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ORIGINAL PAPER

Pulse electrodeposition of Ni/nano-TiO_2 composites: effect of pulse frequency on deposits properties

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Abstract Pure and composite nickel deposits containing nano-TiO_2 particles ($d_m = 21$ nm) were produced under direct-DC and pulse current-PC conditions. The influence of pulse frequency on the codeposition of TiO_2 particles, preferred orientation of Ni crystallites and grain size, as well as microhardness of the composites, was investigated systematically. Composites prepared in PC regime displayed higher incorporation percentage than those obtained under DC conditions, and the highest incorporation rates were achieved at pulse frequencies $v > 100$ Hz. The application of pulse frequency accompanied by the embedding of TiO_2 nanoparticles in the nickel matrix resulted in a strong influence upon the crystalline orientation, the grain size and the corresponding microhardness. All composites exhibited higher microhardness values compared to the pure deposits, independent of the applied current conditions. Overall, when ascribing the observed strengthening effect of composites, not only grain refinement and dispersion strengthening mechanisms but also preferred crystalline orientation should be taken into consideration.

Keywords Electrodeposition · Pulse frequency · Ni/nano-TiO_2 composites · Texture · Crystalline size · Microhardness

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1 Introduction

Electrolytic codeposition is widely used for preparing metal matrix composite coatings in micro to nanodimensions as a low cost and versatile process [1]. In the last years, a lot of study has been performed on the TiO_2 codeposition process, with matrices as Cu [2, 3], Ag [2, 3] and Zn [4, 5]. Specifically, TiO_2 particle-reinforced Ni composite electrodeposits exhibit improved mechanical properties [6–12], accompanied by an interesting photoelectrochemical [3] and electrocatalytical behaviour [13]. Moreover, literature survey has revealed that the incorporation of nano-sized TiO_2 particles into the nickel matrix, under direct current (DC) electrodeposition, leads to the formation of finer structures with reduced grain size [12, 14, 15], decreases the residual tensile stresses [12], increases the hardness [6–12], wear [9–12] and corrosion resistance [6, 10, 12] of the coatings, compared to pure Ni electrodeposits, although controversial results have been reported concerning corrosion resistance [8].

However, only few scientists have examined the textural modifications induced by the presence of TiO_2 particles in the Ni matrix [14, 15], and have attempted to correlate them with the structural and mechanical properties of the coatings. For example, Lampke et al. have made an effort to relate the microhardness of Ni/TiO_2 composites, prepared under DC conditions, with the observed metal matrix textures, and concluded that the hardness is highest when the nickel grains are aligned in a columnar way [8]. Moreover, it has been demonstrated that the presence of TiO_2 nanoparticles in the deposits favours the predominance of [100] texture of the nickel matrix over an extended region of electrodeposition conditions. In addition, TiO_2 embedding leads to the confinement of the [211] and [110] preferred orientation domains and to the transformation of [210] to a random oriented crystalline growth. It has been proposed that during electrodeposition H^+ adsorption/desorption phenomena on the titania surface take place, depending on the pH of the electrolyte, while inhibition of particular chemical species (i.e. $Ni(OH)_2$, H_{ads} and H_2) is occurring, resulting to the imposition of specific modes of nickel crystal growth [14].

Pulse current (PC) deposition is a powerful means of perturbing the adsorption–desorption phenomena occurring at the nickel cathode/electrolyte interface (catholyte), and hence the electrocrystallization process, offering the opportunity to control the structure and the properties of the produced deposits [16–18]. The rather complex perturbation of nickel growth provoked by pulse plating could be summarised as follows: (a) medium perturbations allow the adsorption/desorption of interfacial inhibitors, such as H_2 or $Ni(OH)_2$, and (b) large perturbations lead to the appearance of the [110] mode of growth, which is attributed to a severe growth inhibition due to the presence of H_{ads} [17].

In the case of Ni/particles co-deposition, the application of pulse current techniques results to the production of composite coatings with higher percentages of particle incorporation, reduced grain sizes and a more uniform distribution of particles in the Ni matrix, than those attained under DC regime. Pulse plating has yielded many nickel matrix composites, such as Ni–SiC [19, 20], Ni–Al_2O_3 [21, 22], Ni–ZrO_2 [23], Ni–WC [24] and Ni–diamond [25]. It is worth to be mentioned that relatively less research study has been done in the field of quantitative texture analysis of composite nickel electrodeposits under various PC conditions [11, 19, 24, 26]. Specifically, concerning codeposition of nano-TiO_2 particles in Ni matrix, it seems that there is a lack of a systematic study regarding the influence of the PC parameters on structure, apart from limited reports that refer to restricted pulse plating conditions [27, 28].

Therefore, in this study, based on a previous report concerning textural modifications induced by pulse plating electrolysis of pure nickel [17] and expanding our recent study on Ni/nano-TiO_2 composites prepared [14], we investigate the influence of pulse frequency on the codeposition percentage of nano-TiO_2 particles, surface morphology, grain size and preferred orientation of Ni matrix crystallites, and microhardness of the composites. The electrolysis conditions, like current density and pH value, were chosen so as to produce composites with three 'initial' preferred orientations of nickel matrix ([110], [100] and random oriented) in the DC regime [14]. The term 'initial' is used to emphasise that the selected DC plating conditions correspond to three different Ni crystalline orientations exhibiting the highest degree of texture perfection. These initial orientations will be perturbed progressively by pulse regime. Furthermore, pure nickel deposits under the same experimental conditions and both types of imposed current (DC and PC) were also produced for comparison, to verify any possible textural modifications induced by the presence of titania nano-particles in the matrix.

2 Experimental

Pure Ni and composite Ni–TiO_2 coatings were electrolytically deposited under both DC and PC conditions from an additive-free nickel Watts solution as illustrated in Table 1. The electrodeposition experiments were performed on rotating disc electrodes (RDE) with a constant rotation velocity of 600 rpm. The solution temperature was maintained by water circulation thermostat at 50 ± 1 °C. Nickel plate of 99.9% purity, positioned on the side of the electrolytic cell, was used as anode, while a standard calomel electrode was used as the reference electrode. The initial pH of the bath was adjusted to the constant values of 2.0, 3.5 and 4.0. The concentration of particles in the electrolyte was set at 20 g L^{-1} and the applied peak current density varied from 1 to 20 A dm^{-2}. The corresponding values of current density and pH were chosen properly to produce composite coatings with three well developed textures, i.e. [110], [100] and random [14], as depicted in Table 1. With the application of the pulse current technique, new parameters were introduced, namely, the duty cycle (dc), which was kept constant at 50% and the pulse frequency (v) that varied between 0.1 and 1,000 Hz. It should be noticed that $dc = T_{on}/(T_{on} + T_{off})$, where T_{on} is the time

Table 1 Experimental conditions for the preparation of pure Ni and Ni/nano-TiO_2 composite coatings by electrodeposition

Electrolyte composition			
$NiSO_4 \cdot 6H_2O$	330 g L^{-1}		
$NiCl_2 \cdot 6H_2O$	35 g L^{-1}		
H_3BO_3	40 g L^{-1}		
TiO_2 powder ($d_m = 21$ nm)	0 and 20 g L^{-1}		
Electrodeposition conditions			
Temperature (°C)	50 ± 1		
Substrate	Brass disc (diameter 25 mm)		
Cathode rotation rate (rpm)	600		
Anode	Ni foil		
Magnetic stirring (rpm)	250		
Type of current	DC and PC		
Duty cycle (dc)	50%		
Frequency (v)	0.1, 1, 10, 100 and 1000 Hz		
$T_{on} = T_{off}$	5000, 500, 50, 5 and 0.5 ms		
pH	4	3.5	2
Peak current density (A dm^{-2})	1	5	20
Texture: Ni	[110]	[100]	[210]
Ni/TiO_2	[110]	[100]	Random

period when the pulses are imposed and T_{off} is the relaxation time. All the experiments were performed using a Wenking PGS 95 Potentio-Galvanoscan, and a Kethley 3400 Pulse/Pattern Generator.

The TiO_2 powder (Degussa P_{25}) with a mean diameter of 21 nm was used as received without any pre-treatment. Titania particles were maintained in suspension by continuous magnetic stirring of 250 rpm for at least 24 h before deposition, as well as during the electrolysis process. The substrates were brass discs with a total surface area of 0.05 dm^2 that were mechanically polished and chemically cleaned in an ultrasonic agitated bath before deposition. After electrolysis, the deposits were ultrasonically cleaned in distilled water for 10 min to remove any loosely adsorbed TiO_2 particles from the surface. The thickness of the produced coatings was at least 50 μm so as to obtain fully developed preferred orientations and therefore permit their determination in a comparable and reliable way.

X-ray diffraction analysis was carried out using a Siemens D-5000 diffractometer, with a Cu K_α radiation. In order to describe the structure and estimate quantitatively the preferred orientation of the nickel deposits, the relative texture coefficient $RTC_{(hkl)}$ was calculated [29]. Grain size of the crystallites was determined using the (200) and (220) X-ray diffraction peak broadening according to the Sherrer equation. The full-width-half-maxima of the peaks were estimated after background correction and subtracting the instrumental line broadening, as presented elsewhere [29].

Measurements of the Vickers microhardness (HV in GPa) of pure nickel and Ni/nano-TiO_2 composite deposits were performed on their surface, using a Reichert microhardness tester under 50 g load for 15 s, and the corresponding final values were determined as the average of 10 measurements.

Scanning electron microscopy technique (SEM; FEI QUANTA 200) was applied to study the surface structure and morphology of the Ni/TiO_2 coatings. The concentration of TiO_2 particles on the surface was evaluated using energy dispersive X-ray spectroscopy (EDS, Oxford Instruments). The concentration of TiO_2 codeposited nanoparticles with Ni resulted from the mean value of at least three measurements along the radius of the disk.

3 Results and discussion

3.1 Effect of pulse frequency on TiO_2 nano-particles codeposition percentage

Figure 1 illustrates the incorporation percentages (vol.%) of TiO_2 nano-particles in Ni matrix composites, prepared under both DC and PC conditions, as a function of pulse frequency at various pH and current density values. It is obvious that composite electrodeposits prepared under PC conditions have higher incorporation percentages than those obtained under DC conditions, for all the applied working conditions (pH, current density). This is in accordance with relative results regarding Ni/SiC and Ni/WC composite electrodeposits [19, 24, 26, 30].

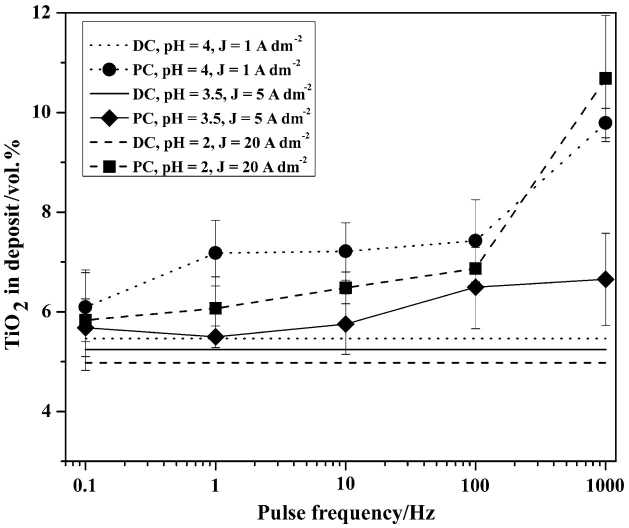

Fig. 1 Volume percentage of codeposited nano-TiO_2 particles in nickel matrix as a function of pulse frequency, under both DC and PC conditions, at various pH and current density values

Moreover, the volume fraction of TiO_2 nano-particles in the composite coatings increases rather gradually as the pulse frequency is increased and achieves the highest value at the pulse frequency of 1,000 Hz, regardless of the pH value or the imposed peak current density. In particular, the highest percentage of embedded TiO_2 nano-particles into the nickel matrix (10.7 ± 1.3 vol.%) is observed at pH = 2, $J_p = 20$ A dm^{-2} and pulse frequency $v =$ 1,000 Hz (Fig. 1). Under specific electrolysis conditions (pH, J) an analogous increment of codeposition percentage with increasing pulse frequency has been observed for Ni/Al_2O_3 composite coatings [22, 31], although contradictory conclusions also exist in literature [21, 32]. Therefore, to elucidate the correlation between pulse frequency and codeposition percentage, this study covers an extended range of pulse frequencies and electrodeposition parameters. Thus, it is proved that systematically the highest incorporation rates are achieved at pulse frequencies $v > 100$ Hz under various values of pH and current density.

Given that all pulse plating experiments were conducted under dc = 50%, it is apparent that the deposition time was equal to the relaxation time. According to Chen et al. [22], prolonged relaxation times T_{off}, i.e. low pulse frequencies, are associated with decreased incorporation, since it is possible that some particles, which were loosely adsorbed on the cathodic surface could be desorbed due to the stirring of the suspension during these long T_{off} times. Consequently, the percentage of incorporated TiO_2

nano-particles increases with increasing the pulse frequency. This experimental finding could also be linked to the suggestion of Podlaha et al. [33] that the maximum particle concentration is realised where the deposits' thickness per cycle approaches the particles diameter size. Therefore, taking into consideration that the TiO_2 particles are in the nanometre scale, small T_{on} values will favour the occlusion. Moreover, according to the codeposition model proposed by Celis et al. [34], a particle will only be irreversibly incorporated in the growing metal matrix when a certain amount of adsorbed ionic species is reduced. Amongst the parameters that affect the reduction process, the applied overpotential is one of the predominant ones [18, 35, 36]. Indeed, in our experimental set-up and at the highest applied frequency, we have observed a high instantaneous current spike induced at the beginning of the T_{on} period—instead of a regular rectangular pulse—followed by a decrease towards a limiting value of peak current density (J_p). This is in accordance with previous results regarding codeposition of submicron alumina particles (0.05 μm) in Au–Co matrix under the same pulse plating conditions [31]. Thus, the higher overvoltage at 1,000 Hz could also result in the enhanced embedding rate of TiO_2 nanoparticles in the nickel matrix.

Figure 1 also illustrates the influence of the pH value of the electrolytic bath on the titania codeposition percentage. However, the pulse frequency and the type of imposed current demonstrate the most pronounced effects. At pH = 3.5, a less prominent improvement of the codeposition percentage in the nickel matrix is observed, when going from DC to PC plating, compared to the deposits prepared under other pH values (4 and 2). This finding is consistent with the results of our previous study concerning TiO_2 particles reactivity with H^+ [14], since the point of zero charge for this system is at pH = 3.5 and consequently, this specific working condition is unfavourable for the codeposition of titania nano-particles.

3.2 Effect of pulse frequency on the structure of pure nickel and Ni/nano-TiO_2 deposits

3.2.1 Perturbation of [110] initial preferred orientation

Figure 2 demonstrates the quantitative X-ray diffraction analysis of the raw data for pure and composite electrodeposits, exhibiting [110] 'initial' preferred orientation under DC conditions, as a function of applied pulse frequency. It is worth to be mentioned that the induced modifications of [110] preferred orientation by pulse plating conditions for both pure nickel and composite coatings have not been investigated thoroughly elsewhere in the literature. First of all, comparing the deposits prepared under DC conditions, it is obvious that the embedding of the nano-TiO_2 particles in the nickel matrix is accompanied by a significant improvement of the quality of [110] preferred orientation (Fig. 2a). The observed enhancement of [110] texture in the presence of 20 g L^{-1} titania in the bath under DC mode is in accordance with our previous results [14].

Regarding pure nickel deposits (Fig. 2a), the application of 0.1 Hz pulse frequency leads to the enhancement of [110] preferred orientation, while for medium pulse frequencies (1 and 10 Hz), the predominance of [211] orientation is revealed. At this point, it should be noticed that the reinforcement of [211] crystalline orientation is concluded by the relative increasing of (311) and (111) diffraction line intensities [29]. However, at higher values of pulse frequency (≥100 Hz), a [110] texture reappears. Under such experimental conditions (pH = 4 and $J_p = 1$ A dm^{-2}), which are close to the boundaries of textural modification [110] → [211] as reported in Ref. [14], nickel deposits with a [211] preferred orientation seem to be favoured at medium pulse frequencies.

In the case of Ni/nano-TiO_2 composites, the 'initial' [110] orientation of the DC deposit is preserved with high perfection (Fig. 2a) by increasing values of pulse frequency, except from the value of $v = 1{,}000$ Hz, where a mixed orientation of [110] and [211] texture is apparent. Comparison of pure and composite coatings reveals that the most pronounced textural modifications are observed at medium frequencies, where the presence of TiO_2 nanoparticles in the deposits induces the [110] Ni crystalline orientation instead of [211]. This alteration, achieved under

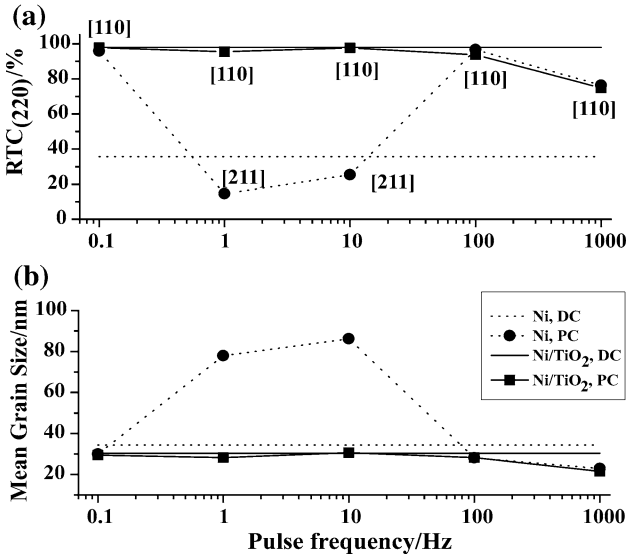

Fig. 2 Influence of imposed current type on (**a**) relative texture coefficient values of (220) diffraction line, and (**b**) average grain size, for pure and composite nickel coatings prepared under pH = 4 and $J_p = 1$ A dm^{-2} (Numbers in *brackets* notify the corresponding nickel preferred orientation of the coating)

these specific electrodeposition conditions, could be correlated with enhanced concentration of H_{ads} in the cathode/electrolyte interface [37] induced by the presence of charged titania particles in the catholyte, which in turn imposes the [110] nickel crystalline orientation against the other modes of nickel growth.

The observed alternations between the preferred orientations (Fig. 2a), provoked either by the engulfing of the TiO_2 nano-particles in the Ni matrix or/and by the different values of imposed pulse frequency, strongly affect the average grain size of the nickel crystallites (Fig. 2b). An almost 'mirror-like' behaviour of the quality of preferred orientation and corresponding average grain size as a function of applied frequency is apparent. The [110] preferred orientation is accompanied by the lowest values of average grain size compared to those exhibiting [211] texture (Fig. 2b). This finding is consisted with literature data [14, 17] and indicates that for both kinds of deposits the preferred orientation of the nickel crystallites and the average grain size are directly correlated.

Moreover, the application of the highest pulse frequency value leads to further reduction of the average grain size of Ni crystallites resulting to the lowest value achieved for pure and composite deposits, which is approximately the same for both kinds of deposits (Fig. 2b), though the highest titania incorporation rate is achieved. Studies concerning the incorporation of TiO_2 nanoparticles in nickel under DC regime have shown that the dispersed nano-particles either increase the nucleation [6, 12] or restrain the crystal size rather by inhibiting crystal growth than by providing new nucleation surfaces [14, 15]. However, it seems that, under these PC conditions, pulse frequency is the main factor determining the average grain size of the Ni crystallites, diminishing the influence of the increased codeposited titania particles. This could be attributed to the formation of increased number of new nuclei on the cathode surface due to high overpotential applied under these pulse plating conditions [18].

3.2.2 *Perturbation of [100] 'initial' preferred orientation*

Figure 3 represents the quantitative analysis deduced from X-ray diffraction raw data, illustrating: (a) the alteration of the quality of [100] 'initial' preferred orientation and (b) the average grain size of pure and composite deposits prepared under increasing values of pulse frequency. Comparing deposits prepared under DC conditions, a certain refinement of the Ni crystals is observed—although the quality of the [100] orientation is similar—due to the incorporation of the titania particles in the nickel matrix. Moreover, all pulse plated deposits exhibit reduced grain size compared to DC deposits. Especially, at very high frequencies, the nickel matrix crystals size can be refined to less than 50 nm.

Regarding pure nickel deposits, the application of increasing values of pulse frequency results to deposits characterised by a decreasing perfection of [100] (Fig. 3a) texture, and consequently to the following sequence of texture modifications: [100] → [211] → [110]. These structural modifications are also discernable in SEM surface images of Fig. 4. For example, at medium frequencies (10 and 100 Hz) crystals oriented through [211] axis are distinguished, and their size increases as the frequency is increased (Fig. 4b, c). This increment is expected since the increase in the quality of the [211] texture (Fig. 3a) is linked to the formation of larger crystallites, in accordance with reports regarding pure nickel deposits under PC conditions [29]. At the highest frequency, the predominance of [110] preferred orientation is revealed (Fig. 3a), which is accompanied by the drastic refinement of crystallites reaching the mean grain size of ~30 nm, as depicted in Figs. 3b and 4d. Overall, electrocrystallization of nickel is once more proved to be a highly inhibited process, in which the proper imposition of pulse frequency leads to the predominance of a crystal orientation, associated with a specific quality, average grain size and consequently, microhardness value.

Concerning composite electrodeposits, it is observed that the 'initial' [100] preferred orientation of the nickel crystallites under DC conditions (Fig. 5a) is preserved up to 100 Hz (Fig. 5b). Surface SEM micrographs illustrate

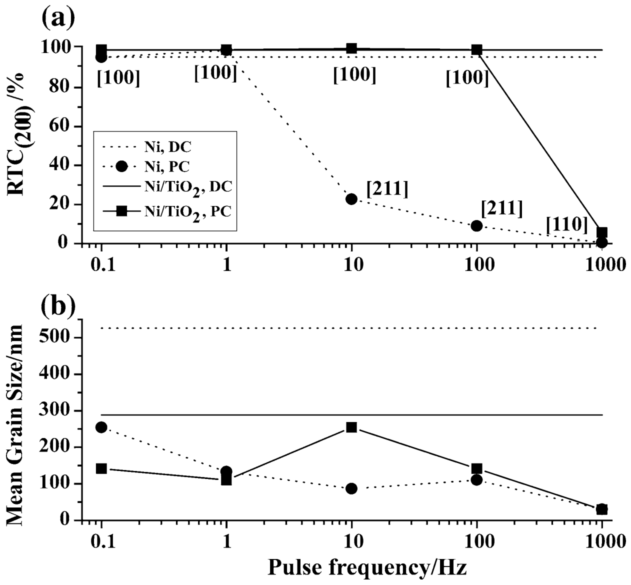

Fig. 3 Influence of imposed current type on (**a**) relative texture coefficient values of (200) diffraction line, and (**b**) average grain size, of pure and composite nickel coatings prepared under pH = 3.5 and $J_p = 5$ A dm^{-2} (Numbers in *brackets* notify the corresponding nickel preferred orientation of the coating)

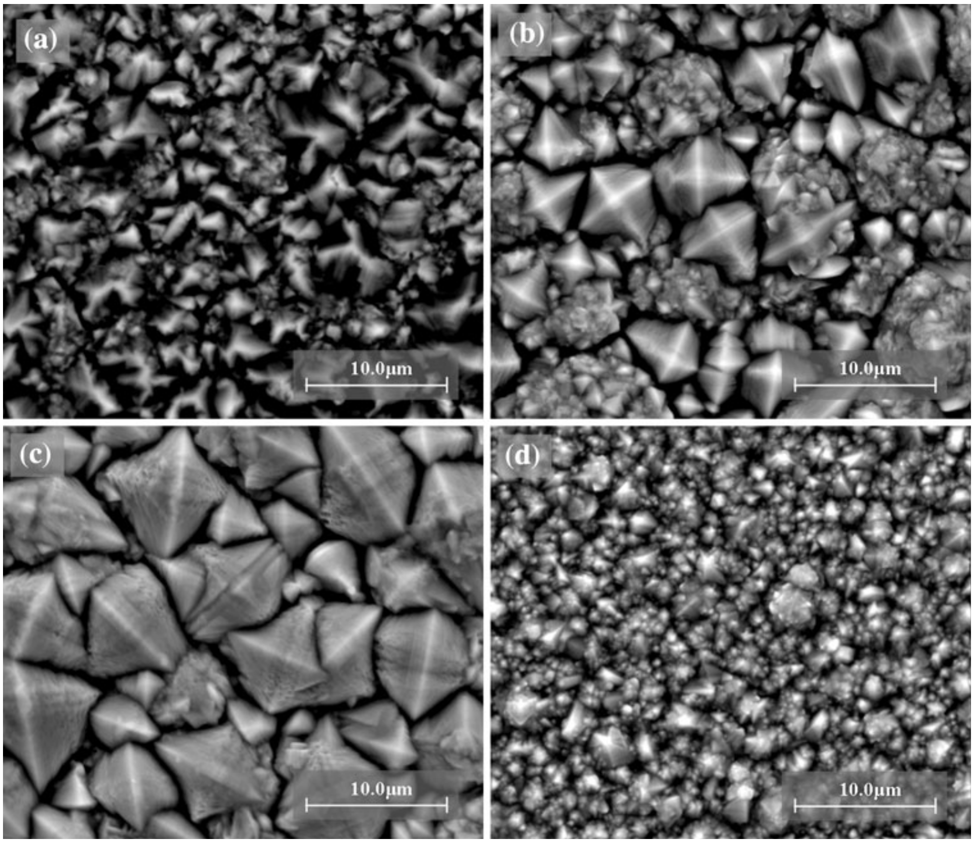

Fig. 4 SEM surface micrographs of pure deposits prepared under: **a** DC conditions with a [100] preferred orientation, **b** $v = 10$ Hz with a [211] preferred orientation, **c** $v = 100$ Hz with a [211] preferred orientation and **d** $v = 1{,}000$ Hz with a [110] preferred orientation. All the deposits were produced under the same experimental conditions (pH = 3.5 and $J_p = 5\ \mathrm{A\ dm^{-2}}$)

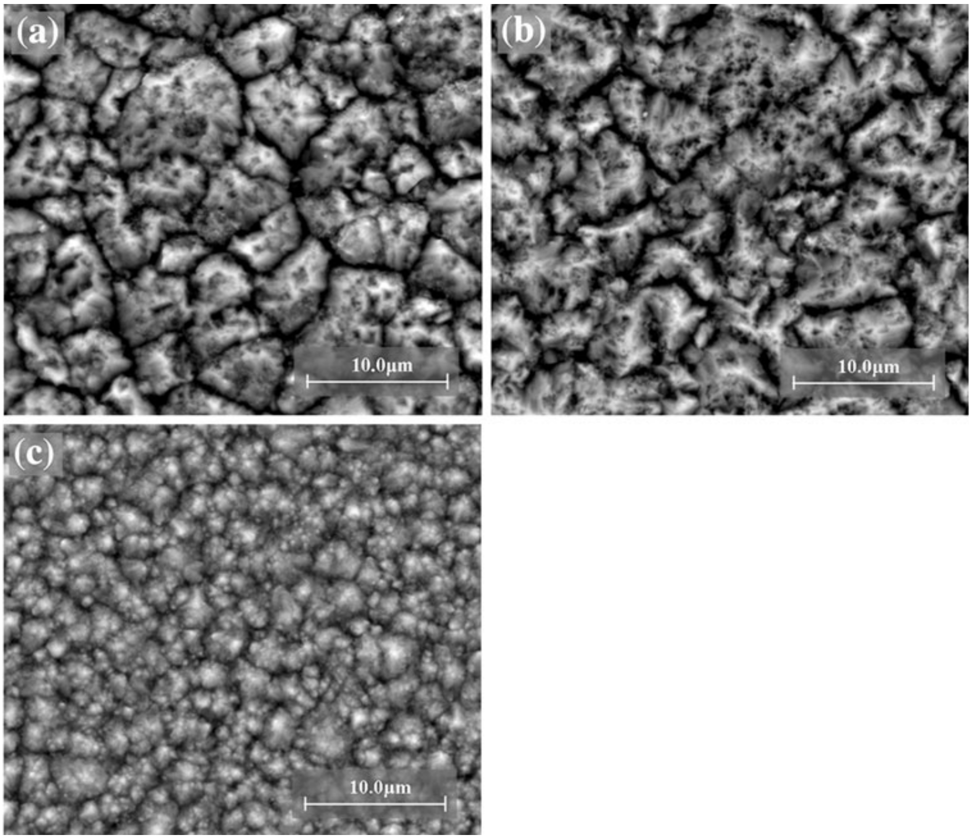

Fig. 5 SEM surface micrographs of composite deposits prepared under: **a** DC conditions with a [100] preferred orientation, **b** $v = 100$ Hz with a [100] preferred orientation, **c** $v = 1{,}000$ Hz with a [110] preferred orientation. All the deposits were produced under the same experimental conditions (pH = 3.5 and $J_p = 5\ \mathrm{A\ dm^{-2}}$)

that the borders of the [100] oriented grains are becoming fuzzy (Fig. 5a, b) compared to pure Ni coating (Fig. 4a), due to the embedding of the nanoparticles. At this region of applied frequencies, the presence of TiO_2 nano-particles in the nickel matrix favours the predominance of the [100] in comparison with pure coatings prepared under the same PC conditions. This observation is in consistency with data of DC-plated composites, which demonstrated that titania incorporation in the matrix favoured the [100] Ni crystalline orientation under a proper combination of pH and current density values [14]. However, the perturbation of the electrocrystallization process seems to be so intense at the highest applied frequency, that both kinds of deposits exhibited crystals oriented through [110] axis. This structural modification is shown in the surface SEM images of pure (Fig. 4d) and composite coating (Fig. 5c). Furthermore, as depicted in Fig. 3b, all Ni/nano-TiO_2 composite deposits that exhibit the same kind of preferred orientation with the corresponding pure ones, are characterised by reduced average grain size. Concluding, it is revealed that regardless of the titania particles presence, deposits with [110] texture demonstrate the lowest values of average grain size, achieved once more at the highest applied frequency, followed by deposits with [211] texture, while the largest grains are detected for coatings oriented though [100] axis.

3.2.3 Perturbation of random 'initial' texture

Figure 6 demonstrates the X-ray diffraction patterns of pure and composite coatings by increasing values of pulse frequency, at the lowest pH and the highest current density applied values. Comparing both kinds of deposits prepared under DC conditions, it is proved that the presence of TiO_2 nano-particles favours the growth of randomly oriented Ni crystallites, in contrast with the corresponding pure deposit that is oriented through [210] axis. It should be noted that the [210] orientation is characterised by the significant enhancement of the intensity of (420) diffraction line (Fig. 6a). This structural modification is expected at these specific plating conditions according to the results of our previous study [14]. In addition, for composite coatings, the presence of TiO_2 nanoparticles in the nickel matrix is also verified by the diffraction lines observed at $2\theta = 25.3°, 38.6°$ as depicted in the inset of Fig. 6b, which cannot be clearly observed otherwise, due to the relatively high intensity of nickel diffraction peaks.

As illustrated in Figs. 6a and 7a, pure nickel deposits preserve the [210] texture at low and medium pulse frequencies (0.1–10 Hz), but at higher frequencies (100–1,000 Hz) a gradual textural modification from [210] to [100] is revealed. Such a transition has been associated with the relief of the cathodic surface from H_{ads} due to the abundant hydrogen formation under these plating conditions [17]. By increasing the pulse frequency, the perfection of [100] texture is increased gradually (Fig. 7a), resulting to increased average grain size values of the pure deposits (Fig. 7b). However, it is noteworthy that the average grain size of the coating characterised by the highest quality of [100] preferred orientation (obtained at the highest frequency), is the lowest one (~93 nm) observed for pure deposits exhibiting the [100] orientation (Figs. 3b, 7b). Therefore, it is revealed that the application of specific values of pulse frequency, pH and current

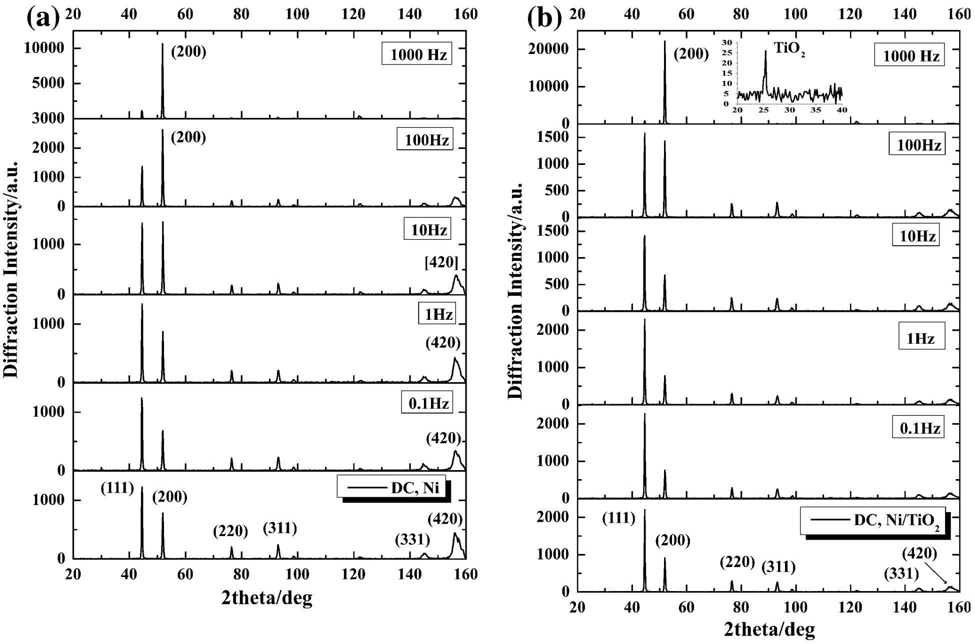

Fig. 6 X-ray diffraction patterns of (**a**) pure Ni and (**b**) composite Ni/nano-TiO_2 deposits, prepared under both types of current and the same experimental conditions ($pH = 2$ and $J_p = 20$ A dm^{-2}), showing the textural modifications imposed by increasing pulse frequency compared to DC deposit exhibiting [210] as an 'initial' preferred orientation

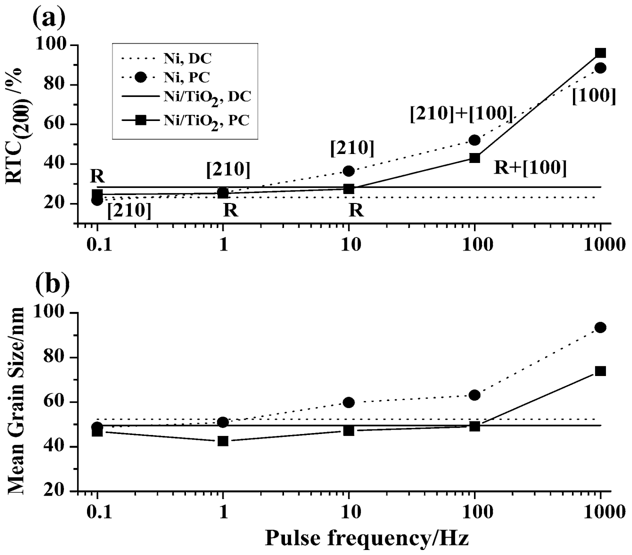

Fig. 7 Influence of imposed current type on (**a**) relative texture coefficient values of (200) diffraction line and (**b**) average grain size of pure and composite nickel coatings prepared under pH = 2 and $J_p = 20$ A dm^{-2} (Numbers in *brackets* notify the corresponding nickel preferred orientation of the coating)

density could lead to considerable grain refinement amongst deposits exhibiting [100] texture.

Regarding composite deposits, as the imposed pulse frequency increases, the texture progressively changes from the 'initial' random one to [100] (Fig. 6b) and, consequently, the quality of (200) diffraction line progressively increases (Fig. 7a). In addition, the same behaviour is observed for the corresponding average grain size (Fig. 7b). At $v = 1000$ Hz applied frequency, a strong [100] preferred orientation is imposed and the highest crystallite size is observed. However, all composites exhibit lower grain size values in comparison with the corresponding pure deposits, indicating once more that the presence of nanoparticles in the matrix induces grain refinement. Furthermore, all deposits randomly oriented are more microcrystalline than those oriented through [210] and [100] axis (Fig. 7b).

Concerning pure Ni coatings, taking into consideration all the above mentioned results, it is obvious that by increasing the values of pulse frequency, a series of structural modifications takes place regardless of the DC 'initial' orientation. However, under the most perturbed conditions, the transition from [211] to [110] preferred orientation was observed. Thus, the [110] mode of growth is stable over a restricted area, where pulse frequency is higher than 100 Hz. Nevertheless, this is not the case for deposits prepared under high value of peak current density (20 A dm^{-2}) and low pH value (2), where the [100] orientation is the predominant one at the most perturbed conditions. This could be possibly correlated with the fact that, according to the texture diagram for pure coatings [14], these specific experimental conditions (pH and current density) are close to the boundaries of the textural modification between [210] and [100]. Thus, increased values of pulse frequency could be related to simultaneous diminution of the amplitudes of the electrode potential [36], which in turn could be connected with a shift of the applied current density to lower values that favour the transition to [100] crystalline orientation. It is should be mentioned that the transition of [100] → [110] is not observed under these specific pulse plating conditions, since it has been detected under more perturbed electrodeposition conditions, as reported in Ref. [17], realised by the application of lower values of duty cycle.

On the other hand, composites prepared under pulse plating conditions tend to preserve or improve the 'initial' orientation, although relative high perturbations are induced. A possible interpretation of the these experimental findings could be proposed, taking into consideration also the results of our previous report under DC conditions [14], where it was noted that H^+ adsorption/desorption phenomena on the titania surface take place depending on the electrolysis parameters and finally associated with specific modes of nickel crystal growth. Hence, the application of low and medium values of pulse frequency in the presence of titania nanoparticles in the cathode/electrolyte interface seems to intervene the electrocrystallization process by either enhancing adsorption/desorption of H_{ads} on the titania surface [14], which finally impose the [110] texture [37], or by hindering the chemical species reactivity related to hydrogen codeposition and consequently, favouring the [100] mode of growth.

However, this specific influence of titania nanoparticles upon the Ni electrocrystallization and thus, on the preferred orientation seems to be restricted at the highest applied frequency, since both pure and composites exhibit the same structural characteristics. Therefore, under the most intense pulse perturbations, even though the highest incorporation rates are observed, pulse frequency appears to be the predominant factor governing nickel textural development against the effect of adsorption/desorption phenomena occurring on the titania particles in the catholyte area. Thus, it is quite possible that the concentration of the inhibiting species on the TiO_2 particles, at these short T_{on} and T_{off} values, could be reduced by two synergistic actions: (a) an enhanced reduction of the ionic species, provoked by the high instantaneous overpotential during the short on-time [34], and simultaneously (b) a restriction of the adsorption of the inhibiting species due to the short T_{off} value, which in turn could inhibit the nickel crystal growth in composites.

3.3 Effect of pulse frequency on microhardness

It is well-established that composite coatings microhardness is strongly affected by the volume fraction of the particles codeposited with the metal matrix and, thus many efforts have been made to correlate the amount of codeposited particles with the electrodeposition parameters, such as pH, current density, etc. [38]. However, the correlation of the structural modifications, induced either by pulse parameters or/and particles incorporation, with the observed mechanical properties of the composite deposits (i.e. microhardness) has been the subject of few studies, like those concerning Ni/SiC [19, 26], and Ni/Al_2O_3 composites [22, 32]. Therefore, the microhardness of the coatings will be assessed from the viewpoint of crystal orientation, grain size, type of imposed current and nanoparticles codeposition percentage.

The microhardness values as a function of imposed current type and pulse frequency, for both types of deposits, are illustrated in Fig. 8, under the highest and lowest values of applied current density and pH. It is obvious that independent of the applied type of current, all Ni/nano-TiO_2 composite coatings exhibit higher microhardness values compared to the pure nickel coatings. All the aforementioned experimental data in Figs. 2 and 7 indicate that the titania incorporation in the nickel matrix significantly influences the crystalline orientation and refine the average grain size. Consequently, this behaviour results to the enhancement of the microhardness.

Figure 8a demonstrates the variation of microhardness for pure and composites prepared under the highest pH and the lowest applied current density value. The lowest values of microhardness for pure deposits are expected at medium to low pulse frequencies, since the application of these PC conditions provokes the textural modification from [110] → [211] (Fig. 2a), accompanied by higher average grain sizes (Fig. 2b). On the other hand, composites under PC conditions up to 100 Hz demonstrate no significant variation of microhardness that could be associated with: (i) the stabilization of the same [110] preferred orientation (Fig. 2a), (ii) the narrow range of grain size in the nanometre scale (25–32 nm; Fig. 2b), and (iii) the almost unchangeable codeposition titania rate (Fig. 1) achieved under these PC conditions. The highest microhardness value is attained at the highest frequency, where the highest incorporation percentage is observed (Fig. 1). It should be noticed that although the same average grain size for both kinds of deposits is achieved (Fig. 2b), it is revealed that the leading factor for determining microhardness value is the presence of codeposited nanoparticles in the matrix. Several studies have shown that specific PC conditions result to more uniform nanoparticles distribution in the metallic matrix, thus this considerable hardness increase may be linked to a dispersion hardening mechanism [19, 26, 32].

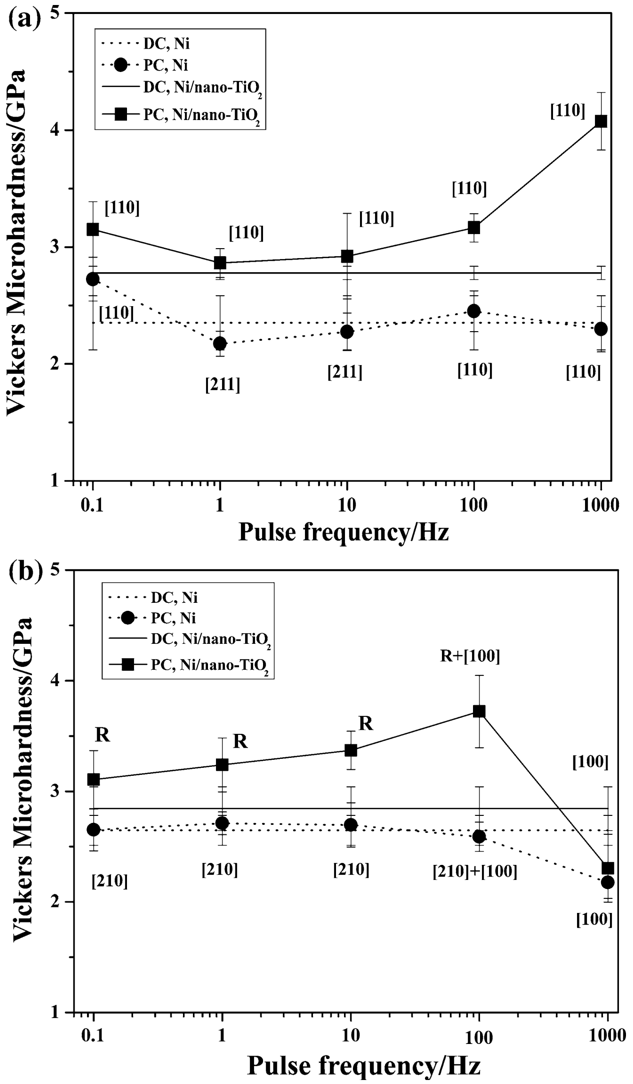

Fig. 8 Variation of microhardness values as a function of pulse frequency for pure and composite coatings prepared under (**a**) pH = 4, $J_p = 1$ A dm^{-2} and (**b**) pH = 2, $J_p = 20$ A dm^{-2} (Numbers in *brackets* notify the corresponding nickel preferred orientation of the coating)

The hardness variation, under the lowest pH and the highest applied current density value for both pure and composite deposits, is presented in Fig. 8b. Microhardness values of pure deposits are almost independent of applied pulse frequency up to 100 Hz, associated with small modifications of the [210] preferred orientation quality (Fig. 7a) and corresponding average grain size (Fig. 7b). However, the increasing intensity of the 'soft' [100] mode of crystalline growth and the simultaneous increasing of grain size, results to a considerable decrease of microhardness. This behaviour is expected, given that amongst the observed nickel preferred crystal orientations, the [100] texture is known to be the 'free mode of growth' for electrodeposited Ni, presenting few structural defects, maximum ductility and low values of grain size, tensile strength, yield strength and microhardness [17, 29, 39]. In contrast, composites exhibit ameliorated microhardness values, which increase with increasing pulse frequency as the deposits preserve their random texture, with similar microcrystalline structures (Fig. 7b) and increased incorporation rates (Fig. 1). Nonetheless, the microhardness is reduced drastically at $v = 1000$ Hz to values close to the corresponding for pure coatings, although the highest incorporation rate is observed. It is noteworthy that similar microhardness variations have been reported for Ni/nano-Al_2O_3 composites prepared under similar pulse plating conditions [22]. In both composite systems, this behaviour could be attributed to the increasing perfection of [100] orientation. Therefore, these results imply that pulse frequency and particles presence in the matrix could influence the microhardness through a synergistic mechanism. In fact, the application of pulse frequency seems to influence the hardness of composite coatings by: (a) provoking changes in the microstructural properties of the deposits, i.e. mode of crystal growth, quality of preferred orientation, crystalline defects, grain size, and (b) affecting the amount of titania incorporated into the nickel matrix, which indirectly has an effect upon the microstructure and thus, on the microhardness.

In an attempt to elucidate further the hardening mechanism of pulse plated composite nickel coatings, the microhardness values of deposits exhibiting three different textures ([110], [100], random) have been plotted as a function of: (a) codeposition percentage and (b) reciprocal square root of average grain size (Fig. 9). Composite deposits with preferred crystalline orientation [100] show the lowest values of microhardness and exhibit the highest average grain size values amongst the other deposits (Fig. 9b). It is worth to mention that although the TiO_2 codeposition percentage was doubled ($\sim$11 vol.%) at $v = 1000$ Hz, pH $= 2$ and $J_p = 20$ A dm^{-2}, the corresponding hardness does not show any significant improvement. On the other hand, randomly oriented composites present considerable increase of microhardness in a narrow grain size (Fig. 9b) and codeposition range (Fig. 9a). However, composites oriented through [110] axis demonstrate enhanced microhardness compared to [100] oriented ones, as well as the lowest mean crystallite sizes amongst the other deposits achieved at a broad range of titania incorporation percentage.

In general, the strengthening mechanisms of polycrystalline metals and composites can be described as follows: (i) grain refinement strengthening from Hall–Petch relationship; (ii) dispersion strengthening due to Orowan mechanism and (iii) crystal orientation [40]. Overall, experimental data of this study reveal that it is crucial to taken into consideration the preferred crystalline orientation in order to define if there is a direct correlation between codeposition rate and microhardness (Fig. 9a). For instance, the alteration of titania nanoparticles incorporation in the nickel matrix reveals a negligible effect on the microhardness for composites oriented through [100] axis, but an almost linear relationship with microhardness for those coatings exhibiting random and [110] textures. In addition, the dependence of hardness values on the mean grain size (Fig. 9b) indicate that for ascribing the strengthening effect of composites both grain refinement and dispersion strengthening mechanisms should be taken into account for a given preferred orientation.

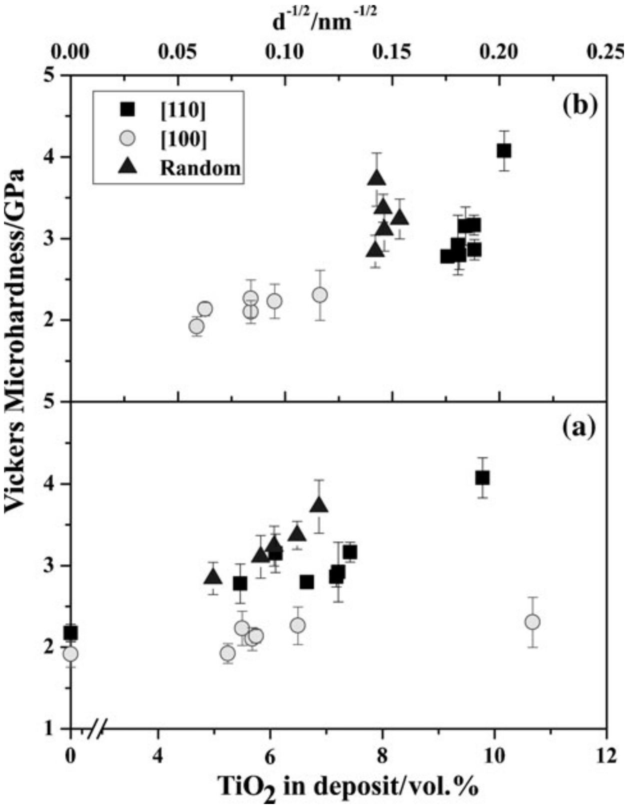

Fig. 9 Variation of composites microhardness values with various textures as a function of (**a**) volume percentage of codeposited nano-TiO_2 particles in nickel matrix and (**b**) $d^{-1/2}$ (d = average grain size)

4 Conclusions

Pulse electrodeposition, under specific electrolysis conditions (pH, J_p), was performed so as to study the perturbations induced by pulse frequency on Ni/nano-TiO_2 coatings with three well-developed textures ([110], [100], random). Pure nickel deposits were also produced for comparison, to elucidate the effect of pulse frequency on codeposition percentage, structural characteristics and microhardness values of the deposits.

Concerning perturbations on the 'initial' textures of pure Ni coatings, a series of structural modifications took place by increasing the pulse frequency, regardless of the DC 'initial' orientation. Specifically, at medium perturbations the [211] preferred orientation was favoured, while at frequencies higher than 100 Hz, the [110] mode of growth was stabilised. On the other hand, composites prepared under the same PC conditions tended to preserve or even improve the 'initial' orientations ([110] or [100]). An interpretation of the experimental findings could be based on possible adsorption/desorption phenomena occurring on the surface of TiO_2 particles, present in the cathode/electrolyte interface, resulting to the imposition of specific modes of crystal growth. However, this influence of titania nanoparticles upon the Ni electrocrystallization seemed to be restricted at the highest applied frequency $v = 1{,}000$ Hz, due to the reduced concentration of chemical species adsorbed on the nanoparticles surface, provoked by the applied short T_{on} and T_{off} values.

As far as codeposition rate is concerned, it has been proven that composites prepared in the PC regime have higher incorporation percentages than those obtained under DC conditions, and systematically the highest incorporation rates were achieved at pulse frequencies $v > 100$ Hz. Moreover, it has been revealed that the nickel average grain size for both pure and composite coatings is directly associated with the induced nickel crystalline orientation, where deposits oriented through [110] axis exhibited the lowest mean grain size when compared to the other preferred orientations.

Overall, the experimental data revealed that the application of pulse frequency affected the microhardness of composites by provoking microstructural changes in the deposits, expressed through alterations of crystal growth, quality of preferred orientation and grain size, as well as by varying the amount of codeposited titania nanoparticles with the nickel matrix. All Ni/nano-TiO_2 composite coatings exhibited higher microhardness values compared to the pure nickel deposits, regardless the applied type current. It has been shown that to ascribe the observed strengthening effect of Ni/nano-TiO_2 composites, it is crucial to taken into consideration the preferred crystalline orientation of the coatings in combination with grain refinement and dispersion strengthening mechanisms.

In conclusion, electrocrystallization of nickel in the presence of titania nanoparticles in the catholyte is once more proved to be a highly inhibited process, in which the proper imposition of pulse frequency leads to specific range of codeposition percentage and the predominance of a crystal orientation, associated with a specific quality, average grain size, and consequently, microhardness value of the Ni/TiO_2 composites.

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