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Microstructural investigation of nickel deposits obtained by pulsed current

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ABSTRACT

Electrodeposited nickel coatings are applied in functional applications to modify or improve corrosion resistance, hardness, wear, magnetic, and other properties. In this work, Nickel deposits were produced by simple pulse electrodeposition using a free-additive Watts bath. It has been shown that pulse current deposition is able to produce coatings with excellent properties in morphology, particle distribution, structure, grain size, hardness and wear resistance. Pulsed techniques present a larger number of variables, so we propose to optimize the parameters which define the pulsed current to obtain deposits with improved properties. The optimization of the conditions of deposition was established and the influence of pulse parameters, namely, pulse on-time, off-time and average current density, on the grain size, surface morphology and crystal orientation was determined. The morphology of the coatings was characterized by observations in scanning electronic microscopy (SEM). X-ray diffraction in symmetric mode was also used to evaluate the structure and principal crystallographic orientations of the deposits. The study showed that pulse current results in better properties of deposits and significantly refined the crystal grain.

1. Introduction

Electroplating is one of the most commonly used surface-finishing processes that can satisfy the requirements of decorative and functional applications. Electrodeposition of metallic coatings is attractive due to: (a) low cost, as it involves minor modification of conventional electrodeposition technologies (b) easy of control, as the electrodeposition parameters can be easily controlled to produce the required crystal grain size, alloy chemistry and texture in order to improve mechanical or electrochemical properties [1–3], and (c) versatility, as the codeposition technology can produce a variety of innovative materials such as nanocomposites [4]. Electrodeposition of nickel has been widely investigated because of its particular mechanical properties in numerous industrial applications. The Ni deposits are used in the industry to improve wear and corrosion resistance, to repair eroded metals, to change the dimensions of small size pieces, to improve magnetic properties, to prepare the substrate surface for glazing or producing the organic coating, and other purposes. A brief summary and usual behavior of nickel electrodeposition is given in Table 1.

Many experimental works were published [13–19] in order to understand the relation between electrodeposition parameters and

metallurgical states of the electrodeposits. The mechanism of nucleation and growth of Ni coatings was thoroughly described and in most cases, illustrated from results coming from Watts baths [20–22]. Watts bath is largely described in literature, even if some recent works suggest that sulfamate based baths permit to reduce internal stresses favoring the elaboration of thick coatings [23].

The synthesis of nickel by pulse electrodeposition has attracted much attention during the last decades [24,25]. Pulse electrodeposition can be used as a mean of producing unique structures with improved properties, i.e., coating with properties not available from direct-current plating [26]. Pulse electrodeposition has been reported to improve the deposition process and deposit properties such as porosity [27], ductility [28], hardness [29] and surface roughness [1].

Pulse electrodeposition yields a finer-structure and more homogeneous surface appearance of the deposit because a higher instantaneous current density is applied during deposition by pulse current electroplating compared with direct current plating. Increase of the cathodic current density during pulse electroplating permits to increase the nucleation rate leading to the formation of finer structures as suggested by Mishra [30,31]. It was recently shown the contrary in cases of sulfamate baths where a finer structure is obtained for the lowest values of

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Table 1
Summary of results of research conducted on the nickel Coating.

Author	Work	Reference
Boukhouiete et al.	Studied the effect of deposition current density on microstructure and surface morphology of electrodeposited nickel coatings. The optimum conditions of deposition were established and the influence of current density on the grain size, surface morphology, and crystal orientation was determined.	[5]
Allongue et al.	Used in situ scanning tunneling microscopy (STM) and cyclic voltammetry (CV), investigated the growth mechanism of ultrathin layers of nickel and cobalt that were electrodeposited from dilute sulphate solutions onto gold.	[6]
Evans et al.	Examined the interaction of additives with the cathode during nickel electrodeposition in the Watts electrolyte	[7]
Serek et al.	Studied the influence of different metallic substrates on nickel electrodeposition from a chloride electrolyte. Cyclic voltammetry and potential step transient measurements were determined for platinum, nickel and iron electrodes.	[8]
Qu et al.	Performed experiments investigating the quality of surface finishes (surface roughening) in pulse and pulse reverse current deposition of nickel. It was shown that pulse deposition produced significantly better deposits in terms of surface roughening.	[9]
Chan et al.	Performed crystallographic texture analysis on samples of nickel deposited from a sulphamate bath for improvement of magnetic and mechanical properties. The specific crystal orientation depends on electrocrystallisation circumstances. It was shown pulse reverse current deposition significantly influences these circumstances.	[10]
Hadian et al.	Performed a comparative study of DC and pulse current deposition in Watts electrolyte. It was shown that pulsing the current lowered the mean stress, increased the microhardness, increased the current efficiency, greatly reduced burning and peeling in high current density areas of the samples and improved deposit distribution.	[11]
Popov et al.	Reported that with increasing pause to pulse ratio in pulsating current deposition leads to a decrease in the size and increase in the number of growing grains.	[12]

current densities. An evolution of the coating texture was reported when current densities decrease, from a strong (100) orientation at high current densities, to a non textured (random orientation) microstructure at low current densities [32]. The reduction of the nodule size was attributed to the incorporation of impurities, essentially light element like oxygen, hydrogen or nitrogen that could affect the growth of the nickel nucleus, this assumption was supported by the fact that cathodic efficiency also decreases in the same way.

It has been reported that pulse plating strongly modifies the properties, the structure, the surface morphology and the macroscopic characteristics of nickel coatings. Pulse electrolysis is thus a powerful means to disturb the metal-catholyte interface and hence offers an opportunity of preparing nickel deposits with well-defined properties and significantly refined the crystal grain [33,34]. The reduction of grains sizes has been found to offer substantial grains in the properties of the deposited metal such as the hardness and the corrosion resistance.

In simple pulse (sp) electrodeposition process, the average current

Table 2
Range of variation of electrochemical parameters during sp electrodeposition.

j_p (mA/cm ²)	$10 < j_p < 1820$
t_{on} (ms)	$3 < t_{on} < 15$
t_{off} (ms)	$10 < t_{off} < 100$
γ (%)	$3 < \gamma < 100$

density (j_m) is equivalent to the current density applied in the continuous electrodeposition process and is defined as:

$$j_m = j_p \cdot t_{on} / t_{on} + t_{off}$$

Where j_m is the average current density, j_p is the peak current density applied during the synthesis of the coating, t_{on} is the time of the cathodic pulse (on time) and t_{off} is the time between pulses (off time).

During the off time, it was reported that a relaxation occurs at the cathode interface permitting to renew the composition of the electrolyte that was previously disturbed during the on time cycle. It was also reported that adsorption and desorption of impurities like light elements could occur during this stage and would modify the growth of the nucleus [35].

In general, the results of pulse-plating experiments obtained by different researchers are difficult to compare and, in many cases, contradictory. This is because of (1) the complexity of the electrodeposition process, (2) the rather large number of experimental variables involved in pulse plating and (3) the lack of a clarified and standardized procedure in investigating the general effect of a particular pulse-plating parameter. Regarding the last point, most researchers [36,37] usually cite the influence of duty cycle, γ or pulse frequency, f , on deposit structure and morphology. However, these parameters are mathematical extracted quantities from the compelled pulse parameters, namely, pulse on-time (t_{on}) and pulse off-time (t_{off}), and therefore do not reflect the effects of these parameters. For example, the effects of pulse on and off time on electrodeposition of nickel, by varying the pulse frequency at constant duty cycle and peak current density were reported [36,37]. However, by varying the pulse frequency in this manner, both the on-time and off-time change simultaneously and hence it is difficult to ascertain the influence of on-time or off-time separately. It seems that it is quite complex to determine clearly the impact of each parameters on the morphology and structure of the nickel based deposits, so we have investigated the comparison of the nickel deposits obtained from conventional direct-current (DC) methods with coatings resulting from simple pulse plating methods, conserving the global deposit charge as constant during this approach.

2. Materials and methods

Nickel coatings were deposited galvanostatically using a free-additive Watts bath. No additives were used in order to limit the incorporation of pollutants resulting from surface adsorption or electro-activity of these compounds. The bath contained 300 g/L NiSO₄·7H₂O, 45 g/L NiCl₂·6H₂O, and 45 g/L H₃BO₃. Solutions were prepared by dissolving pure salts in ultrapure water (18.2 MΩ cm) and pH was then adjusted to 4.5 by adding sodium hydroxide.

A nickel sheet of 99.99% purity contained in a polypropylene anode bag was used as a soluble anode and quite pure 99.5% polycrystalline nickel (obtained from Goodfellow society) with an exposed surface of 2 cm² as cathode materials.

Prior to deposition, the nickel substrates were mechanically polished with silicon carbide (paper of 600–4000 grits), sonicated for 2 min, rinsed with ultrapure water and dried.

The coatings thickness was fixed at about 50 μm by controlling the plating time. Gravimetric measurements were previously performed in order to check the cathodic efficiency and then to correct the deposit time in order to reach the required thickness.

Electroplating was performed in a three-electrode cell by using a VSP Biologic potentiostat/galvanostat coupled to a current amplifier VMP 3B-10 and driven by EC-lab software.

A specific support was designed in order to keep constant the distance between each electrode during electroplating. Anode-cathode distance is kept constant at 3 cm. The reference electrode was a saturated calomel electrode (SCE) inserted to the cell through a Luggin-Haber capillary tube. The distance between the capillary tube tip and the working

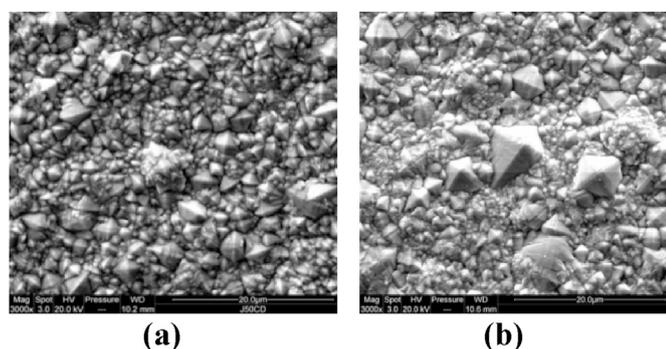


Fig. 1. SEM images of nickel coatings electrodeposited under direct current at (a) 50; (b) 100 mA/cm².

Table 3

Evolution of the average nodule size deduced from SEM observations of Nickel coatings prepared by direct-current from a Watts Bath.

j (mA/cm ²)	d_{SEM} (μm)
50	1.48 ± 0.74
100	1.82 1.38

Table 4

Parameters of pulsed electrodeposition of Nickel at constant t_{on} and j_m .

t_{on} (ms)	t_{off} (ms)	j_m (mA/cm ²)	j_p (mA/cm ²)	γ (%)
5	10	50	150	33
5	50	50	550	9.1
5	90	50	950	5.2
5	100	50	1050	4.7

electrode was 2 mm. The plating temperature was kept constant at 60°C using a Julabo cryothermostat and the solution was mechanically stirred during the deposition.

Coatings were prepared in galvanostatic mode either with direct-current (DC) or with pulsed conditions. Simple pulse (sp) electrodeposition was used for the synthesis of the coatings.

Parameters like on-time (t_{on}), off-time (t_{off}) and pulse current density (j_p) were varied in order to assess to their influence on the morphology and microstructure of the coatings. Table 2 presents the range of evolution of these parameters.

Surface morphology of the deposits was studied by scanning electron microscopy using a SEM-FEG Quanta Philips 200F operating at 20 kV as acceleration voltage.

The deposit structures under various plating were characterized by X-ray diffraction using a Brucker apparatus (AXS D8-Advanced) diffractometer equipped with a Cu-K α radiation ($\lambda = 0.15405$ nm). Diffractograms were recorded with a step size of 0.04° for 2θ ranging from 40° to 100° and the K α 2 peak and background were removed.

3. Results and discussion

3.1. Ni coatings deposited under direct current

For reference two coatings were prepared from Watts bath in continuous mode at current densities of 50 and 100 mA/cm². Fig. 1 illustrates SEM observations of the surface of these samples. It can be seen that Surface morphology of nickel deposit is heterogeneous and composed of many large pyramidal-shaped crystallites and a few fine grains at is surrounding. This pyramidal growth is typical way of field-orientation texture that is the preferential growth in the direction of electric field [38].

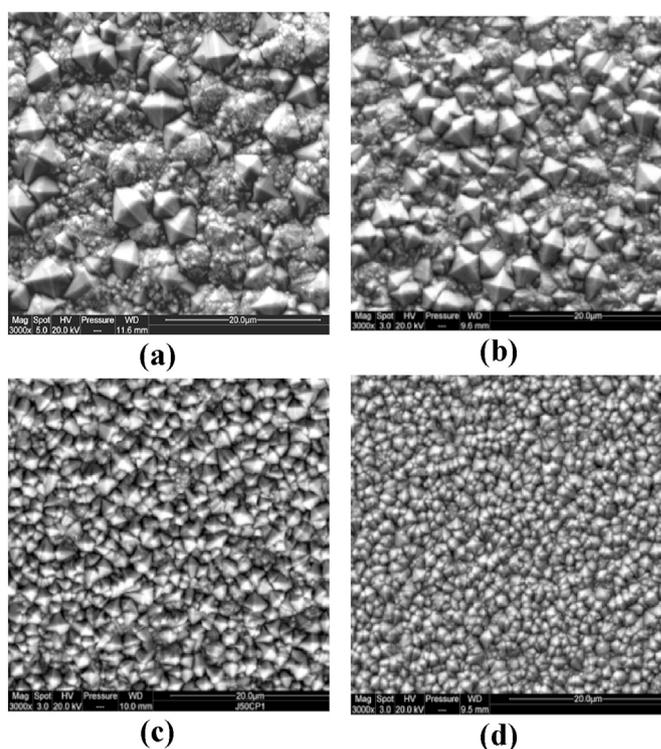


Fig. 2. Influence of t_{off} on surface morphology of nickel deposited from a Watts Bath at 60° with constant t_{on} of 5 ms and j_m of 50 mA/cm²: (a) 10; (b) 50; (c) 90; (d) 100 ms.

Table 3 presents the average sizes of the nodules deduced from the SEM surface observations, and evaluated for different configurations at the same magnification using the intersection methods through the two image diagonals. The average size of nodules effectively increases with the current density.

3.2. Ni coatings deposited under pulse regime

3.2.1. Effect of off-time

Table 4 illustrates the pulse plating parameters and average current densities j_m used to investigate the influence of pulse off-time on surface morphology and crystal orientations.

Fig. 2 presents the SEM observations of the different coatings performed when off time is increased. The average current density was fixed at 50 mA.cm⁻², corresponding to an heterogeneous microstructures previously described. For values of t_{off} between 10 and 20 ms, the morphology (Fig. 2a) is heterogeneous presenting large pyramids interconnected by a finer matrix. This type of morphology has already been observed in continuous mode and corresponds to the formation of instabilities on the interface that promotes the local growth of grains compare with the rest of the matrix for which growth rate seems to be quite constant. We can assume that the presence of these large coarse pyramids is probably due to heterogeneities in the growth rate probably associated to local chemical variation of the species concentration at the vicinity of the electrode during the restauration period. Furthermore, it was shown that small values of t_{off} are not sufficient to restore the initial concentration of electroactive species in the electrolytic interfacial layer. Decrease of the concentration of Ni²⁺ cations in the diffusion layer will promote the reaction of reduction of the proton due to the low hydrogen overvoltage on nickel. However, the competition between the reduction reaction implying these two cations Ni²⁺ and H⁺ slows down the reduction kinetics of nickel reduction.

For high values of t_{off} (90 and 100 ms), the morphology becomes more homogeneous, smoother, more compact and composed of very fine

Table 5

Evolution of the average nodule size deduced from SEM observations with the off-time value.

t_{off} (ms)	j_p (mA/cm ²)	γ (%)	d_{SEM} (μ m)
10	150	33	1.96 \pm 1.26
50	550	9.1	1.65 \pm 0.98
90	950	5.2	1.18 \pm 0.52
100	1050	4.7	0.77 \pm 0.35

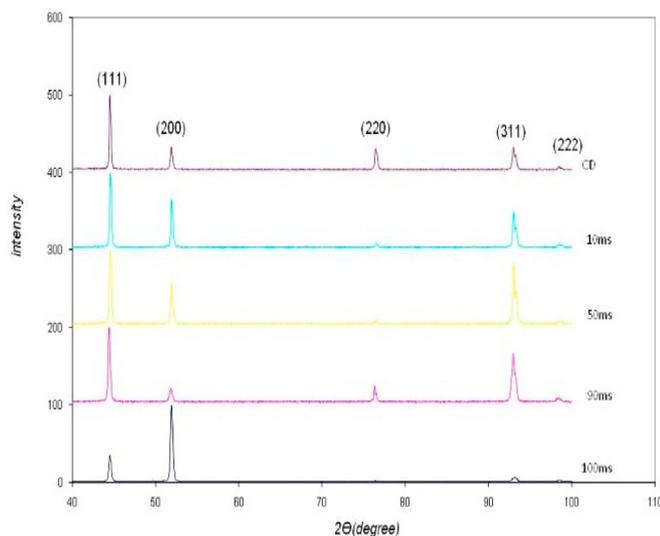


Fig. 3. XRD patterns showing the influence of t_{off} on the crystal orientation of nickel deposits with constant average current density j_m of 50 mA/cm² and t_{on} of 5 ms.

pyramids as observed in Fig. 2c and 2d. We also note the disappearance of the large coarse pyramids. We can deduce that the increase of t_{off} has a beneficial effect on the morphology of deposits. It is known that a long off-time is required for desorption of non required species adsorbed on the surface or inserted into the solid phase [39]. Moreover, the redistribution of hydrogen near the electrode during the off-time permits to activate additional nucleation sites favoring homogeneous microstructure. Increase of the off-time is associated with a drastic increase of the current density linked to the pulse plating. So the density of nucleation sites normally increases with the current density of the pulse. So the formation of smaller nuclei is favored. Furthermore, the off-time increase permits to limit the metallic ions depletion in the electrolyte double layer, leading to homogenous coating morphology. But this parameter should be optimized because the off-time period was also reported as promoting the growth of the nucleus.

Table 5 presents the average size of the nickel nodules deduced from SEM observations presented in Fig. 2. As it was noticed, when the current density of the pulse (j_p) is increased, the size of the nodules is slightly reduced from 1.96 to 0.77 μ m. The evolution of off-time period can not be easily associated with the nodule size evolution. The morphology becomes more uniform as the range of nodule size also becomes narrow. So the off-time evolution probably affects the growth mechanism permitting a more uniform and narrow distribution of nickel nodules.

Finally, it seems that the off-time value of 100 ms would be optimal for obtaining a fine and uniform morphology. Electrocrystallization mechanism of nickel from the Watts bath were largely investigated in the literature [30,31,33,40–42], and it was reported that the rate-determining stage corresponds to the step associated to charge transfer leading to adsorbed species and replenishing double layer of electroactive species. Increasing the t_{off} can not lonely explain the structure refinement, because it is combined with high pulse current

Table 6

Evolution of the texture index with the current density for coatings deposited in pulsed regime for different t_{off} values.

Plating conditions			Texture index				
j_m (mA/cm)	t_{on} (ms)	t_{off} (ms)	$N_{(111)}$	$N_{(200)}$	$N_{(220)}$	$N_{(311)}$	$N_{(222)}$
50	5	100	0.751	1.161	0.374	2.345	0.954
50	5	90	0.883	0.426	1.033	2.495	1.243
50	5	50	0.769	0.963	0.308	2.680	1.012
50	5	10	0.853	1.240	0.337	1.772	1.018

density j_p that allows the activation of a larger number of nucleation sites.

The X-ray diffraction diagrams, presented in Fig. 3, of the deposits obtained in pulsed mode by varying the value of t_{off} show that the spectra are quite similar to those of deposits prepared in direct current. For low values of off time, the coating morphology is quite similar to that obtained in direct current, and a random orientation characterizes the microstructure of the coating. When the t_{off} is increased (and so on the pulse current density), the morphology becomes more homogeneous and the nodule size is progressively reduced. The nodules present a pyramidal shape for the whole conditions, and a preferentially (200) orientation is marked when t_{off} reaches 100 ms. According to Amblard et al. [43,44], the free mode of growth for electrolytic Ni, which corresponds to $\langle 100 \rangle$ texture, is associated with the adsorbed intermediate (NiOH)_{ads}. More recently, the effect of hydrogen adsorption on nickel adatoms mobility and on other events occurring at the growing interface was theoretically evaluated [45]. These calculations suggest that the effects of hydrogen adsorption strongly depend on surface orientation. So, the off-time period favors the desorption of interfacial inhibitors such as H₂ or Ni(OH)₂ promoting the growth of specific crystal orientation.

It was found that the application of the pulse current technique influences the composition of the electrolyte at the electrode interface owing the desorption of impurities during the relaxation time that would modify the structure and the properties of the deposits [2,46]. However, it is necessary to limit the off-time because it was reported that high values lead to morphological and microstructural deterioration of the coating.

Table 6 presents the texture index deduced from XRD patterns of the coatings synthesized at different values of off-time. The relative texture coefficient $N_{(hkl)}$ was used to determine the preferred crystalline orientations of the deposits and to evaluate their qualities [47]. $N_{(hkl)}$ is defined as:

$$N_{(hkl)} = \frac{IF_{(hkl)}/I_{P(hkl)}}{\sum_1^5 (IF_{(hkl)}/I_{P(hkl)})} \cdot 100 \%$$

where $IF_{(hkl)}$ and $I_{P(hkl)}$ are the diffraction intensities of the (hkl) plane measured in the diffractogram for the deposit and the standard Ni powder sample (JCPDS n°04–0850). A value of $N_{(hkl)} > 1$ indicates a preferred orientation of the (hkl) reflection compared with the random distribution of the grains. According to Table 6, the texture index values do not permit to distinguish eventual preferential orientations, it can only be observed that for high off-time values, the $\langle 111 \rangle$ index slightly

Table 7

Plating conditions of nickel coatings deposited at 60°C in pulsed mode with constant values of t_{off} and j_m .

t_{on} (ms)	t_{off} (ms)	j_m (mA/cm) ²	j_p (mA/cm) ²	γ (%)
3	100	50	1716.66	2.91
5	100	50	1050.00	4.76
9	100	50	605.55	8.25
15	100	50	383.33	13.04

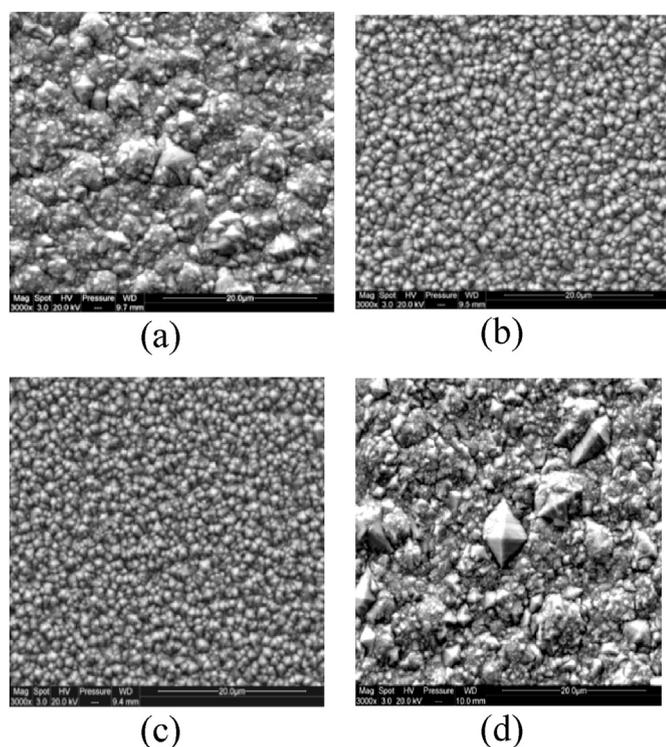


Fig. 4. SEM micrographs showing the influence of t_{on} on surface morphology: (a)3; (b)5; (c)9 (d)15 ms.

decreases and the $\langle 100 \rangle$ becomes predominant. In the range of experimental parameters, the evolution of texture index is not enough significant so as to suggest modification of the growth mechanism with off-time evolution.

3.2.2. Influence of on-time on plating deposits

The influence of on-time parameter on crystal morphology and orientation of nickel deposits was investigated with constant pulsed current density and off-time (Table 7). The latter parameter was fixed at $t_{off} = 100$ ms as this value leads to a drastic improvement of the coating morphology.

Fig. 4 presents the SEM observations of the coatings performed at different values of on-time ranging from 3 to 15 ms. The influence of the on-time on the morphology of nickel deposits shows that the morphology of the deposit is strongly influenced by the change of on time. For $t_{on} = 3$ ms, the texture of deposits is formed by heterogeneous large pyramids surrounded by uniaxial crystallites. The density of large pyramids is very low for small values of t_{on} . Between $t_{on} = 5$ and 9 ms, the structure changes drastically and becomes more uniform, more fine, formed by very thin well-faceted pyramidal-shaped crystallites. By increasing the t_{on} to 9 ms particle size is much fine, which is surprisingly due to the fact that intensity of the pulse is less important compared with $t_{on} = 3$ ms and 5 ms. A further increase of the on-time parameter to 15 ms results in the reappearance of the larger pyramidal-shape crystallite structure (Fig. 4d) and the structure becomes randomly oriented. This difference in morphology could be linked to a local modification of the nucleation-growth mechanism of nickel. As reported by many studies, high cathodic overpotentials favor great nucleation rate promoting a refinement of the microstructure. When the on-time parameter is decreased, the pulse current progressively becomes higher, so the cathodic overpotential should favor the formation of small crystallite. But we can observe that the lowest value of t_{on} effectively leads to a refinement of the crystallite, but heterogeneities are observed due to local coalescence of few crystallites.

Another explanation for the refinement of crystallite when on-time

Table 8

Evolution of the average nodule size deduced from SEM observations with the on time value.

t_{on} (ms)	j_p (mA/cm ²)	γ (%)	d_{SEM} (μ m)
3	1716.66	2.91	2.04 ± 0.75
5	1050	4.76	0.77 ± 0.35
9	605.55	8.25	0.71 ± 0.17
15	383.33	13.04	2.11 ± 1.19

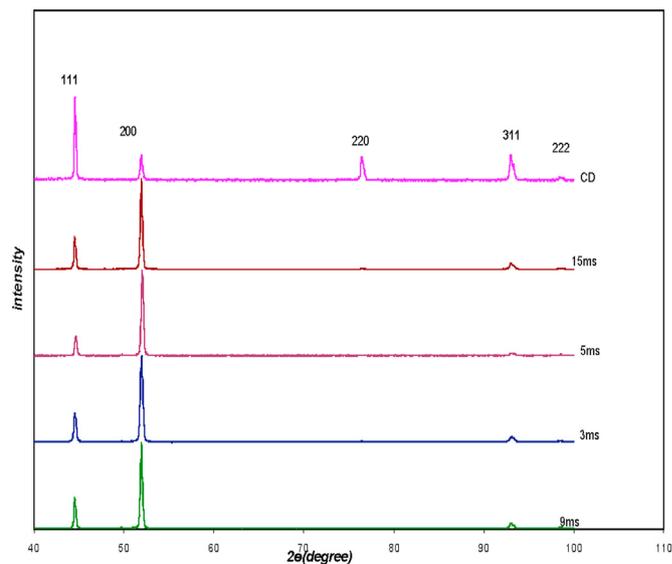


Fig. 5. XRD patterns showing the influence of t_{on} on the crystal orientation of nickel deposits with constant j_m of 50 mA/cm² and t_{off} of 100 ms.

decreased that longer on-time lead to an increase in the amount of hydrogen that provokes the shift of the pH of the nickel/electrolyte interface toward more basic values, enhancing the adsorption and co-deposition of basic insoluble compounds such as Ni(OH)₂. The adsorption or incorporation of these insoluble species at the active growth sites is believed to have inhibiting effect leading to finer-grained structure [48]. Explanation of the reappearance of large pyramids at high t_{on} values (15 ms) could be associated with the redistribution of partial current reduction of nickel and hydrogen. Hydrogen evolution becomes significant [48], it is assumed that the major part of the applied current is consumed by the reduction of the proton leading to a low current of deposition of nickel favoring the formation of larger grains. Yoshimura [49] reported such a decrease in the current efficiency for palladium deposition and a corresponding increase in co-deposition hydrogen at longer t_{on} . On-time value close to 9 ms seems to be the optimal value in order to reach finer structures (see Table 8), compact and homogeneous texture. So it was shown that t_{on} must be smaller than the value of pulse limiting current density (j_L). The pulse t_{on} must be short to stay below the (j_L), but sufficiently long to fully charge the double layer [47]. But, the changes of microstructure and properties of deposits can not only

Table 9

Evolution of the texture index with the current density for coatings deposited in pulsed regime for different t_{on} values.

Plating conditions			Texture index				
j_m (mA/cm ²)	t_{on} (ms)	t_{off} (ms)	N ₍₁₁₁₎	N ₍₂₀₀₎	N ₍₂₂₀₎	N ₍₃₁₁₎	N ₍₂₂₂₎
50	3	100	0.466	2.999	0.143	0.399	0.489
50	5	100	0.751	1.161	0.374	2.345	0.954
50	9	100	0.505	3.092	0.0996	0.412	0.434
50	15	100	0.489	2.986	0.094	0.412	0.413

Table 10
Parameters of pulsed electrodeposition of Ni coatings at constant ton and toff.

t_{on} (ms)	t_{off} (ms)	j_m (mA/cm ²)	J_p (mA/cm ²)	γ (%)	d_{SEM} (μ m)
9	100	50	605.55	8.25	0.71 ± 0.17
9	100	100	1211.11	8.25	0.43 ± 0.11
9	100	150	1816.66	8.25	1.05 ± 0.24

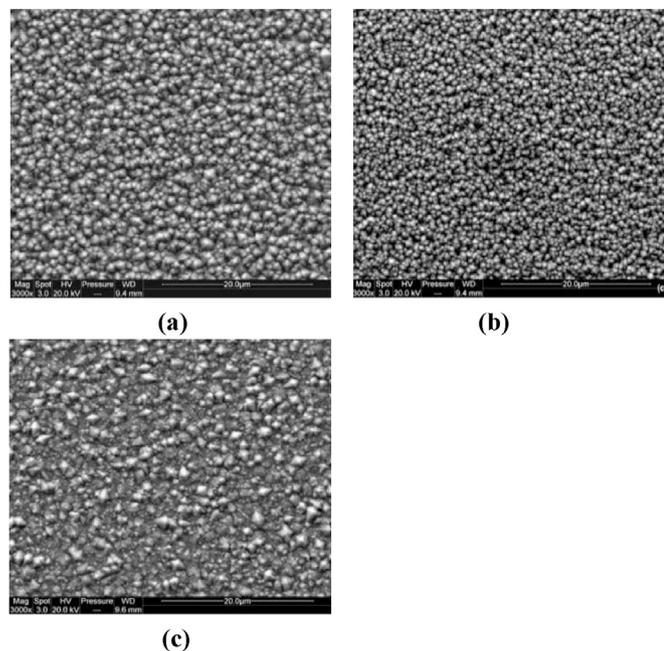


Fig. 6. Influence of j_m on surface morphology of nickel deposits with t_{off} of 100 ms and t_{on} of 9 ms (a) 50 (b) 100 and (c) 150 mA/cm².

attributed to the change of t_{on} , because when t_{off} and average current density (J_m) were kept constant, t_{on} was increased, however, J_p could not be kept constant, it was unable to determine whether changes on the surface morphology and microstructure of electrodeposits were caused by changes of t_{on} and/or J_p . Then, it may be concluded that increasing of the pulse on-time and the peak current density (J_p) can refine grains. Evidently, with the increase of J_p cathode polarization increases correspondingly, at higher overpotential, the nucleation rate increases so the deposits are thinner.

Fig. 5 presents the diffraction diagrams of the coatings realized at

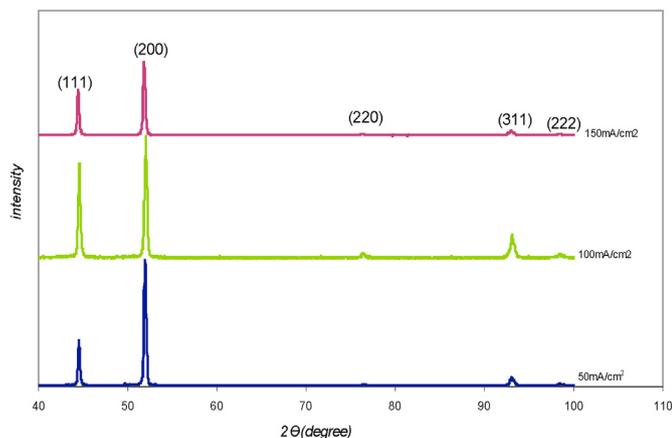


Fig. 7. XRD patterns showing the influence of the average current density on the crystal orientation of nickel deposits with constant on time of 9 ms and off time of 100 ms.

Table 11
Evolution of the texture index with the current density for coatings deposited in pulsed regime for constant t_{on} and t_{off} values.

Plating conditions			Texture index				
j_m (mA/cm ²)	t_{on} (ms)	t_{off} (ms)	$N_{(111)}$	$N_{(200)}$	$N_{(220)}$	$N_{(311)}$	$N_{(222)}$
50	9	100	0.505	3.092	0.099	0.412	0.434
100	9	100	0.725	2.076	0.281	0.857	0.752
150	9	100	0.698	2.525	0.145	0.339	0.416

different values of t_{on} with an average current density corresponding to 50 mA/cm². The diffraction diagrams of the coating synthesized at the same current density in direct current mode is also presented as reference. The reference sample presents a randomly oriented texture whereas the XRD diagrams of all the coatings performed at different t_{on} values reveal the presence of preferential (200) orientation, as demonstrated in **Table 9** where the texture index of (200) orientation is largely higher than 1.

The texture of the deposits is mainly due to the effect of t_{off} as it has been already reported in previous paragraph. According to the literature [35], the modification of t_{on} affect mainly the evolution of the chemical composition of the double layer and determines the surface morphology of the electrodeposited film, especially for thick film. Moreover, it was demonstrated that the transition from the randomly crystalline orientation to the plane (200) preferential orientation may be due to the deposition of colloidal species like Ni(OH)₂ and/or the hydrogen away from the cathode surface [13] formed during the active period (t_{on}) on the surface of the cathode [16]. According to our results, the texture evolution is directly related to events occurring during the resting stage.

3.2.3. Influence of the average current density j_m on deposit

The influence of the average current density j_m on the microstructure and morphology of the deposits was investigated. Values of $t_{on} = 9$ ms and $t_{off} = 100$ ms were selected as optimized values. The electrodeposition conditions are described and reported in **Table 10**.

Fig. 6 presents SEM observations of coatings deposited at different values of average current density from 50 to 150 mA/cm². We notice that the deposits present a pyramidal shape characterized by a homogeneous and uniform distribution of grains. There is a strong influence of current density on the morphology of deposit. Indeed, by increasing the average current density of 50–100 mA/cm², the morphology becomes finer and more homogeneous. However at 150 mA/cm², the morphology becomes less homogeneous and it is composed of very fine pyramids interconnected by a continuous background that seems very thin. These results are consistent with many studies on the deposition of nickel in Watts bath by pulsed current [35,48,49].

Grain refinement in pulse plating is favored by the enhancement of nucleation rates due to high overpotentials which result from high pulse current densities. It seems that the off-time also influence the nucleation and growth mechanism, essentially through the renewing of the solution between pulses that is directly dependent on the level of the pulse current density. Thus, the evolution of the morphology could also be related to local changes at the interface like interfacial alkalination and evolution of the nature of metal species (intermediates compounds, adsorbed complex) at the interface, as it was noticed in the case of cobalt: the conditions of hydrogen evolution are modified [16], on the other hand, the instantaneous pulse current strongly modifies the mass transport processes at the electrode-electrolyte interface. At the same average current density, the nodule size, deduced from SEM observations, obtained in pulse current electrodeposition is smaller and more homogenous than that in direct current electrodeposition. It can be explained by a higher peak current density used in pulse current electrodeposition.

XRD diagrams of the different coatings are presented on **Fig. 7**. Increasing the average current density for a couple of t_{on} and t_{off} constant, does not induce any significant change in the structure of the

deposits (see Table 11). Moreover, it has been argued that the plan (200) is a free mode of growth that is not affected by the action of interfacial inhibitors [17,45,46]. Changes in the crystal growth may therefore be related to process of adsorption, desorption occurring at the interface nickel/electrolyte.

The average current density of 100 mA/cm² presents the most uniform morphology of the coatings probably due to an adequate balance between the increase of the nucleation sites due to the high applied overpotential and the renewing of the electrolyte during the off time.

4. Conclusions

Fine-grained Nickel coatings were produced by pulse electrodeposition from Watts bath without using any additives. The effect of, pulse on-time, off-time, and average current density on the surface morphology and microstructure of Nickel electrodeposit was investigated. The results obtained, revealed that low values of ton and toff lead to morphology and structure of the deposits quite similar to those obtained in continuous mode. When toff increases to 100 ms, finer grain size and more Homogeneous microstructure could be obtained. A pulse on-time of 9 ms seems to be the optimal value to reach better uniformity, finer structures, compact and smoother texture. It was also found an ultra-fine-grained deposit can be obtained by increasing the applied average current density during plating. In addition, the crystal orientation progressively changed from a (111) texture to a strong (200) texture with Variations in pulsed current parameters.

In conclusion, These results suggest that adjustment of ton, toff and jm of the pulse current, can lead to the desired quality of nickel deposits.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Cl J, Puipe, Leaman F, editors. *Theory and Practice of Pulse Plating*. Orlando, Florida: AESF; 1986.
- Ding J, Li X, Zhou L, Yang R, Yan F, Su B. Electrodeposition of nickel nanostructures using silica nanochannels as confinement for low-fouling enzyme-free glucose detection. *J. Mater. Chem. B*. 2020;8:3616–22. <https://doi.org/10.1039/C9TB02472G>.
- Youssef Kh MS, Koch CC, Fedkiw PS. Improved corrosion behavior of nanocrystalline zinc produced by pulse-current electrodeposition. *Corrosion Sci*. 2004;46:51–64. [https://doi.org/10.1016/S0010-938X\(03\)00142-2](https://doi.org/10.1016/S0010-938X(03)00142-2).
- Talbot JB. Electrodeposition of nanocomposite films, *Plat. Surf. Finish*. 2004;91:60–5.
- Boukhouiete A, Boumendjel S, Sobhi NE. Effect of current density on the microstructure and morphology of the electrodeposited nickel coatings. *Turk. J. Chem*. 2021;45:1599–608. <https://doi.org/10.3906/kim-2102-46>.
- Allongue P, Cagnon L, Gomes C, Gündel A, Costa V. Electrodeposition of Co and Ni/Au(111) ultrathin layers. Part I: nucleation and growth mechanisms from in situ STM. *Surf. Sci*. 2004;557(1):41–56. <https://doi.org/10.1016/j.susc.2004.03.016>.
- Evans P, Scheck C, Schad R, Zangaric G. Electrodeposition of epitaxial nickel films on GaAs. *J. Magn. Mater*. 2003;260:467–72. [https://doi.org/10.1016/S0304-8853\(02\)01403-8](https://doi.org/10.1016/S0304-8853(02)01403-8).
- Serek A, Budniok A. Production of electrolytic nickel and nickel-phosphorous composite layers containing titanium. *Curr. Appl. Phys*. 2002;2:193–9. [https://doi.org/10.1016/S1567-1739\(02\)00062-7](https://doi.org/10.1016/S1567-1739(02)00062-7).
- Qu NS, Chan KC, Zhu D. Surface roughening in pulse current and pulse reverse current electroforming of nickel. *Surf. Coating. Technol*. 1997;91(3):220–4. [https://doi.org/10.1016/S0257-8972\(97\)00523-9](https://doi.org/10.1016/S0257-8972(97)00523-9).
- Chan KC, Qu NS, Zhu D. Quantitative texture analysis in pulse reverse current electroforming of nickel. *Surf. Coating. Technol*. 1998;99(1–2):69–73. [https://doi.org/10.1016/S0257-8972\(98\)00523-9](https://doi.org/10.1016/S0257-8972(98)00523-9).
- Hadian SE, Gabe DR. Residual stresses in electrodeposits of nickel and nickel-iron alloys. *Surf. Coating. Technol*. 1999;122:118–35. [https://doi.org/10.1016/S0257-8972\(99\)00328-X](https://doi.org/10.1016/S0257-8972(99)00328-X).
- Popov KI, Maksimović MD, Stevanović RM, Krstajić NV. Fundamental aspects of pulsating current metal electrodeposition VIII: the effect of pause-to-pulse ratio on microthrowing power of metal deposition. *Surf. Technol*. 1984;22:155–8. [https://doi.org/10.1016/0376-4583\(84\)90051-7](https://doi.org/10.1016/0376-4583(84)90051-7).
- Orináčková R, Trnková L, Gálová M, Šupicová M. Application of elimination voltammetry in the study of electroplating processes on the graphite electrode. *Electrochim. Acta* 2004;49:3587. <https://doi.org/10.1016/j.electacta.2004.03.027>.
- Bockris JOM, Drazic D, Despic AR. The electrode kinetics of the deposition and dissolution of iron. *Electrochim. Acta* 1961;4:325–61.
- Gomez E, Pollina R, Vallés E. Morphology and structure of nickel nuclei as a function of the conditions of electrodeposition. *J. Electroanal. Chem*. 1995;397:111. [https://doi.org/10.1016/0022-0728\(95\)04202-1](https://doi.org/10.1016/0022-0728(95)04202-1).
- Kollia C, Spyrellis N. Textural modifications in nickel electrodeposition under pulse reserved current. *Surf. Coating. Technol*. 1993;57:71–5. [https://doi.org/10.1016/0257-8972\(93\)90338-O](https://doi.org/10.1016/0257-8972(93)90338-O).
- Amblard J, Froment M, Maurin G, Spyrellis N, Trevisan-Souteyrand E. Nickel electrocrystallization—from nucleation to textures. *Electrochim. Acta* 1983;28:909–15. [https://doi.org/10.1016/0013-4686\(83\)85166-4](https://doi.org/10.1016/0013-4686(83)85166-4).
- Das P, Samantaray B, Dolai S, et al. Combined effect of sodium lauryl sulphate and saccharin on microstructure and corrosion performance of electrodeposited nickel prepared from modified watts bath. *Metall. Mater. Trans*. 2021;52:1913–26. <https://doi.org/10.1007/s11661-021-06202-y>.
- Mahidashti Z, Aliofkhaezrai M, Lotfi N. Review of nickel-based electrodeposited tribo-coatings. *Trans. Indian Inst. Met*. 2018;71:257–95. <https://doi.org/10.1007/s12666-017-1175-x>.
- Mockute D, Bernotiene G, Vilkaite R. Reaction mechanism of some benzene sulfonamide and saccharin derivatives during nickel electrodeposition in Watts-type electrolyte. *Surf. Coat. Technol*. 2002;160:152–7. [https://doi.org/10.1016/S0257-8972\(02\)00385-7](https://doi.org/10.1016/S0257-8972(02)00385-7).
- Lemaire G, Hébant P, Picard GS. DFT analysis of interfacial processes occurring in the first steps of electrodeposition of nickel from chloride melt. *J. Mol. Struct*. 1997;419:1–10. [https://doi.org/10.1016/S0166-1280\(97\)00250-9](https://doi.org/10.1016/S0166-1280(97)00250-9).
- Watts OP. Rapid nickel plating. *Trans. An. Electrochem. Soc*. 1916;23:395–403.
- Godon A, Creus J, Feaugas X, Conforto E, Pichon L, Armand C, Savall C. Characterization of electrodeposited nickel coatings from sulphamate electrolyte without additive. *Mater. Character* 2011;62:164. <https://doi.org/10.1016/j.matchar.2010.11.0.11>.
- Ma C, Zhao D, Liu W, Xia F, Jin P, Sun C. Magnetic assisted pulse electrodeposition and characterization of Ni-TiC nanocomposites. *Ceram. Int*. 2020;46(11):17631–9. <https://doi.org/10.1016/j.ceramint.2020.04.065>.
- Xia F, Li Q, Ma C, Liu W, Ma Z. Preparation and wear properties of Ni/TiN-SiC nanocoatings obtained by pulse current electrodeposition. *Ceram. Int*. 2020;46(6):7961–9. <https://doi.org/10.1016/j.ceramint.2019.12.017>.
- Xia F, Li C, Ma C, Li Q, Xing H. Effect of pulse current density on microstructure and wear property of Ni-TiN nanocoatings deposited via pulse electrodeposition. *Appl. Surf. Sci*. 2021;538:148139. <https://doi.org/10.1016/j.apsusc.2020.148139>.
- Popov KI, Keca DN, Vuksanovic BI. The effect of the overpotential of deposition on the porosity of metal deposits. *J. Appl. Electrochem*. 1977;7:185–8.
- Raub CJ, Knodler A. Pulse-Plated gold, plat. *Surf. Finish*. 1978;65:32–4.
- Youssef Kh MS, Koch CC, Fedkiw PS. Influence of additives and pulse electrodeposition parameters on production of nanocrystalline zinc from zinc chloride electrolytes. *J. Electrochem. Soc*. 2004;151:C103–11.
- Mishra R, Basu B, Balasubramaniam R. Effect of grain size on the tribological behavior of nanocrystalline nickel. *Mater. Sci. Eng*. 2004;373:370. <https://doi.org/10.1016/j.msea.2003.09.107>.
- Kollia C, Spyrellis N, Amblard J, Froment M, Froment M, Maurin G. Nickel plating by pulse electrolysis textural and microstructural modifications due to adsorption/desorption phenomena. *J. Appl. Electrochem*. 1990;20:1025–32.
- Godon A, Creus J, Cohendoz S, Conforto E, Feaugas X, Girault P, Savall C. Effects of grain orientation on the Hall-Petch relationship in electrodeposited nickel with nanocrystalline grains. *Scr. Mater*. 2010;62:403–6. <https://doi.org/10.1016/j.scriptamat.2009.11.038>.
- Saitou M, Oshikawa W, Mori M, Makabe A. Surface roughening in the growth of direct current or pulse current electrodeposited nickel thin films. *J. Electrochem. Soc*. 2001;148:C780.
- Pavlatou EA, Raptakis M, Spyrellis N. Synergistic effect of 2-butyne-1,4-diol and pulse plating on the structure and properties of nickel nanocrystalline deposits. *Surf. Coating. Technol*. 2007;201:4571. <https://doi.org/10.1016/j.surfcoat.2006.09.113>.
- El-Sherik AM, Erb U, Page J. Microstructural evolution in pulse plated nickel electrodeposits. *Surf. Coat. Technol*. 1996;88:70–8. [https://doi.org/10.1016/S0257-8972\(96\)02928-3](https://doi.org/10.1016/S0257-8972(96)02928-3).
- Zhang H, Xia F, Wang J, Xu F. Influence of duty cycle and pulse frequency on structures and performances of electrodeposited Ni-W/TiN nanocomposites on oil-gas X52 steels. *Coatings* 2021;11:1182. <https://doi.org/10.3390/coatings1110.1182>.
- Kim W, Weil R. Property enhancement of nickel electrodeposits by anodic current pulses. *Surf. Coat. Technol*. 1987;31:143–50.
- Budevski E, Staikov G, Lorenz WJ. *Electrochemical phase formation and growth. In: Advances in Electrochemical Science and Engineering*. first ed. Wiley-VHC; 1996.
- Wiart R. Elementary steps of electrodeposition analysed by means of impedance spectroscopy. *Electrochim. Acta* 1990;35:1587–93.
- Saraby-Reintjes A, Fleischmann M. Kinetics of electrodeposition of nickel from watts baths. *Electrochim. Acta* 1984;29:557–66. [https://doi.org/10.1016/0013-4686\(84\)87109-1](https://doi.org/10.1016/0013-4686(84)87109-1).
- Epelboin I, Wiart R. Mechanism of the electrocrystallization of nickel and cobalt in acidic solution. *J. Electrochem. Soc*. 1971;118:1577–82.
- Amblard J, Froment M, Spyrellis N. Origine des textures dans les depots électrolytiques de nickel. *Surf. Technol*. 1977;5:205–34. [https://doi.org/10.1016/0376-4583\(77\)90047-4](https://doi.org/10.1016/0376-4583(77)90047-4).

- [43] Haug K, Jenkins T. Effects of hydrogen on the three- dimensional epitaxial growth of Ni (100), (110), and (111). *J. Phys. Chem. B* 2000;104:10017. <https://doi.org/10.1021/jp0012092>.
- [44] Lajevardi SA, Shahrabi T. Effects of pulse electrodeposition parameters on the properties of Ni-TiO₂ nanocomposite coatings. *Appl. Surf. Sci.* 2010;256:6775–81. <https://doi.org/10.1016/j.apsusc.2010.04.088>.
- [45] Abdulin VS, Chernenko VI. The current efficiency and mechanical properties of nickel deposited in a pulse mode. *Protect. Met.* 1982;18:777.
- [46] Yoshimura S, Chida S, Sato E, Kubota N. Pulsed current electrodeposition of palladium. *Met. Finish.* 1986;84:39–42.
- [47] Chandrasekar MS, Pushpavanam M. Pulse and pulse reverse plating-Conceptual, advantages and applications. *Electrochim. Acta* 2008;53:33133322. <https://doi.org/10.1016/j.elect.acta.2007.11.054>.
- [48] Xuetao Y, Yu W, Dongbai S, Hongying Y. Influence of pulse parameters on the microstructure and microhardness of nickel electrodeposits. *Surf. Coat. Technol.* 2008;202:1895. <https://doi.org/10.1016/j.surfcoat.2007.08.023>.
- [49] Qu NS, Zhu D, Chan KC, Lei WN. Pulse electrodeposition of nanocrystalline nickel using ultra narrow pulse width and high peak current density. *Surf. Coating. Technol.* 2003;168:123. [https://doi.org/10.1016/S0257-8972\(03\)00014-8](https://doi.org/10.1016/S0257-8972(03)00014-8).