Nucleation and Growth Mechanism of Ni/TiO₂ Nanoparticles Electro-Codeposition

Lidia Benea* and Eliza Danaila

Competences Center, Interfaces-Tribocorrosion-Electrochemical Systems, Faculty of Engineering, Dunarea de Jos University of Galati, RO-800008 Galati, Romania

The mechanism of TiO₂ nanoparticles electro-codeposition with nickel is studied. In-situ different electrochemical techniques such as cyclic voltammetry, electrochemical impedance spectroscopy, chronoamperometry, and chronocoulometry are used. The nucleation and growth mechanism of nickel in absence and presence of different nanoparticles concentration are analyzed through a mathematical model. The nucleation process of pure Ni system tends to follow the progressive model with three-dimensional fashion, while Ni/TiO₂ codeposition follows an instantaneous nucleation model. The presence of nanoparticles on the cathode offers many favorable sites for nickel crystallization nucleation, promote electrodeposition process and change the preferred orientation of nickel to a random one. 

© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0591613jes] All rights reserved.

The opportunity to codeposit inert nanoparticles from electrolytic baths has been widely used in metal electrodeposition in order to obtain structured nanocomposite coatings. Among the various techniques for producing nanostructured materials, electro-codeposition is technologically feasible and economically superior because this method can easily provide metal matrix nanocomposite coatings on surfaces of different sizes and shapes without porosity, with layer thicknesses from a few nanometers to hundreds of micrometers, or as a multilayer. Also this electrochemical method shows high production efficiency and the technological transfer from the laboratory to the existing infrastructure in the electroplating industry is easy. Compared to pure metal coatings, the nanostructured materials exhibit a wide range of new properties, such as increased resistance to wear and corrosion, improved mechanical properties (hardness, tensile strength, yield strength) and good electrocatalytic properties. Although the electro-codeposition process has aroused over time the interest of researchers for the development and characterization of metal matrix nanocomposites able to meet specific requirements, the theory of particles incorporation mechanisms is not well studied, being yet unclear. In addition such incorporating mechanism depends on each separate system (metal matrix–dispersed phase).

In order to improve the properties to microhardness, wear and corrosion of the pure nickel coating, a variety of micro and nanometric sized particles such as Al₂O₃, SiC, WC, ZrO₂, TiO₂ have been successfully codeposited in the nickel matrix. The nucleation process of pure Ni system tends to follow the progressive model with three-dimensional fashion. 

Titanium oxide (TiO₂) features properties very similar to those of an ideal semiconductor, being designed primarily for photocatalytic applications. Also TiO₂ is the most widely oxide after Al₂O₃ and ZrO₂ due to its high stability, low cost and safety to health and environment. Environmental and energy applications of this material include: air and water decontamination, degradation of pesticides, optical devices, solar cells, sensors, anticorrosive coatings, production of H₂ as an energy source, etc. Composite coatings of Ni/TiO₂ obtained by electrodeposition can meet various features that are significantly improved compared to pure Ni coatings. These characteristics can be listed as follows: hardness, corrosion and wear resistance, self-cleaning behavior, reduction of nickel recrystallization temperature, etc. Baghery and co-workers have prepared by electrodeposition Ni/TiO₂ nanocomposite coatings which have been characterized in terms of composition, hardness and resistance to corrosion and wear. The results showed that the microhardness, corrosion and wear resistance increase with increasing content of TiO₂ nanoparticles in the coating. Spanou et al. have obtained Ni/TiO₂ composite coatings with self-cleaning properties as a result of TiO₂ nanoparticles codeposition in the nickel matrix. Lin and co-workers have developed Ni/TiO₂ composite coatings by electrodeposition, with improved hardness as compared with pure nickel coating. Although in the scientific journals, many papers dealing with the electro-codeposition of Ni/TiO₂ composite coatings and their performance the literature reporting the nucleation and growth mechanisms involved in the electro-codeposition of Ni/nano-TiO₂ layers by electrochemical methods is still scarce. Nucleation and growth kinetics of the composite layers are the most important steps that determine the physico-chemical properties of the electrodeposited material and therefore these are crucial issues in understanding and controlling composite coatings. The electrochemical characterization of the nucleation process is generally done by collecting different types of transient current obtained when potential pulses are imposed at the metal–electrolyte interface.

The electrochemical methods employed in the study of the nucleation process are as follows: cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy. Similar electrochemical methods were used also by other researchers in order to study the nickel electrocrystallization with different particles such as: nano-Al₂O₃ particles, cysteine and nano–SiC particles.

This work aims at investigating the electro-kinetic processes, nucleation and growth of Ni electrodeposition in the presence of TiO₂ nanoparticles (10 nm mean diameter) using electrochemical techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronoamperometry and chronocoulometry. The experimental data are verified by a mathematical model in order to explain the differences between the diagrams performed during electrodeposition of pure nickel and codeposition of TiO₂ nanoparticles in the same electropolating conditions. The X-ray diffraction analyses are used to determine the presence of TiO₂ nano dispersed phases into nickel matrix and to confirm the effect of TiO₂ nanoparticles on performed electrochemical diagrams.

**Experimental**

To study the kinetics and mechanism of electro-codeposition of nano TiO₂ dispersed phase in nickel matrix, a potentiostat/galvanostat with frequency response analyzer (FRA) and a standard three-electrode electrochemical cell have been used, Figure 1. The electrochemical cell consisted of a copper cylinder with an area of 10 cm², which was used as working electrode (WE), a circular electrode of pure nickel used as a counter electrode and a saturated calomel electrode (SCE, KCl saturated solution (E = + 241 mV vs. normal hydrogen electrode–NHE)), which served as the reference electrode.

---

* Electrochemical Society Member.
* E-mail: Lidia.Benea@ugal.ro

---
surface morphology of resulted electrodeposited Ni/nano TiO$_2$ (10 g L$^{-1}$) nanocomposite coating is shown in Figure 2b. From this figure it can be seen that TiO$_2$ nanoparticles reveal a tendency to form spherical agglomerates uniformly distributed over the whole surface of the coating, leading to cauliflower surface morphology.

The X-ray diffraction analyses were performed at room temperature on Seifert 3003 T with Cu Kα radiation, operated at 40 kV and 40 mA, in order to determine the presence of dispersed phases into nickel matrix and the preferred orientation of the deposits. The scan rate was 0.02° over a 20 range from 10 to 100° and measuring time 2 s per step.

Before codeposition the nickel electrolyte was stirred for at least 60 minutes to obtain a uniform dispersed solution and a uniform adsorbed ionic film on nanoparticles surface. During the electrodeposition a stirring rate of 300 rpm was used, which resulted to be optimal to preserve the homogeneous dispersibility of the TiO$_2$ nanoparticles. The electrolytic bath had a pH of 4.04 and its temperature was maintained at 42 ± 1°C.

**Results and Discussion**

**Cyclic voltammetry.**—Cyclic voltammetry method was used to determine the potential range in which the electro–crystallization of nickel occurs. The cyclic voltammetry curves of pure Ni and Ni/nano–TiO$_2$ composite systems with different concentration of TiO$_2$ nanoparticles recorded at a scan rate of 5 mV/sec are shown in Figure 3.

Going from open circuit potential to the cathodic direction, in presence of TiO$_2$ nanoparticles from Figures 3a, 3b it can be seen that in the electro–codeposition of Ni/nano-TiO$_2$ composite systems, the current density gradually increases with increasing the potential starting from the values of −580 mV (vs. SCE for Ni/nano–TiO$_2$ - 20 g L$^{-1}$) and from −590 mV (vs. SCE for Ni/nano–TiO$_2$ - 10 g L$^{-1}$), which is the nucleation and growth processes of composite layers. For the pure nickel system only after −690 mV (vs. SCE) the current density begins to increase gradually with increasing potential. This behavior may reflect the influence of TiO$_2$ nanoparticles on the nucleation and growth process of nickel electrodeposition.

As shown in Figure 3a, the addition of TiO$_2$ nanoparticles in solution results in a displacement of the nickel reduction curve to more positive potential values with increasing TiO$_2$ nanoparticles concentration. The same behavior is reported in the case of nano–SiC particles on nickel electrodeposition from a nickel sulfate–chloride electrolyte.\textsuperscript{16}

The shift of reduction potential can be caused by TiO$_2$ nanoparticles added into electrolyte thus changing the nickel nucleation mechanism during electro–codeposition.

---

**Figure 1.** Electrochemical cell setup to study the nano–TiO$_2$ dispersed phase codeposition into nickel matrix during electroplating process: (1) – potentiostat / galvanostat – FRA with a computer interface; (2) – electrolytic cell with the electrolyte inside; (3) – cylinder working electrode (WE); (4) – reference electrode (RE); (5) – Ni circular counter electrode (anode); (6) – nano sized TiO$_2$ particles surrounded by ionic clouds from nickel plating electrolyte; (7) – magnetic stirrer.

**Figure 2.** SEM morphology of the (a) nanometric TiO$_2$ dispersed phase and (b) electrodeposited Ni/nano–TiO$_2$ nanocomposite coating.

**Figure 3.** Comparative cyclic voltammograms for (1) Ni/nano–TiO$_2$ (0 g L$^{-1}$), (2) Ni/nano–TiO$_2$ (10 g L$^{-1}$) and (3) Ni/nano–TiO$_2$ (20 g L$^{-1}$) systems, (a) full representation and (b) zoom in the beginning of cathodic domain.
The semiconductive TiO2 nanoparticles surrounded by the ionic cloud, under the effect of electric field are transported and loosely adsorbed on the cathode surface. Here, under the effect of electric field, the ionic shells are broken and followed by a strong adsorption of TiO2 nanoparticles. These positively charged particles adsorbed on the cathode surface increase the active surface and provide more nucleation sites for the Ni2+ ions reduction. Some other authors studied the zeta potential of TiO2 nanoparticles as function of pH in ultra–pure water. They found a positive value of zeta potential at the pH value of 4.04 like that used in the electrolyte for TiO2 electro-codeposition with nickel, thus confirming our assumption about the mechanism with positively charged TiO2 nanoparticles.

Considering a constant value of the cathodic potential of −1.4 V (vs. SCE), in Figure 3a it is noted that the current density takes the lowest cathodic value for the Ni/nano–TiO2 (0 g L−1) system (pure Ni system), being equal to −19.30 mA/cm2 (t = 80 sec). For the Ni/nano–TiO2 (10 g L−1) system, the current density reveals an increased cathodic value of −22.64 mA/cm2 (t = 80 sec) and for the Ni/nano–TiO2 (20 g L−1) system a further increased value of −23.60 mA/cm2 (t = 80 sec). The results presented confirm the activation of the Ni matrix in the presence of TiO2 dispersed nanoparticles. This behavior demonstrates that one of the intermediate stages of the particles codeposition is the adsorption of metal ions on the particles surface and their migration to the cathode. Practically, the Reactions 1 and 2 take place, in the case of pure nickel electrodeposition.

\[
Ni^{2+} + e^{-} \rightarrow Ni^{0}_{\text{ads}} \quad [1]
\]

\[
Ni^{0}_{\text{ads}} + e^{-} \rightarrow Ni^{0} \quad [2]
\]

The effect of TiO2 nanoparticles on the Ni electrodeposition can be described by the following steps:

\[
Ni^{2+} + TiO_2 \rightarrow Ni^{2+}_{\text{ads}}(TiO_2) \quad [3]
\]

\[
Ni^{2+}_{\text{ads}}(TiO_2) + e^{-} \rightarrow Ni^{0}_{\text{ads}}(TiO_2) \quad [4]
\]

\[
(Ni^{+})_{\text{ads}}(TiO_2) + e^{-} \rightarrow Ni/TiO_2
\]

Nickel matrix with embedded TiO2 nanoparticles [5]

The activation of the entire process of nickel electro–reduction is described by the Reactions 3, 4 and 5, by adsorbing the positive nickel ions on TiO2 nanoparticles and thus participating in the electro–reduction steps of nickel ions and having as a result the inclusion of nanoparticles into nickel matrix.

**In situ electrochemical impedance spectroscopy.**—The measurements of electrochemical impedance spectroscopy (EIS) were performed in the nickel electrolyte with and without TiO2 nanoparticles to observe the effect of nanoparticles on the electrodeposition mechanism. These measurements have been made at different cathodic potentials ranging from −700 to −1100 mV (vs. SCE). The EIS Nyquist representations are shown in Figure 4, where the symbols represent the experimental data and the dashed lines represent the simulated data. Simulated data are obtained using the equivalent circuit shown in Figure 5, using the ZView software. In this circuit, \( R_s \) designates the resistance of the solution being measured between the working electrode and the reference one. More specifically it represents the ohmic resistance of the double layer or electron transfer capacitance of the electrode/electrolyte interface. \( CPE \) is the constant phase element that correlates the high frequency capacitance loop. In parallel with \( R_s \) describes reduction of ions on the working electrode surface. The parallel connection between \( R_{ct} \) and \( CPE \) is used to describe the high frequency capacitance loop. In parallel with \( R_{ct} \) is placed the series connection between the resistor \( R_{ad} \) and inductor \( L_{ad} \) indicating the existence of an adsorption process.

The values of fitting EIS elements for pure nickel and Ni/TiO2 under different deposition potential are tabulated in Table I. The factor \( \alpha \) (Table I) is related to the angle of rotation of a purely capacitive line on the complex plane plots. The value of \( \alpha \) is associated to the non-uniform distribution of current as the result of surface inhomogeneity.

**Figure 4.** EIS Nyquist plots and simulated plots for (■) Ni/nano–TiO2 (0 g L−1), (●) Ni/nano–TiO2 (10 g L−1) and (▲) Ni/nano–TiO2 (20 g L−1) systems, at different negative potentials: (a) \( E = -700 \text{ mV (vs. SCE)} \) and (b) \( E = -800 \text{ mV (vs. SCE)} \).
(roughness, structure, defects). Depending on α, CPE can represent a circuit parameter with limiting behavior as a capacitor for α = 1, a resistor for α = 0, an inductor for α = −1 or Warburg impedance for α = 0.5.

From Figures 4a, 4b it becomes obvious that the applied potential has a significant effect on the Nyquist impedance diagrams. Thus, at a potential value of E = −700 mV (vs. SCE) (Figure 4a), the EIS spectra show a large and complete capacitive loop (a capacitive semicircle) and a small and incomplete inductive loop (an inductive semicircle). With the achievement of a negative potential step of E = −800 mV (vs. SCE) (Figure 4b), the capacitive loops become smaller and the inductive loops become complete. The capacitive semicircle occurs at high frequencies and this behavior is due to the interfacial capacitance (capacitance of the double layer) which is parallel to the charge transfer resistance. The inductive semicircle occurs at very low frequency due to the adsorption of the electrochemically active species.

At the same reduction potential of E = −700 mV (vs. SCE), the characteristic inductive loops observed at low frequency are larger for pure nickel reduction than that for codeposition of TiO2 nanoparticles with nickel. The similar behavior was reported by Benea et al.,15 who have studied the influence of SiC nanoparticles on nickel electrodeposition. They have explained that the inductive loop could also have studied the influence of SiC nanoparticles on nickel electrodeposition. These results suggest that the presence of TiO2 nanoparticles at different cathodic potentials (ranging from −700 mV to −1100 mV (vs. SCE)), for a deposition time of 300 seconds. Figure 6 shows the current–time curves under various step cathodic potential: E = −900 mV (vs. SCE) (Figure 6a), respectively E = −1000 mV (vs. SCE) (Figure 6b) for different concentrations of TiO2 nanoparticles added into the electrodeposition solution (0 g L−1, 10 g L−1 and 20 g L−1).

From Figures 6a, 6b it can be seen that the cathodic value of current density increases with increasing concentration of the TiO2 nanoparticles dispersion phase during Ni electrodeposition at the same potential. These results suggest that the presence of TiO2 nanoparticles influences the nucleation of the nickel coatings, which imply that nano–TiO2 particles may encourage the reduction of metallic ions adsorbed on the particle surface. It may be considered that nano–TiO2 particles adsorbed on electrode may change the conformation of electric double layer on electrode surface.

A similar behavior is reported by Chengyu et al.14 who have studied the influence of nano–Al2O3 particles on the electrochemical potentials. Thus, as shown in Figure 4a and Table I the charge transfer resistance is about 123 Ω cm−2 for Ni/nano–TiO2 (0 g L−1) system deposition, decreases to 98 Ω cm−2 for Ni/nano–TiO2 (10 g L−1) system and decreases even more at 76 Ω cm−2 for Ni/nano–TiO2 (20 g L−1) system deposition, at the same reduction potential (−700 mV). By increasing the TiO2 nanoparticles concentration the nickel reduction is activated and also is enhanced the ionic transport and, therefore Rct decreases.

**Chronoamperometry (current transients I vs. t).—**In this research work the chronoamperometry technique is used to determine the mechanism of nickel electrodeposition in the presence and absence of TiO2 nanoparticles at different cathodic potentials (ranging from −700 mV to −1100 mV (vs. SCE)), for a deposition time of 300 seconds. Figure 6 shows the current–time curves under various step cathodic potential: E = −900 mV (vs. SCE) (Figure 6a), respectively E = −1000 mV (vs. SCE) (Figure 6b) for different concentrations of TiO2 nanoparticles added into the electrodeposition solution (0 g L−1, 10 g L−1 and 20 g L−1).

From Figures 6a, 6b it can be seen that the cathodic value of current density increases with increasing concentration of the TiO2 nanoparticles dispersion phase during Ni electrodeposition at the same potential. These results suggest that the presence of TiO2 nanoparticles influences the nucleation of the nickel coatings, which imply that nano–TiO2 particles may encourage the reduction of metallic ions adsorbed on the particle surface. It may be considered that nano–TiO2 particles adsorbed on electrode may change the conformation of electric double layer on electrode surface.

A similar behavior is reported by Chengyu et al.14 who have studied the influence of nano–Al2O3 particles on the electrochemical potentials. Thus, as shown in Figure 4a and Table I the charge transfer resistance is about 123 Ω cm−2 for Ni/nano–TiO2 (0 g L−1) system deposition, decreases to 98 Ω cm−2 for Ni/nano–TiO2 (10 g L−1) system and decreases even more at 76 Ω cm−2 for Ni/nano–TiO2 (20 g L−1) system deposition, at the same reduction potential (−700 mV). By increasing the TiO2 nanoparticles concentration the nickel reduction is activated and also is enhanced the ionic transport and, therefore Rct decreases.

**Table I. Parameters obtained from equivalent circuit fitting during the electrodeposition of Ni with different concentration of TiO2 nanoparticles at different step potentials.**

| Cathodic potential [mV] | TiO2 nanoparticles [g L−1] | Rct [Ω cm2] | α | Rct [Ω cm2] | Rad [Ω cm2] | Lad [H cm2] |
|------------------------|---------------------------|-------------|---|-------------|-------------|-------------|
| −700                   | 0                         | 24.46       | 0.88 | 123         | 335         | 28.21       |
| −700                   | 10                        | 23.55       | 0.81 | 98          | 224         | 18.87       |
| −800                   | 20                        | 22.71       | 0.78 | 76          | 162         | 11.85       |
| −800                   | 0                         | 24.75       | 0.99 | 23          | 33.46       | 2.55        |
| −800                   | 10                        | 23.9        | 0.96 | 21          | 33.25       | 2.8         |
| −800                   | 20                        | 23.4        | 0.95 | 20          | 30.16       | 2.54        |

**Figure 6.** (a) Chronoamperometry of Ni in the presence of different concentrations of TiO2 nanoparticles: (1) Ni/nano–TiO2 – 0 g L−1, (2) Ni/nano–TiO2 – 10 g L−1 and (3) Ni/nano–TiO2 – 20 g L−1 at the applied potentials of −900 mV. (b) Chronoamperometry of Ni in the presence of different concentrations of TiO2 nanoparticles: (1) Ni/nano–TiO2 – 0 g L−1, (2) Ni/nano–TiO2 – 10 g L−1 and (3) Ni/nano–TiO2 – 20 g L−1 at the applied potentials of −1000 mV (vs. SCE).
behaviors of Ni electro–deposition on copper substrates from Watts–type acidic electrolyte.

It is well known that in the process of metal electrodeposition, increasing the current density determines the increase of nucleation centers. Thus it can be concluded that in the case of the Ni/TiO 2 (10 g L −1 and 20 g L −1) nanocomposite coatings, the increase in the nucleation centers is higher compared with pure Ni coatings and therefore the amount of metal to be deposited in the presence of dispersed phase is higher. This behavior is due to the metallic electroactive species that are adsorbed or formed on the surface of the TiO 2 nanoparticles and which are reduced at the cathode. In the increased thickness of the metallic coating being electrodeposited and which is the result of the competition between the nucleation and crystal growth, TiO 2 nanoparticles act as catalysts to reduce the metal. This could account for the increased number of active nucleation centers for the Ni/TiO 2 nanocomposite coatings.

Also in Figures 6a, 6b it can be seen that for the same system studied, with the cathodic deposition potential displacement to more negative values, the cathodic value of current density increases. This means that the number of nucleation centers increases resulting in a higher nucleation rate.

In the literature, many authors such Armstrong et al., 19 Abyaneh and Fleishmann, 20,21 Scharifker and Hills, 22 Heerman and Tarallo 23 etc., have developed nucleation and growth mathematical models that are frequently used to describe the growth process using chronoamperometry. At present, the most used nucleating model for describing the electro–crystallization process is the one developed by Scharifker and Hills (SH). 14,15,24,25 Thus, Zhau et al. 24 have evaluated their results on electrodeposition of Cu on n-type single–crystal GaN(001) electrode from a sulfate solution through SH mathematical model. Also Im et al. 26 have compared their experimental current transient curves of Cu electrodeposited using a neutral Cu–NH 4 citrate electrolyte with SH theoretical curves of instantaneous and progressive nucleation. This model has a three-dimension growth fashion. According to this model, two limiting nucleation mechanisms can be distinguished: instantaneous and progressive. Instantaneous nucleation corresponds to immediate activation of all nucleation sites, forming them instantly after it is applied the potential step. The number of the nuclei remains constant during the growth process, in other words the rate of further nuclei formation is negligible in the time frame of the experiment. In progressive nucleation, the number of nuclei increases gradually with the deposition time, so the rate of new nuclei formation in the time frame of the experiment is not negligible. The expressions for instantaneous and progressive nucleation with 3D growth are given by Eq. 6 and Eq. 7, respectively: 21

\[
\left( \frac{I}{I_{\text{max}}} \right)^2 = \frac{1.9542}{t/t_{\text{max}}} \left(1 - \exp \left[-1.2564 \left( \frac{t}{t_{\text{max}}} \right) \right] \right)^2
\]

Instantaneous nucleation [6]

\[
\left( \frac{I}{I_{\text{max}}} \right)^2 = \frac{1.2254}{t/t_{\text{max}}} \left(1 - \exp \left[-2.3367 \left( \frac{t}{t_{\text{max}}} \right)^2 \right] \right)^2
\]

Progressive nucleation [7]

where \( I_{\text{max}} \) is the maximum current density from the \( I − t \) transients during the electrodeposition process (Figure 6) and \( t_{\text{max}} \) is the corresponding peak time.

The experimental and theoretical plots, derived from Scharifker–Hills equations for instantaneous and progressive nucleation, are shown in Figures 7a–7c for Ni electrodeposition in the presence of different concentrations of TiO 2 nanoparticles (0 g L −1, 10 g L −1, 20 g L −1). These non-dimensional diagrams plotted as \( (I/I_{\text{max}})^2 \) vs. \( t/t_{\text{max}} \), correspond to the cathodic potential \( E = −900 \text{ mV (vs. SCE)} \). Scharifker–Hills model allows determining the type of nucleation by analyzing the ascending parts of the chronoamperograms, prior to the overlap of nuclei diffusion zones. 26

Analyzing the ascending part of the diagrams from Figure 7a it can be seen that the electrodeposition of Ni ions without the TiO 2 nanoparticles is closer to progressive nucleation. The increase of the TiO 2 nanoparticles concentration will result in a larger deviation from the progressive nucleation mechanism of the Ni ions, being very near to instantaneous nucleation theoretical curves. This behavior confirms the effect of TiO 2 nanoparticles on nickel electrocrystallization by activating the electro-reduction.

**Chronocoulometry.**—Figures 8a, 8b shows the charge vs. time curves measured at the cathodic potentials of −900 mV (vs. SCE) and −1000 mV (vs. SCE) respectively, for the various concentrations of TiO 2 nanoparticles added to the electropolating solution (0 g L −1, 10 g L −1, 20 g L −1). From Figure 8a corresponding to the cathodic potential \( E = −900 \text{ mV (vs. SCE)} \) it can be seen that the lower charge is consumed by pure Ni system, which has an cathodic value of −1.38 C/cm 2 at the end of the 300 seconds. With the increase of dispersed phase concentration to 10 g L −1 and 20 g L −1, the charge cathodic values increase to −1.65 C/cm 2 and −1.76 C/cm 2 respectively, for the same deposition time of 300 seconds. In Figure 8b the same trend of increasing the charge is maintained with increasing dispersed phase concentration, corresponding to the cathodic potential \( E = −1000 \text{ mV (vs. SCE)} \). In this case the amount of charge increases from the cathodic value of −2.44 C/cm 2 for pure Ni system, to the values of −2.58 C/cm 2 and −2.68 C/cm 2 corresponding to the nanocomposite systems with 10 g L −1 and 20 g L −1 concentration of TiO 2. In both Figures 8 there are drawn the diagrams recorded in the first 3 seconds of nucleation and growth of nanocomposite layers, denoted as a-1 and b-1. From these graphs it can be seen the increased Q values from the first steps of nucleation and growth of layers with added TiO 2 nanoparticles, confirming the influence of such nanoparticles in the mechanism and growth kinetic of nickel during electro-codeposition.

The XRD patterns of the nanocomposite systems studied, the charge values increases with increasing value of the cathodic potential from \( E = −900 \text{ mV (vs. SCE)} \) to \( E = −1000 \text{ mV (vs. SCE)} \). Increasing the charge amount during the codeposition of dispersed TiO 2 nanoparticles can be explained by the increase of the active surface.

Current efficiency (CE) is the ratio of the mass of metal deposited at a given time to the mass that would be deposited if all of electric current were used in the electrolytical process (Equation 8).

\[
CE = \frac{\int \frac{zF}{M} \Delta m}{\Delta t}
\]

where: \( z \) is the number of electrons involved in the electrochemical reaction (for nickel, \( z = 2 \)), \( F \) is the Faraday constant (96487 Coulomb/mol), \( M \) is atomic weight (58.69 g mol −1 for nickel), \( m \) is the mass electroprocessed during the time interval \( \Delta t \) (g), and \( I \) is the electric current (A).

The current efficiency of deposited layers was calculated depending on the current densities applied (ranging between 40–72 mA/cm 2) at 15 minutes time of electrodeposition. It was found a current efficiency between 83–87 for nickel electrodeposition, between 86–89 for 10 g L −1 TiO 2 added in the electrolyte and between 88–93 for 20 g L −1 TiO 2 added in the electrolyte, being higher for nanocomposite electro-codeposition. The current efficiency confirms the results found and discussed during electrochemical measurements about the influence of nano TiO 2 particles on nickel cathodic reduction.

**XRD patterns.**—In order to determine the phase structure of the nickel films XRD technique was employed. In Figures 9a–9c there are presented the diffractograms, in logarithmic scale of intensity counts, resulted from the deposits obtained in absence and in presence of TiO 2 nanoparticles into nickel plating Watts bath at 40 mA/cm 2 current density and 15 minutes deposition time.

From diffractograms presented in Figure 9 it can be observed that the nickel films are characterized by diffraction peaks corresponding to (111), (200), (220), (311) and (222) planes. The peaks corresponding to TiO 2 nanoparticles appear in the XRD patterns of nanocomposite layers at lower intensity counts due to very small size of TiO 2 nanoparticles (10 nm), as it is shown on Figures 9b, 9c.
Figure 7. Non-dimensional plots in form of $(I/I_{max})^2$ vs. $t/t_{max}$ recorded at the cathodic potential $E = -900 \text{ mV (vs. SCE)}$ for different concentrations of TiO$_2$ nanoparticles: (a) Ni/nano-TiO$_2$ – 0 g L$^{-1}$, (b) Ni/nano–TiO$_2$ – 10 g L$^{-1}$ and (c) Ni/nano–TiO$_2$ – 20 g L$^{-1}$.

Figure 8. Chronocoulometric curves for different concentrations of TiO$_2$ nanoparticles: (1) Ni/nano–TiO$_2$ – 0 g L$^{-1}$, (2) Ni/nano–TiO$_2$ – 10 g L$^{-1}$ and (3) Ni/nano–TiO$_2$ – 20 g L$^{-1}$ recorded at the cathodic potentials: (a) $E = -900 \text{ mV (vs. SCE)}$ and (b) $E = -1000 \text{ mV (vs. SCE)}$. 

Downloaded on 2018-07-20 to 207.241.231.82. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
Figure 9. XRD diffraction patterns of: (a) pure Nickel deposits having 0 g L$^{-1}$ dispersed TiO$_2$ nanoparticles; (b) Ni/nano–TiO$_2$–10 g L$^{-1}$ dispersed TiO$_2$ nanoparticles into electrolyte; (c) Ni/nano–TiO$_2$–20 g L$^{-1}$ dispersed TiO$_2$ nanoparticles into electrolyte.

Figure 9a shows the typical XRD pattern obtained for electrodeposited Ni films in which it is possible to observe the preferential orientation corresponding to (111) and (311) crystallographic planes. By adding TiO$_2$ nanoparticles (Figures 7b, 7c) into nickel Watts bath, the preferred orientation along (111) planes of Ni matrix did not change, on the contrary, the intensity of peak corresponding to (111) plane increases with increasing of TiO$_2$ nanoparticles concentration in the plating bath. Oppositely, the intensity peaks corresponding to (311) plane decrease after addition of 10 g L$^{-1}$ TiO$_2$ nanoparticles into solution but increase with increasing of TiO$_2$ concentration into solution, also the intensity peak of (200) plane increases simultaneously.

The increasing of TiO$_2$ nanoparticles concentration into electrolytic bath from 10 g L$^{-1}$ to 20 g L$^{-1}$ decreases the intensity peak of (200) plane and increases the intensity peak of (220) plane.

The addition on TiO$_2$ nanoparticles into nickel electrolyte causes a competition between the nucleation and crystal growth and the preferred orientation of the nickel matrix from nanocomposite deposit is disturbed by nanoparticles inclusion.

Benea et al. have been reported that the presence of nanoparticles provides more nucleation sites by increasing the surface area of the cathode and thus perturbs the nickel growth. The obtained nanocomposite coatings with TiO$_2$ nanoparticles embedded into nickel matrix show a perturbation of the nickel matrix growth as compared with the crystalline orientation of pure nickel deposited layers.

Figures 9b, 9c shows the characteristic peaks of TiO$_2$ nanoparticles included into nickel matrix to obtain Ni/nano–TiO$_2$ nanocomposite layers, confirming the effect of TiO$_2$ nanoparticles on the nickel electrodeposition obtained on the performing electrochemical diagrams.

The relative texture coefficients corresponding to the planes (111), (200) and (311) for pure nickel and Ni/nano–TiO$_2$ nanocomposite layers have been calculated according to Equation 9:

$$RTC_{hkl} = \frac{I_{hkl}}{\sum I_{hkl}} \cdot 100\%$$

where $I_{hkl}$ are the relative intensities of the (hkl) reflections, $\sum I_{hkl}$ is the sum of all intensities, in our case (111), (200), (220), (311) and (222). $I_{hkl}^0$ is the relative intensities of a randomly oriented nickel powder sample, from JCPDS no. 4–850 (Joint Committee on Powder Diffraction Standards).

The relative texture coefficients of deposited layers have been calculated function of the TiO$_2$ nanoparticles concentration into electrolytic bath (0 g L$^{-1}$, 10 g L$^{-1}$, 20 g L$^{-1}$). The RTC(111) of pure Ni layer revealed a value of 14.23, while the Ni/nano–TiO$_2$ nanocomposite layers showed the values of 22.75 for 10 g L$^{-1}$ TiO$_2$ added in the electrolyte and 20.58 for 20 g L$^{-1}$ TiO$_2$ added in the electrolyte. The RTC(200) of pure Ni layer showed a value of 9.79 and the Ni/nano–TiO$_2$ nanocomposite layers revealed the values of 25.15 and 16.26 corresponding to the TiO$_2$ concentration of 10 g L$^{-1}$ TiO$_2$ and respectively 20 g L$^{-1}$ TiO$_2$. The RTC(311) of pure Ni layer revealed a value of 51.61, while the Ni/nano–TiO$_2$ nanocomposite layers showed the values of 25.86 for 10 g L$^{-1}$ TiO$_2$ concentration and 27.02 for 20 g L$^{-1}$ concentration.
It was found that the addition of TiO$_2$ nanoparticles in the bath, causes an increase in the RTC$_{111}$ and RTC$_{200}$ with increasing of TiO$_2$ nanoparticles concentration compared to pure Ni coating, while the RTC$_{311}$ value decreases.

Conclusions

Nickel electrodeposition from a Watts nickel plating bath mixed with various concentrations of TiO$_2$ nanoparticles was studied under various potentials (vs. SCE) by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) chronoanperometry and chronocoulometry.

The cyclic voltammetry study reveals that the addition of TiO$_2$ nanoparticles in solution leads to a displacement of the nickel reduction curve to more positive potential values with increasing concentration, thus affecting the nickel nucleation mechanism.

Impedance spectra is influenced by the addition of TiO$_2$ nanoparticles, and, therefore, the charge transfer resistance was decreased compared with pure Ni system. By increasing the TiO$_2$ nanoparticles concentration the nickel reduction is activated, the ionic transport is enhanced as well as the density of nucleation sites.

The analysis of current-time transients performed by nonlinear fitting procedure shows that the pure nickel nucleation proceeds as a 3D instantaneous nucleation according to the same model.

The XRD patterns confirm the inclusion of dispersed TiO$_2$ nanoparticles into the nickel matrix and the resulted structural modifications due to nanoparticles, which are also observed by electrochemical methods.

As final conclusion the nano–TiO$_2$ particles induce structural modification of the nickel matrix by increasing the number of favorable sites for nickel nucleation.

Acknowledgments

UEFISCDI - Ministry of Education and Research is acknowledged for the financial support to Competences Centre Interfaces - Tribocorrosion and Electrochemical Systems (CC-ITES) - Dunarea de Jos University of Galati - Research Project: HyBioElect, contract 10/30-08-2013 (2013-2016) in the frame of National Research Programme Romania - PN II PCE.

Lidia Bacea conceived and designed the experiments; Eliza Danaila performed the experiments; Lidia Bacea and Eliza Danaila analyzed the data and contributed to the interpretation of the experimental results and writing the paper.

The authors declare no conflict of interest.

References

1. C. T. J. Low, R. G. A. Wills, and F. C. Walsh, Surf. Coat. Technol., 201, 371 (2006).
2. M. Torabi and A. Dolati, J. Appl. Electrochem., 40, 1941 (2010).
3. I. Gurrappa and L. Binder, Sci. Technol. Adv. Mater., 9, 1 (2008).
4. A. Goral, Nowak, M. Marek, K. Berent, Kania, and B. Bogusz, J. Alloys Compd., 615, S406 (2014).
5. D. K. Singh and V. B. Singh, J. Electrochem. Soc., 158, D114 (2011).
6. D. K. Singh, M. K. Tripathi, and V. B. Singh, Int. J. Mater. Sci. Appl., 2, 68 (2013).
7. F. Hou, Wang, W. Wei, and Guo H. Hetong, Appl. Surf. Sci., 252, 3812 (2006).
8. A. K. Chaudhuri and V. B. Singh, Int. J. Electrochem. Sci., 9, 7021 (2014).
9. A. J. Haider, Aus, A. Najim, and Malik A. H. Muh, Opt. Commun., 370, 263 (2016).
10. A. Fujishima, X. Zhang, and D. A. Tryk, Surf. Sci. Rep., 63, 515 (2008).
11. P. Bagherly, M. Farzam, A. B. Mousavi, and M. Hosseini, Surf. Coat. Technol., 204, 3804 (2010).
12. S. Spanou, A. I. Kontos, A. Siokou, A. G. Kontos, N. Vaenas, P. Falaras, and E. A. Pavlatou, Electrochim. Acta., 105, 324 (2013).
13. C. S. Lin, C. Y. Lee, C. F. Chang, and C. H. Chang, Surf. Coat. Technol., 200, 3690 (2006).
14. T. Chengyu, C. Hang, H. Wei, L. Yu, and Z. Zaqiao, Rare Metal Mat. Eng., 39, 0010 (2010).
15. M. Ebadi, W. J. Basirun, Y. L. Sim, and M. R. Mahmoudian, Metall. Mater. Trans. A., 44, 5096 (2013).
16. L. Bacea, P. L., A. Borello Bonora, S. Martelli, F. Wenger, P. Ponhaiaux, and J. Galland, J. Electrochem. Soc., 148, C461 (2001).
17. J. M. Berg, A. Romoser, N. Banerjee, R. Zebda, and C. M. Says, Nanotoxicology, 3(4), 276 (2009).
18. N. Soltani, N. Tavakkoli, M. Khayatkashani, M. R. Jalali, and A. Mosavizade, Corros. Sci., 62, 122 (2012).
19. R. D. Armstrong, M. Fleischmann, and H. R. Thirsk, J. Electroanal. Chem., 11, 208 (1966).
20. M. A. Abyaneh and M. Fleischmann, J. Electroanal. Chem., 119, 187 (1981).
21. M. A. Abyaneh and M. Fleischmann, J. Electroanal. Chem., 119, 197 (1981).
22. B. Scharifker and G. Hills, Electrochim. Acta., 28, 879 (1983).
23. L. Heerman and A. Tarallo, J. Electrochem. Soc., 9, 7021 (2014).
24. Y. Zhao, F. X. Deng, L. F. Hu, Y. Q. Liu, and G. B. Pan, Electrochim. Acta., 130, 537 (2014).
25. B. Im and S. Kim, Electrochim. Acta., 130, 52 (2014).
26. D. Grjicic and B. Pesic, Electrochim. Acta., 51, 2678 (2006).
27. L. Bacea, P. L. Bonora, A. Borello, S. Martelli, F. Wenger, P. Ponhaiaux, and J. Galland, Solid State Ionics, 151, 89 (2002).
28. S. Spanou, E. A. Pavlatou, and N. Spyrellis, Electrochim. Acta., 54, 2547 (2009).