



## Nickel deposits obtained by continuous and pulsed electrodeposition processes

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### Abstract

Metallic coatings are used for protection against corrosion of metal structures. The protection provided depends on the physico-chemical coatings. Three factors are crucial to have good resistance to corrosion morphology, crystallographic orientation and composition of layers. These can be modified in view of improving the corrosion resistance [1] by using appropriate organic additives. A promising alternative is also possible by the dedicated implementation of the electrodeposition technique in pulsed mode [2]. This technique allows an improvement of the characteristics of metals and alloys deposited compared to coatings obtained by conventional routes. This work is part of that objective. Thus we propose to optimize the parameters of development, pulsed coatings of nickel. Morphology of coatings was characterized by observations in scanning electron microscopy (SEM-FEG). The X-ray diffraction in symmetric mode was used to evaluate the structure and the main crystallographic orientations of the deposits. The results obtained, showed that the development in pulsed induced a marked improvement in the morphology and grain refinement.

**Keywords:** Nickel coating, Pulse plating, Direct current, Morphology, Microstructure.

### 1. Introduction

Electroplating is one of few surface-finishing processes that can satisfy the requirements of decorative and functional applications. It promotes the appearances, extends the life, and improves the performances of materials and products in different media. Electrochemical methods of coating metallic layers are 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, and (c) versatility, as the codeposition technology can produce a variety of novel materials such as nanocomposites [3]. Electrodeposition of nickel has been investigated intensively for decades because of its particular mechanical properties in numerous applications in industry. Many experimental works were published [4]. And many mathematical models of Ni electrodeposition were suggested [5]. The first nickel bath was formulated by Watts [6] in 1916, and this bath still used today because of its simplicity to control and low cost to operate. Recently, the synthesis of nickel by pulse electrodeposition has attracted much attention. Pulse electrodeposition can be used as a means of producing unique structures with improved properties, i.e., coating with properties not obtainable by D.C plating.

In the pulsed electrodeposition process, the average current density ( $j_m$ ) is equivalent to the current density applied in the continuous electrodeposition process and is defined as:  $j_m = j_p t_{on} / (t_{on} + t_{off})$  where  $j_m$  is the average current density,  $j_p$  is the peak current density,  $t_{on}$  is the time of the cathodic pulse (on-time) and  $t_{off}$  is the time between pulses (off-time).

The present investigation was undertaken to verify the modifications in morphology and microstructure of deposits of Ni obtained by continuous and pulsed electrodeposition.

## 2. Materials and methods

### 2.1. Synthesis of nickel coating

Nickel coatings were deposited on nickel substrates by direct (D.C) and pulsed (P.C), using watts bath. A nickel sheet (10X5cm) of 99.99% purity contained in anode bag was used as a soluble anode. A commercial pure nickel (obtained from goodfellow society) was used as cathodes. The exposed surface area of each cathode was 2cm<sup>2</sup>. Prior to deposition, the nickel substrates were mechanically polished with silicon carbide paper of 600, 800, 1000, 1200, 2500, 4000 grits. The coatings thickness was fixed about 50µm by controlling the plating time. The plating temperature was kept constant at 60°C, when a Haake D8 cryostat was used. The pH was adjusted to a constant value of 4.5 by adding NaOH to rise it. The stirring rate was kept constant at 200rpm.

**Table 1:** Bath composition and plating conditions for Ni deposition from watts bath.

NiSO <sub>4</sub> .7H <sub>2</sub> O	300 g /L
NiCl <sub>2</sub> .6H <sub>2</sub> O	45 g /L
Boric acid	45 g /L
pH	4.5
Temperature	60°C

Electrodepositions were carried out using a electrochemical experiment were performed in a conventional three-electrode cell, using VSP Biologic Science Instruments potentiostat-galvanostat. Working electrode was placed vertically in the electroplating cell of 250 mL with magnetic stirring, parallel to the anode, with anode-cathode distance of 3cm. The reference electrode was a saturated calomel electrode (SCE) attached to the cell through a Luggin-Haber capillary tube. The distance between the capillary tube tip and the working electrode was 2 mm.

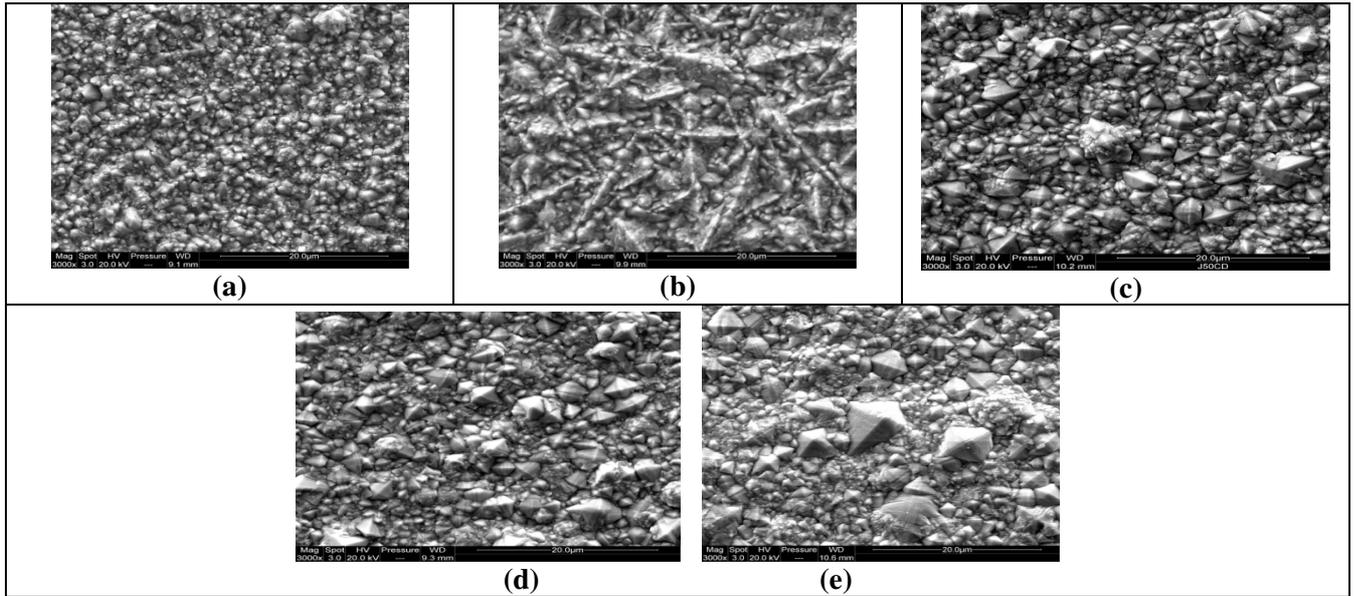
Surface morphology of the deposit was studied by scanning electron microscopy (MEB-FEG quanta 200F). The deposit structure under various plating was charaterised by X-ray diffraction using Bruker D8 advance diffractometer, with Cu-K $\alpha$  radition. Diffractograms were recorded with a step size of 0.04° for 2 $\theta$  ranging from 40 to 100°.

## 3. Results and discussion

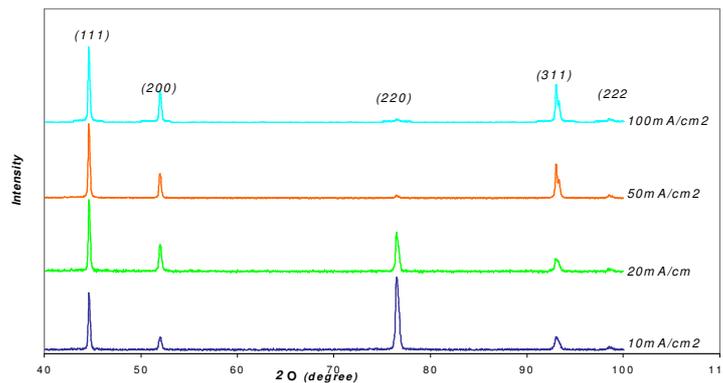
### 3.1. Nickel deposits under direct current regime

Figure 1 shows the scanning electron microscope images for nickel deposits prepared from Watts bath under direct current at different values of current densities. It can be seen that the grain size of nickel deposits increases with increasing deposition current density (idep). The smallest grain size was produced at idep = 10mA/cm<sup>2</sup>. It can be seen that for the higher idep (Figure 1b, 1c), the surface morphology of the deposit consists of large well-faceted pyramidal-shaped crystallites sur-rounded by unfaceted finer grains. The pyramidal growth is typical of a field-orientation texture, which exhibits preferential growth habit in the direction of electric field [7].

Figure 2 presents the X-ray diffraction (XDR) patterns of the electrodeposited Ni films deposited at direct current. At low current density  $j= 10 \text{ mA/cm}^2$ , the (220) peak becomes predominant. It was reported that this kind of structure appears preferentially at low current densities and for pH values between 1 and 5, the formation of this orientation can be attributed to a specific inhibition by H<sub>ads</sub> [8]. When the current density increases, the intensity of the (220) peak is strongly reduces whereas the obtained patterns seem to be close to a random orientation. The intensity of (111) fiber orientation increases with an increase in the current density when it ranges from 20 to 100 mA/cm<sup>2</sup>. A quite random orientation is obtained a high current densities, probably due to the heterogeneous morphology and large distribution of nodule sizes. In direct current electrodeposition, a uniform distribution of nodule size is obtained whereas coalescence of nodules in pyramidal-shape happens for higher current densities. So coarse large pyramidal nodules are formed in a matrix composed of smaller nodules.



**Figure 1:** SEM images of nickel coatings electrodeposited under direct current at (a) 10; (b) 20; (c) 50; (d) 70 and (e) 100 mA/cm<sup>2</sup>



**Figure 2:** X-ray diffraction patterns of Ni coatings electrodeposited by direct current at different values of current densities from the Watts bath at 60°C.

### 3.2 Ni coatings deposited under pulse regime

#### 3.2.1 Effect of off-time

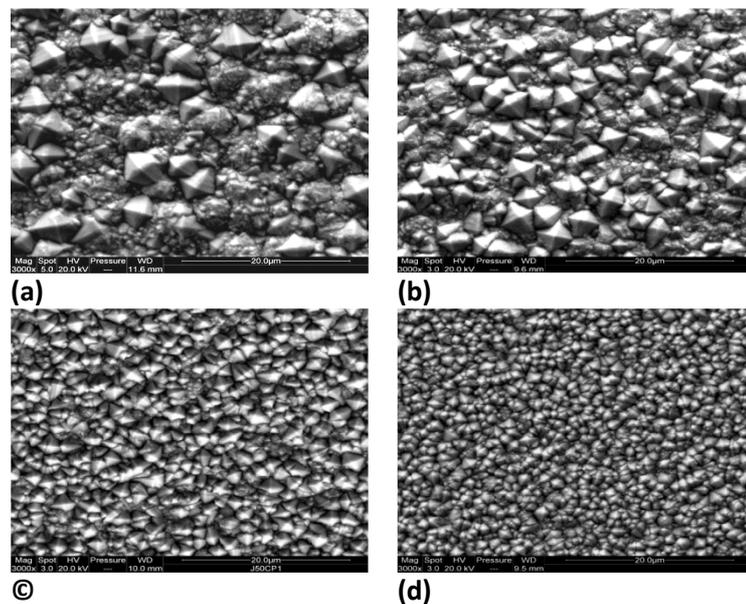
Table 2 illustrates the pulse plating parameters and duty cycle  $\theta$  used to investigate this effect of pulse off-time on surface morphology and crystal orientations.

**Table 2:** Parameters of pulsed electrodeposition of Nickel at constant  $t_{on}$  and  $j_m$

$t_{on}$ (ms)	$t_{off}$ (ms)	$j_m$ (mA/cm) <sup>2</sup>	$J_p$ (mA/cm) <sup>2</sup>	$\theta$ (%)
5	10	50	150	33
5	50	50	550	9.1
5	90	50	950	5.2
5	100	50	1050	4.7

Figure 3 presents the SEM observations of the different coatings performed when off-time is increased. The average current density was fixed at 50 mA.cm<sup>-2</sup>, corresponding to an heterogeneous microstructures previously

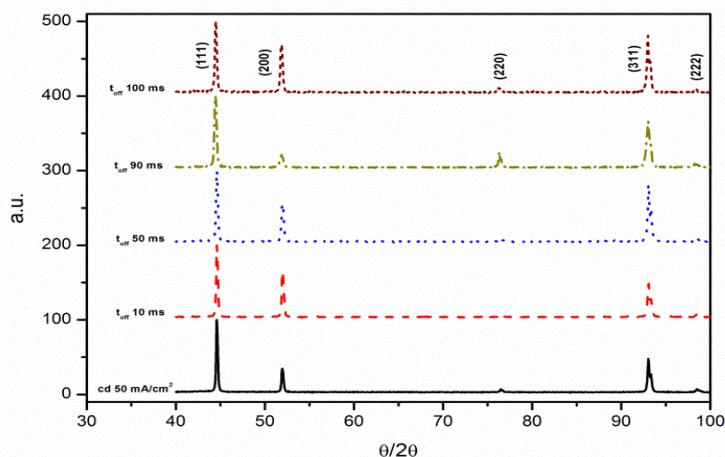
described. For values of  $t_{off}$  between 10 and 20 ms, the morphology (Figure 3a) is heterogeneous presenting large pyramids interconnected by a finer matrix. This type of morphology has already been observed in continuous mode and corresponds to the formation of instabilities on the interface that 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  $Ni^{2+}$  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  $Ni^{2+}$  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 pyramids as observed in figures 3c and 3d. 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 know that a long off time is required for desorption of non required species adsorbed on the surface or inserted into the solid phase. Finally, it seems that the off time value of 100ms would be optimal for obtaining a fine and uniform morphology. But, the changes of microstructure and properties of deposits can not only attributed to the change of  $t_{off}$ . Because when  $t_{on}$  and average current density ( $J_m$ ) were kept constant,  $t_{off}$  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  $t_{off}$  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.



**Figure 3:** Influence of  $t_{off}$  on surface morphology of nickel deposited from a Watts Bath at  $60^\circ$  with constant  $t_{on}$  of 5 ms and  $j_m$  of  $50 \text{ mA/cm}^2$  (a) 10; (b) 50; (c) 90; (d) 100 ms.

The X-ray diffraction diagrams, presented in figure 4, 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. This is , because the morphologies of the deposits made by direct current and pulsed mode are comparable, since in both cases, the morphology has a pyramidal shape in contrast to  $t_{off}=100$  ms, the deposit is predominantly textured (200). The(200) crystal orientation is considered to be the most free mode of growth, independent of any kind of chemical inhibition [8]. Moreover, it was noted in the literature that this mode of growth is attributed to the desorption of impurities or undesirable species adsorbed or inserted into the solid phase and redistribution of hydrogen formed during the active period. This means that the toff–time gives the cathodic layer an opportunity

for the desorption of interfacial inhibitors such as  $H_2$  or  $Ni(OH)_2$ . It was found that the application of the pulse current technique influences the composition of the catholyte owing to the desorption phenomena occurring during the relaxation time and modifies the structure and the properties of the deposits [9].



**Figure 4:** 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/cm<sup>2</sup> and  $t_{on}$  of 5 ms.

## Conclusion

The results obtained, revealed that the current density in continuous mode has an important influence on the surface morphology of electrodeposited Ni coatings. This behavior may be explained by a change of the growth mechanism with current density. However, grain refinement was observed with decreasing deposition current density. The study of the influence of parameters that define the current signal pulse has shown that low values of  $t_{off}$  lead to morphology and structure of the deposits quite similar to those obtained in continuous mode. Moreover, increasing  $t_{off}$  provokes a refinement of grain size and improves the crystalline quality of deposits. We were also able to identify the optimal value of pause time ( $t_{off}$ ) for obtaining a fine and homogeneous deposit. Increasing the  $t_{off}$  can not lonely explain the structure refinement, because it is combined with high pulse current density  $j_p$  that allows the activation of a larger number of nucleation sites. In summary the predominant role of the pause is to standardize the structure, reduce impurities and rate of occluded gases which could lead to deposits of high purity. However, it is necessary to limit the pause time if the state of abandonment is a deterioration of the coating.

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