscopy

Table 1
Experimental conditions for the preparation of Ni/WC composite electrodeposits

Solution composition	
Electrolyte (Watts)	
$NiSO_4 \cdot 7H_2O$	300 g/l
$NiCl_2 \cdot 6H_2O$	35 g/l
H_3BO_3	40 g/l
WC powder (mean diameter of 0.2 μm)	20 g/l

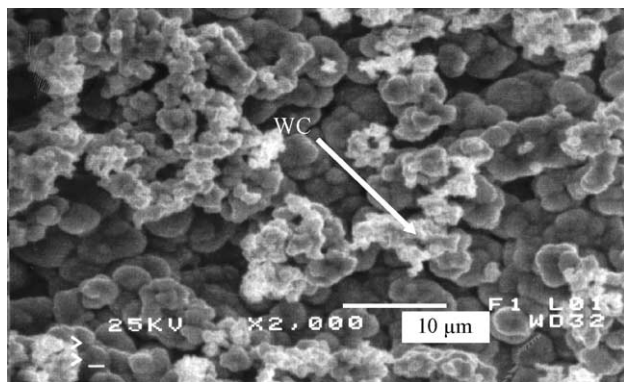| Electrodeposition conditions	
pH	4.40
Temperature (°C)	50
Substrate	brass discs (diameter 25 mm)
Cathode's rotation velocity ω (rpm)	200, 400, 600, 800, 1000, 1200
Agitation of electrolyte	Magnetic stirring (250 rpm)
Current density	7 A/dm^2
Type of current	Direct (DC) and Pulse (PC)
Duty cycle (d.c. %)	50%
Pulse frequency (v)	0.1 Hz

Fig. 1. SEM micrograph presenting the surface morphology of the Ni/WC deposit prepared under DC conditions at cathode rotation velocity of ω=200 rpm.

(EDS). The domain of EDS analysis was a region of 150×100 μm and the determined concentration of codeposited particles WC with Ni resulted from the mean value of at least three measurements along the radius of the disk. The preferred crystalline orientation of the nickel was examined by applying X-ray diffraction (XRD) technique. The diagrams were obtained using a Cu K_α radiation on a Siemens D-5000 diffractometer.

3. Results and discussion

3.1. Composite coatings prepared under DC conditions

A typical microstructure of the surface of the Ni/WC composites prepared under DC conditions at ω=200 rpm is presented by the SEM micrograph in Fig. 1. The overall appearance is representative of an "open-like" structure consisted of WC particles (gray-colored areas) arranged on the Ni crystallites (dark-colored areas) that a "cauliflower" surface morphology is evident. It should be noticed that the EDS spot analysis on the gray particles revealed a spectrum with a high content of tungsten and small amounts of nickel. In spite of the submicron size of used WC particles, many agglomerates of WC are observed.

Representative SEM micrographs of the cross-sectional profile of the composites are depicted in Fig. 2, in which a highly porous structure is revealed. The produced coatings prepared under DC conditions present a structure full of voids and a "dendrite-like" Ni crystal growth, containing considerable amounts of WC particles, is apparent. Moreover, the deposits exhibit a rather rough surface. The estimated cooperation percentages of WC particles in these deposits are 12 and 4.8 wt.% for the surface and cross-section of composites, respectively. The distribution of the WC particles in the Ni matrix is fairly uniform with areas of agglomerated particles (Fig. 2b). Moreover, it seems that in the first few micrometers of deposit growing, only Ni is exclusively deposited on the substrate, and since the first WC particles are embedded in the metal matrix the "dendrite-

like" growth of Ni crystals is motivated, and progressively larger amounts of WC particles are codeposited with Ni (Fig. 2b). It is noteworthy, that such kinds of structures have been also reported in CoNi/WC electrodeposits produced with the use of electrolytes without surfactant [19].

The XRD patterns of the Ni/WC deposit prepared in the regime of DC as well as the corresponding of the used tungsten carbide powder are illustrated in Fig. 3a and b, respectively. The presence of the WC particles in the Ni matrix is also confirmed by the presence of the most intense diffraction lines of the used powder. It is apparent that the embedding of WC particles in the metal matrix leads to an almost random orientation of Ni crystallites in the composites, while in the case of the pure Ni deposition, prepared at the same experimental conditions, a high quality [100] preferred orientation is revealed [31]. It should be noticed that the [100] texture mode of crystal growth is considered as free from inhibiting chemical species [32]. Apparently, the
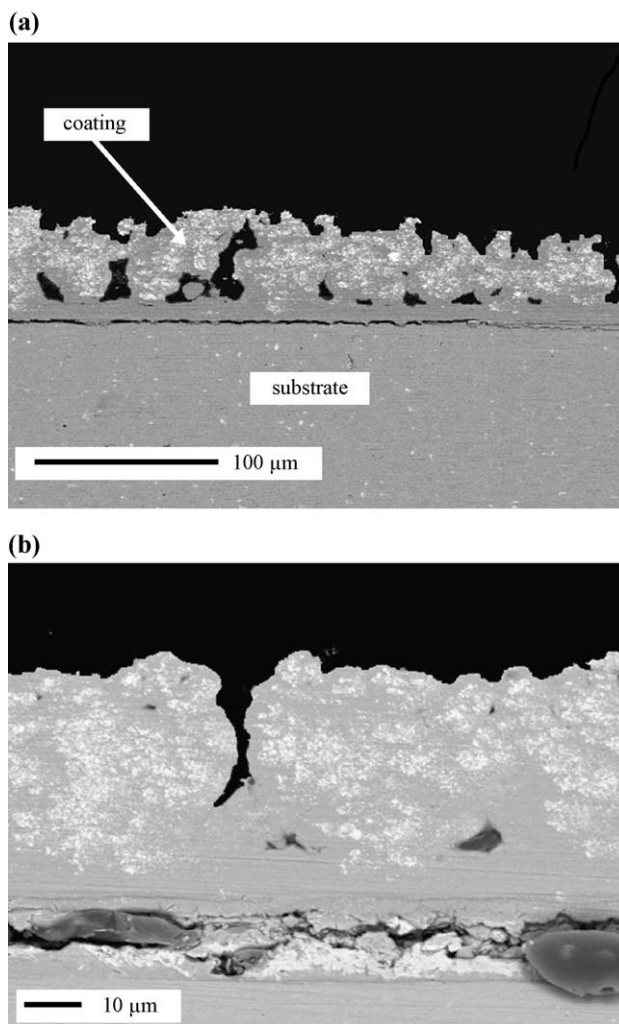

Fig. 2. (a) Backscattered SEM micrograph of the cross-section of the Ni/WC deposit prepared in the DC regime at cathode rotation velocity of ω=200 rpm, showing a highly porous structure. (b) Detail view of the deposit presenting the uniform distribution of WC particles in Ni matrix.
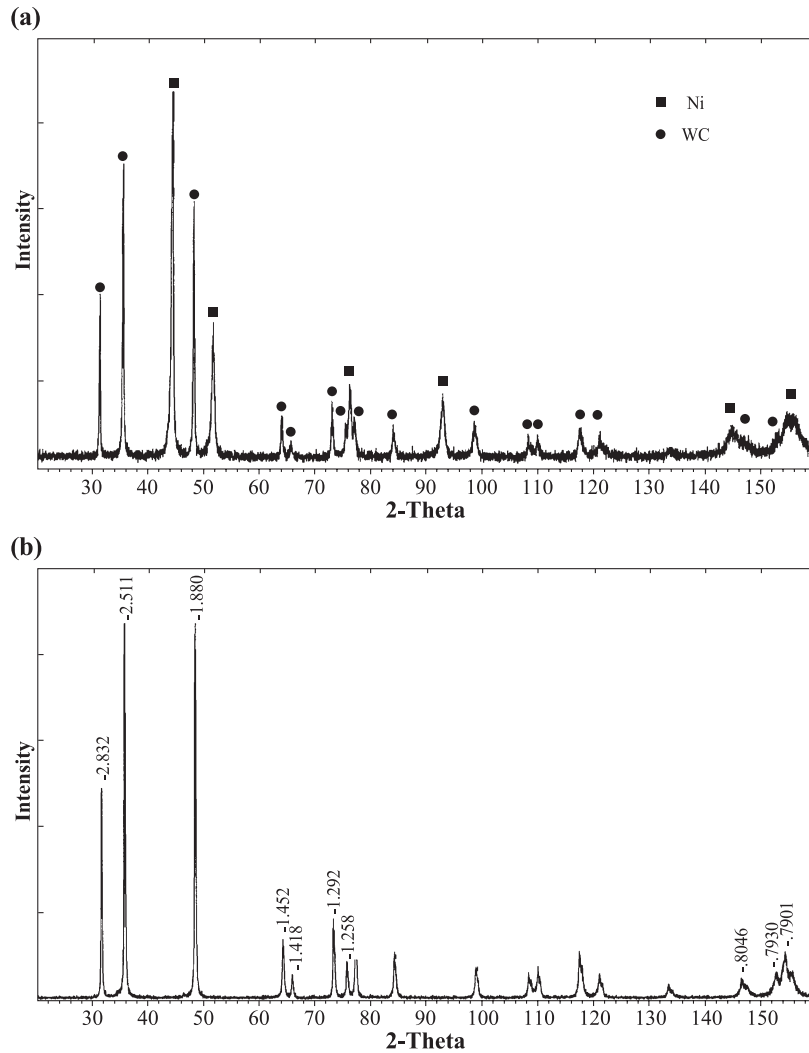
(a)

(b)

Fig. 3. (a) XRD diagram of the Ni/WC composite coating prepared under DC conditions and at cathode rotation velocity of 200 rpm. (b) XRD diagram of the as-received WC powder.

simultaneous embedding of the WC ultrafine particles in the matrix perturbs significantly the "free" mode Ni crystal growth. Thus, the codeposition of WC particles modifies the adsorption–desorption phenomena occurring on the metallic surface that results in change of the catholyte composition. This alteration exerts a much more intense inhibition to the

Ni crystal growth, which leads to the formation of micro-crystalline and almost random oriented deposits.

Although the Ni crystallites are almost random oriented, a careful analysis of the intensities of the diffraction lines (Table 2) shows that there is a slight reinforcement of the [210] orientation, as denoted by the enhanced intensity of the line correspondent to [420] orientation. It should be noticed that the [210] texture, which is attributed to the presence of molecular hydrogen in the catholyte area during the cathodic process, has not been observed at pH higher than 3.0 [33]. Hence, the reinforcement of the [210] texture could be correlated with the enhanced production of molecular hydrogen during the electrocodeposition process, due to the presence of WC particles in the metal matrix.

3.2. Composite coatings prepared under PC conditions

Composite Ni/WC coatings were produced also under PC conditions, i.e., $v = 0.1$ Hz and d.c.=50%, at different

Table 2
X-ray diffraction data of the Ni/WC deposits prepared under DC conditions at $\omega = 200$ rpm in comparison with the standard diffraction data of Ni powder

[hkl]	Ni powder		Ni/WC deposit	
	d (Å)	$[I/I_o]_{[hkl]}$	d (Å)	$[I/I_o]_{[hkl]}$
111	2.0338	100	2.0390	100
200	1.7617	42	1.7646	34
220	1.2461	21	1.2471	19
311	1.0625	20	1.0631	18
400	0.8810	4	0.8836	5
420	0.7880	15	0.7890	22

rotation rates of the RDE. A typical SEM micrograph on the surface of a Ni/WC composite prepared in pulse regime is depicted in Fig. 4. The comparison of Figs. 1 and 4 indicates that the "cauliflower" surface morphology is preserved, although a more coherent structure is revealed. Additionally, the concentration of WC embedded particles is higher than those observed for coatings prepared under DC conditions.

Therewithal, a considerable improvement regarding the quality of deposits is disclosed with application of PC in relation with those obtained by DC electrodeposition, as shown in Fig. 5. There is a continuous amelioration as the rotation velocity of the RDE is increased. The produced deposit at ω=200 rpm presents a great number of pores (Fig. 5a), but less than those observed under DC conditions (Fig. 2). At ω=800 rpm, the deposit becomes rather compact (Fig. 5b) and eventually, at ω=1200 rpm (Fig. 5c) the pores have vanished and thus the produced deposit could be characterized in whole compact. The formation of the pores could be attributed to the simultaneous production of molecular hydrogen on the cathode. It seems that two synergistic phenomena facilitate the removal of the generated hydrogen and are responsible for the elimination of pores: increasing values of rotation velocity of RDE by shear agitation and the application of pulse current that permits the removal of the hydrogen during the relaxation time of the induced pulses.

Concerning the distribution of the embedded WC particles in the Ni matrix, the amelioration is prominent in comparison with deposits produced under DC regime (Fig. 2b), as depicted in Fig. 6. A homogeneous dispersion of WC particles in the Ni matrix is observed for all deposits prepared under PC conditions and consequently a considerable improvement of the mechanical properties could be expected.

The variation of percentage of the codeposited WC particles on the surface and the cross-section of the deposits, as a function of the RDE velocity is presented in Fig. 7a and b, respectively. The obtained curves present maxima at certain values of rotation velocity. Apparently, the highest
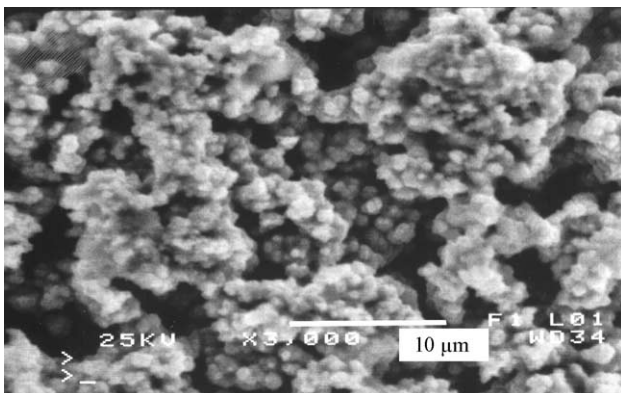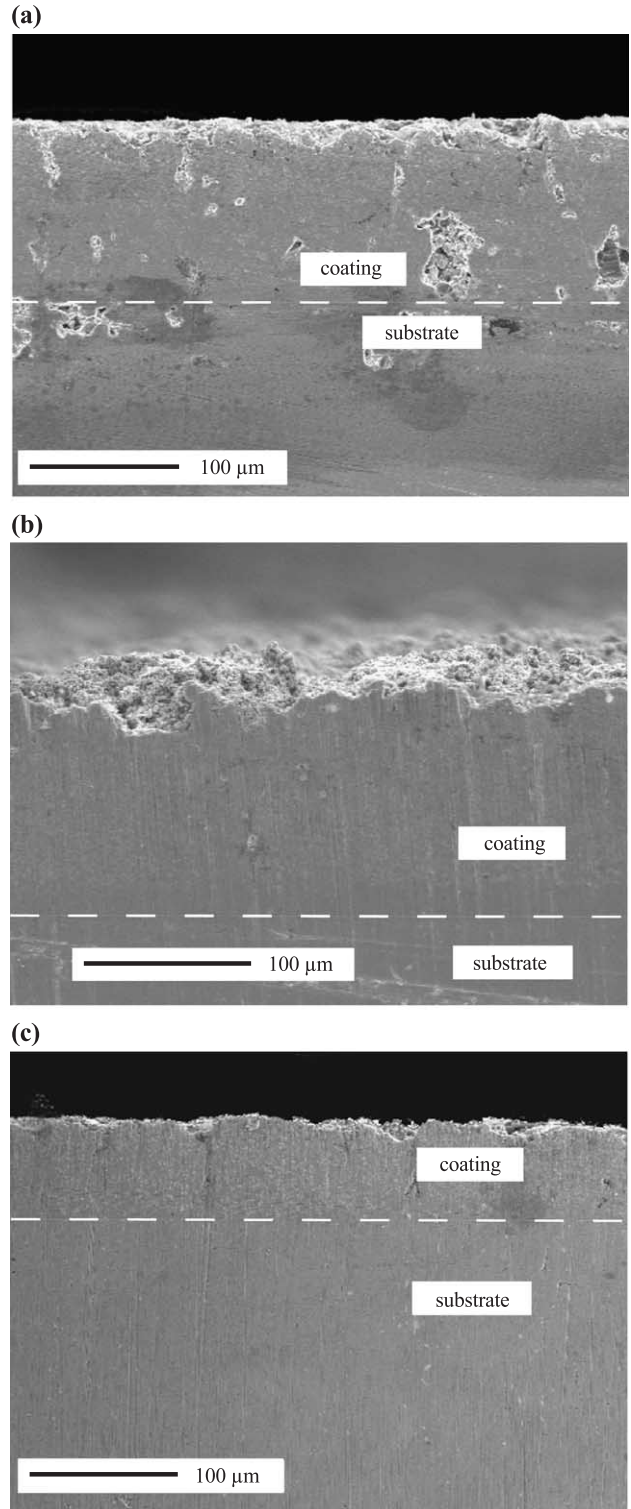
(a)

(b)

(c)

Fig. 5. SEM micrographs presenting the cross-sectional profile of the Ni/WC deposits prepared under PC conditions at cathode rotation velocity of (a) 200 rpm, (b) 800 rpm and (c) 1200 rpm.

Fig. 4. SEM micrograph presenting the surface morphology of the Ni/WC deposit prepared under PC conditions and at cathode rotation of ω=600 rpm.

percentage of embedded WC particles in the Ni/WC coatings—33 wt.% on the surface and 8 wt.% on the cross section of the deposit—is achieved by the imposition of pulse electrodeposition using a RDE with rotation velocity
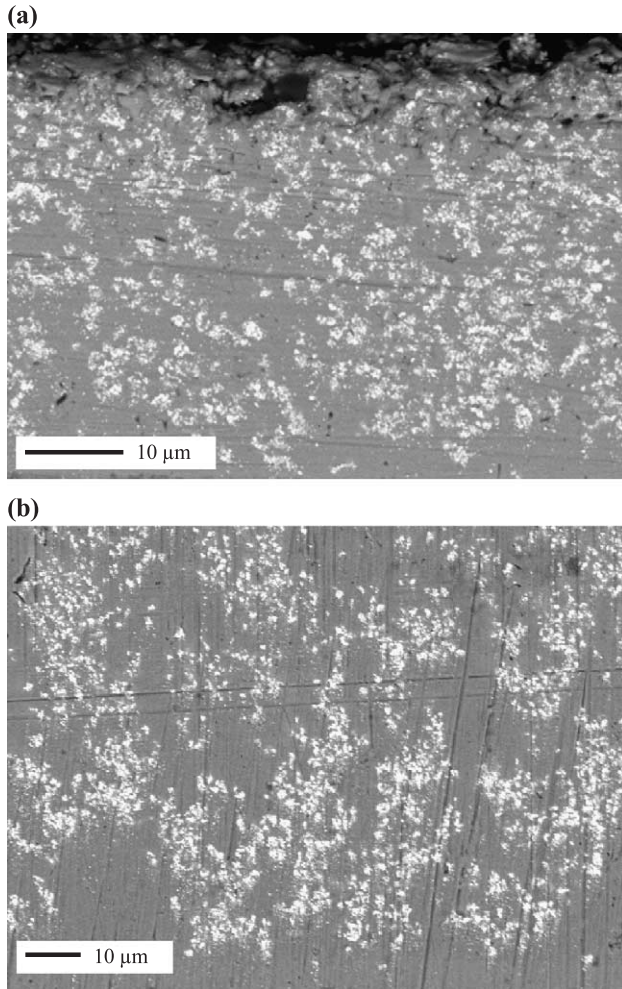
(a)

(b)

Fig. 6. Backscattered SEM micrographs of the cross-profile of the Ni/WC deposits prepared in the PC regime at cathode rotation velocity of (a) 200 rpm and (b) 1200 rpm showing a rather uniform distribution of WC particles in the Ni matrix.

in the range of 600–800 rpm. The reported difference between the percentage of embedded particles on the surface and in the bulk might be correlated with the fact that a number of loose attached particles on the surface are removed and not engulfed in the metal matrix. In general, as the rotation velocity is increased, a beneficial effect on the particle incorporation is revealed, which might be attributed to an increased convective flow towards the disc electrode. On the other hand, the codeposition percentage tends to decrease at very high rotation velocities. In this case, intense radial flow tends to remove the attached particles before they become engulfed in the metal matrix. In the pulse electrodeposition, it appears necessary to control the hydrodynamic conditions of the electrolytic bath, in order to obtain a homogeneous and compact composite coating.

The XRD data of the Ni/WC coatings prepared by pulse electrodeposition at various rotation velocities of RDE are listed in Table 3. A rather random orientation of Ni crystallites is observed for these composite coatings along
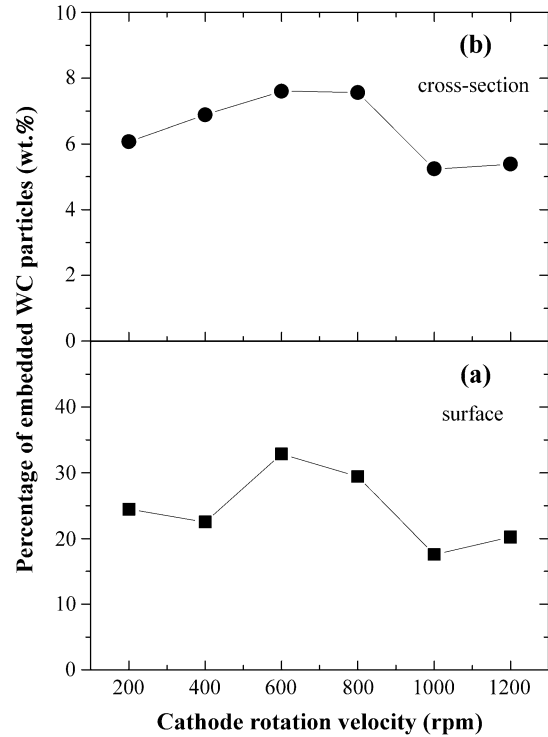

Fig. 7. Dependence of percentage of embedded WC particles (a) on the surface and (b) on the cross-section of the composite coatings.

with a reinforcement of the [210] line. In the case of deposits prepared at ω=200 rpm, this reinforcement is clear and much more pronounced than in the case of deposits produced at higher velocities. This effect could be related to the presence of pores observed in the first deposit (Fig. 5a). An enhanced local production of molecular hydrogen provokes the formation of these pores. Moreover, the presence of molecular hydrogen influences the crystal growth of neighboring nickel crystallites and imposes on those the [210] preferential orientation. On the contrary, the lack of pores in the rest deposits (Fig. 5b and c) indicates the minimization of local production of molecular hydrogen and consequently, the quantity of Ni crystallites oriented along [210] axis is slightly higher than those corresponding to randomly oriented deposits.

Table 3
X-ray diffraction data of the Ni/WC deposits prepared under PC conditions at various rotation velocities of RDE in comparison with the standard diffraction data of Ni powder

[hkl]	Ni/WC, ω=200 rpm		Ni/WC, ω=1200 rpm		Ni powder	
	d (Å)	$[I/I_o]_{[hkl]}$	d (Å)	$[I/I_o]_{[hkl]}$	d (Å)	$[I/I_o]_{[hkl]}$
111	2.0358	100	2.0299	100	2.0338	100
200	1.7615	42	1.7590	30	1.7617	42
220	1.2467	28	1.2453	22	1.2461	21
311	1.0630	26	1.0620	19	1.0625	20
400	0.8817	16	0.8869	10	0.8810	4
420	0.7878	46	0.7892	19	0.7880	15

3.3. Mechanism of nickel electrocrystallisation in the presence of WC particles

WC is thermodynamically unstable and is oxidized in the presence of water or oxygen at room temperature. XPS studies [34,35] showed that the as-received WC powder is oxidized on the surface, and the oxidized surface layer mainly consists of WO_3. Electrophoretic measurements of WC powder in aqueous solutions [35] showed that in the pH range of 3–11, the zeta-potential of the powder is highly negative. This behavior is typical of an acidic oxide with a very low isoelectric point. The WO_3 could be hydrated and –OH groups dominate the surface. These surface groups can result in a negative surface charge according to the reaction:

$$\equiv W - OH \Leftrightarrow \equiv W - O^- + H^+ \tag{1}$$
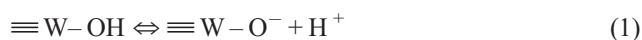
Adopting a surface complexation model reported in the literature [35,36], surface complexes could be formed at the interface of WC particles in a Ni^{+2} acidic aqueous solution, by a reaction such as:

$$\equiv W - OH + Ni^{+2} + Cl^- \Leftrightarrow \equiv W - O \cdot Ni^+ Cl^- + H^+ \tag{2}$$
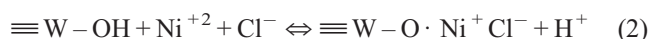
This specific adsorption of Ni^{+2} on the WC particles consequently creates discrete areas with high concentration of Ni^{+2} on the particles and H^+ in the particles' area vicinity. Thus, the adsorption of Ni cations facilitates their reduction and considering the local high nickel concentration it could explain the "dendrite-like" crystal growth of nickel. On the other hand, the massive reduction of H^+ in the discrete areas of H^+ with high concentration elucidates the formation of pores in composites prepared under DC conditions and at low rotation velocity of the cathode. Moreover, this intense reduction of H^+ provokes the alkalization of the catholyte and eventually the precipitation of $Ni(OH)_2$, which in turns imposes the random oriented crystal growth of nickel [25,32]. In parallel, the abundant production of molecular hydrogen imposes in several nickel crystals the [210] orientation [33].

The observed amelioration regarding the quality of deposits prepared under pulse plating conditions could be attributed to the accomplished homogeneity of the solution in the catholyte area, which is achieved during the relaxation time. In addition, the increasing of rotation velocity of RDE leads to a similar effect. Hence, compact deposits without pores are produced under both pulse plating conditions and high rotation velocities.

4. Conclusions

Ni matrix composite electrocoatings containing ultrafine WC particles were produced under direct and pulse current conditions from an additive-free nickel Watts' type bath. It has been shown that deposits prepared in direct regime are highly porous with a fairly uniform distribution of WC particles in the nickel matrix. On the contrary, the application of pulse plating regime joint with the increase of cathode's rotating velocity, improves the quality of Ni/WC deposits by decreasing the number of pores and achieving dense deposits with higher amounts and uniform distribution of WC particles in the metal matrix. Under pulse current conditions and at rotation velocity of the cathode in the range of 600–800 rpm, the embedding particle percentage attains the value of 8 wt.% in the bulk of the deposits and the number of pores is drastically decreased. At 1200 rpm, the percentage of incorporated particles of WC is 5.5 wt.% and the pores are almost vanished and hence, compact deposits are produced. Moreover, it has been observed that the embedding of WC particles in the metal matrix leads to an almost random orientation of Ni crystallites in the composites along with a reinforcement of [210] orientation.

A mechanism of Ni electrocrystallization in the presence of ultrafine WC particles is proposed. Adopting a surface complexation model, a specific adsorption of Ni^{+2} on the WC particles turns up, which creates discrete discharging areas of nickel and hydrogen cations. That comprises an attempt to explain the "dendrite-like" crystal growth of nickel, the formation of pores and the observed crystalline orientation in composite coatings. The application of pulse plating and the increasing of rotation velocity of the cathode contribute to the homogeneity of the electrolytic solution in the catholyte area, which leads to the production of compact composite coatings without pores.

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