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Abstract: The aim of this work is to obtain nanocomposite layers having a cobalt matrix with zirconium oxide nanoparticles (mean diameter 30 nm) through the electrodeposition process. The plating electrolyte suspension is prepared by adding ZrO2 nanoparticles in a sulfate-chloride cobalt electrolyte at a concentration of 0 and 10 g \cdot L⁻¹. The electrodeposition is performed at room temperature, using three current densities of 23, 48 and 72 mA \cdot cm⁻² and three deposition times of 30, 60 and 90 min. The influence of current density, time and nanoparticles concentrations on the characteristics of the obtained nanostructured layers are also discussed. ZrO₂ ceramic nanoparticles as a dispersed phase in the cobalt deposition electrolyte modify the mechanism of its electro-crystallization, so they participate in this process by increasing the rate of cobalt deposition, confirmed by the thickness of the nanocomposite layers obtained. The paper presents some of the comparative results obtained regarding the thickness of the layers, the current efficiency and the inclusion of the nanoparticles into nanocomposite layers depending on the current density and time of the electrodeposition process. The analysis of Co/nano-ZrO₂ nanocomposite layers with the help of optical light microscopy and electronic microscopy in cross-section highlights the good degree of adhesion of the layers to the metallic substrate made of 304L stainless steel. The results of the study show that as the current density and time increase, the thickness of the composite layers increases. The efficiency of the process is improved compared to the electrodeposition of pure cobalt layers. The degree of inclusion of ZrO₂ nanoparticles increases with time and decreases with increasing of imposed current density on the electrodeposition process. The distribution of the dispersed phase in the cobalt metallic matrix is uniform. The layers obtained in this study can be applied in aircraft technology, in the automotive industry, as well as in biomedical applications in order to improve the properties and to increase the corrosion or tribocorrosion resistance in a specific environment.

Keywords: dispersed ZrO₂; cobalt matrix; nanocomposite layer; layer thickness; current efficiency; electrodeposition

1. Introduction

In the context of huge economic losses worldwide due to corrosion and wear degradation of metallic materials, the most advantageous solutions for surface modification are constantly being sought in order to improve their resistance to corrosion and wear [1–4]. Metallic layers and nanocomposites are considered to be the most advantageous forms of corrosion protection and wear resistance of metallic and non-metallic materials in the industrial and biomedical fields [5–7]. A nanocomposite material is a compact material consisting of two or more phases with components separated by interfaces that can be natural or artificial. One of the phases is the matrix (phase I) which is continuous and is in a crystalline or amorphous state, inside the matrix are discretely distributed nanoparticles.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). These nanoparticles represent phase II (or dispersed phase) and can be in solid, liquid or gaseous state [4,5,7].

Nanocomposites occupy a major area in the current research. Recent research has focused in particular on improving the physical–chemical properties of the materials on which they are deposited, in order to obtain layers resistant to wear, abrasion, corrosion, active layers for catalysis, with self-lubricating properties or for better biocompatibility in the case of materials with biomedical applications [8]. The field of functional surfaces is in a continuous and rapid expansion, with a huge number of possible combinations between two or more components. The major advantage of nanocomposite layers is the possibility of obtaining in this way a wide range of materials whose use is to cover almost all areas of activity [7]. Electrochemical deposition of nanocomposite layers on various surfaces in order to increase wear stability, durability, corrosion or biological performances has a number of advantages such as making layers with appropriate structures and properties, ease of obtaining a compact layer, excluding further machining [9–12].

However, insufficient information on manufacturing technologies, working parameters, and the properties of the materials obtained make their industrial application worldwide still limited [13]. The realization or formation of nanocomposite layers by the electrodeposition method depends on a series of factors such as the nature of the electrolyte, the nature of the dispersed phase, the nature of the matrix and the electrodeposition conditions [2–5]. In the literature, relatively limited data about the electrodeposition of dispersed phases into cobalt matrix are found, as follow: Al_2O_3 [14], ZrO_2 [1,15,16], CeO_2 [4], SiC [17], La_2O_3 [18]. As applications, nanocomposites offer opportunities for the automotive industry [19], biomedical [20,21], aerospace [22] or even nuclear [23], etc. Zirconium oxide is a highly resistant ceramic material, which is used, for example, in aircraft technology, in the manufacture of kitchen knives, industrial cutting tools and components resistant to thermomechanical forces in the automotive industry, as well as in biomedical applications such as in dentistry [1,15,24,25].

The novelty of the study is the results showing the new nanocomposite layer as $Co/nano-ZrO_2$. The efficiency of the process is improved compared to the electrodeposition of pure cobalt layers. The degree of inclusion of ZrO_2 nanoparticles increases with time and decreases with increasing current density imposed on the electrodeposition process. The distribution of the dispersed phase in the cobalt metallic matrix is uniform.

No published work has been found on the research study presented. The aim of this research is to highlight the influence of deposition parameters such as time and current density at a constant concentration of ZrO_2 nanoparticles of 10 g/L on the thickness of the obtained layers, the efficiency of the current or the efficiency of the electrodeposition process and the degree of inclusion of nanoparticles in the Co/nano-ZrO₂ nanocomposite layers.

2. Materials and Methods

2.1. Materials

The deposition of nanocomposite and pure cobalt layers is performed at room temperature, 25 ± 0.5 °C, on an electrochemical workstation. The experimental setup regarding the electrochemical cell used to obtain the nanocomposite layers is composed of an anode (Co of 99% purity, with an active surface of 6.25 cm²) and the cathode used, respectively, the substrate on which the pure cobalt and nanocomposite layers are electrodeposited is a 304L stainless steel with an active surface area of 4.25 cm². The support used for deposits (304L stainless steel) is purchased from Direct Line Inox Company (Bucharest, Romania), in the form of sheets with the dimensions of 250 mm × 250 mm × 1.5 mm, later being cut to the required dimensions. The chemical composition of 304L stainless steel is shown in Table 1.

Cr	Mn	Si	Р	S	Ni	Cu	Мо	Fe
19.79	1.74	0.17	0.028	0.005	10.02	0.86	0.74	Balance

Table 1. Chemical composition of 304L stainless steel [%].

The dispersed phase of zirconium oxide is purchased from Inframat Advanced Materials USA (Manchester, NH, USA) and the average diameter of the nanoparticles is between 20 and 60 nm, as specified by the manufacturer as presented in Figure 1.



Figure 1. Transmission electron microscopy (TEM) micrograph of ZrO₂ nanoparticles (provider).

Figure 1 shows the TEM micrograph (JEOL USA, Peabody, MA, USA) of ZrO_2 nanoparticles. It can be seen that they have a spherical shape, with a diameter between 20 and 60 nm. Given that the diameter set by the manufacturer is 30 nm, it can be considered as an average of the values resulting from the TEM image.

2.2. Deposition Methods

The plating electrolyte used is composed of $CoSO_4 \times 7H_2O = 300 \text{ g/L}$, $CoCl_2 \times 6H_2O = 50 \text{ g/L}$, $H_3BO_3 = 30 \text{ g/L}$ and $C_{12}H_{25}NaO_4S = 1 \text{ g/L}$ plus distilled water [4,26]. The amount of electrolyte used for deposition is 450 mL and the pH throughout the deposition period is maintained at a value between 4.0–4.5, and is adjusted as needed with HCl (p.a).

For a better dispersion of the nanoparticles, a magnetic stirrer is used, establishing an optimal rotation speed of 300 rpm. Prior to each deposition, the samples were mechanically cleaned, chemically degreased and chemically pickled. Mechanical cleaning is performed with abrasive sanding paper of different sizes in order to remove micro-irregularities from the working electrode surface. The chemical degreasing of the samples is performed with an alkaline sodium hydroxide solution of 50 g/L by immersing the samples in the sodium hydroxide solution, for 10 min at a temperature of 70–80 °C.

Chemical pickling is performed with a 1:1 hydrochloric acid solution for 1–2 min for the cobalt counter electrode and 5 min for the working electrode, 304L stainless steel.

After the cleaning protocol is applied, the samples are rinsed with distilled water and then immediately introduced into the electrochemical cell. Schematically, the process of obtaining the $Co/nano-ZrO_2$ nanocomposite layers is shown in Figure 2.



Figure 2. Schematic drown of electrochemical cell used to obtain electrodeposited Co/nano-ZrO₂ nanocomposite layers: (1)—electrochemical workstation; (2)—electrochemical cell; (3)—electrolyte plating cobalt solution; (4)—anod (CE)—pure Co; (5)—cathode (WE)—304L stainless steel; (6)—ZrO₂ nanoparticles (30 nm mean diameter); (7)—ZrO₂ nanoparticles immersed into plating solution surrounded by ionic cloud; (8)—magnetic stirrer to maintain homogenous dispersion; (9)—Co/nano-ZrO₂ electrodeposited layer. (10)—Co/nano-ZrO₂ layer with 13.20 µm thickness; (11)—Co/nano-ZrO₂ layer with 25.32 µm thickness; (12)—Co/nano-ZrO₂ layer with 36.63 µm thickness.

As working parameters, the current density varies between 23 and 72 mA·cm⁻² and deposition time between 30–90 min. The concentration of ZrO_2 nanoparticles used is $0 \text{ g} \cdot \text{L}^{-1}$ for pure Co layers and 10 g·L⁻¹ for nanocomposite layers. All tests are repeated three times to verify the reproducibility of the experimental data.

2.3. Characterization Techniques and Methods

The measurement of the thickness of the layers is determined with the help of optical microscopy Reichert-Jung-type optical microscope (AMETEK Reichert, Depew, NY, USA) on the samples with processed layers in cross-section. In order to visualize the samples in cross-section to obtain the thickness of the electrodeposited layers with the help of optical microscopy, the samples are cut, embedded in epoxy resin and polished.

For the compositional analysis of the studied layers, scanning electron microscopy with energy dispersive X-ray spectroscopy, SEM-EDX JEOL JSM-T220 A, is used.

The scanning electron microscope used is JEOL JSM-T220 A (Oxford Instruments, Abingdon, UK). EDX analysis is a complex quantitative method that uses X-rays. By applying it, the local chemical composition can be determined to an accuracy of about 1% by mass and the qualitative analysis of the chemical change of the analyzed material.

For the chemical analysis and the distribution of the chemical elements in the studied layers, a series of work steps are necessary, such as cutting the samples in cross-sections, embedding the samples in epoxy resin, polishing with abrasive paper of different sizes, then with diamond paste with dimensions of 3 and 1 μ m, ethanol cleaning then hot air drying. The samples are covered with a thin gold film for 40 s and glued to a carbon strip for good electrical conductivity.

With the help of EDX analysis, it is possible to calculate the percentage of incorporation of ZrO_2 nanoparticles in the Co matrix. The standard atomic mass of the element Zr has a value of 91.22 g/mol. For the calculation of the current efficiency, Faraday's law is applied according to relation (1):

1

$$\eta = \frac{m_p}{m_t} \cdot 100[\%] \tag{1}$$

where: η is current efficiency, m_p —practical electrodeposited layer, m_t —theoretical electrodeposited layer calculated according to Faraday's laws.

3. Results and Discussion

3.1. Effect of Current Density and Electrodeposition Time on Layer Thicknesses—Optical Micrographs

The study of the thickness of the nanocomposite layers compared to the thickness of the pure cobalt layers was obtained according to the electrodeposition parameters, such as deposition time, current density and concentration of nanoparticles in the electrolyte solution are shown in Figures 3–7. The thicknesses of the nanocomposite layers of Co/nano-ZrO₂ (0 g/L) or pure cobalt and Co/nano-ZrO₂ (10 g/L) are compared according to the electrodeposition parameters such as current density of 23, 48 and 72 mA·cm⁻², deposition time of 30, 60 and 90 min, and the stirring rate remains constant at an optimum value of 300 rpm, established by previous tests.

From Figure 3 it is observed that at constant current density and time the thickness of the layers increases slightly with the addition of the dispersed phase concentration of ZrO_2 . If the Co/nano- ZrO_2 layer (0 g/L) has a value of 13.05 µm when adding 10 g·L⁻¹ ZrO_2 nanoparticles to the cobalt electrolyte, the thickness of the layer reaches a value of 13.20 µm. The difference, in this case, is small but significant at about 0.15 µm.



Figure 3. Optical microscopy micrographs of the layer thicknesses of the electrodeposited layers at the current density of 23 mA·cm⁻² and the time of 30 min for: (a) Co/nano-ZrO₂ (0 g·L⁻¹ nanoparticles in the cobalt electrolyte), (b) Co/nano-ZrO₂ (10 g·L⁻¹) nanoparticles in the cobalt electrolyte.

By increasing the current density to $48 \text{ mA} \cdot \text{cm}^{-2}$ and keeping the same deposition time of 30 min, Figure 4, an increase in the thickness of the layers is observed with the addition of ZrO₂ nanoparticles in the electrolyte, compared to the current density of 23 mA·cm⁻². For the layer without the addition of nanoparticles, the increase in the layer thickness from the current density of 23 to 48 mA·cm⁻² is 9.61 µm, while for the Co/nano-ZrO₂ layer (10 g·L⁻¹) the layer thickness has an increase of 10.06 µm.



Figure 4. Optical microscopy micrographs of the layer thicknesses of the electrodeposited layers at the current density of 48 mA·cm⁻² and the time of 30 min for: (a) Co/nano-ZrO₂ (0 g·L⁻¹ nanoparticles in the cobalt electrolyte), (b) Co/nano-ZrO₂ (10 g·L⁻¹) nanoparticles in the cobalt electrolyte.

If at the current density of 23 mA·cm⁻² the difference in increasing the thickness of the layers between Co/nano-ZrO₂ (0 g·L⁻¹) and Co/nano-ZrO₂ (10 g·L⁻¹) is 0.41 μ m we notice that as the current density increases to 48 mA·cm⁻²; this difference increases approximately 6 times reaching a value of 2.6 μ m.

In Figure 5 it is observed that at the highest studied current density of 72 mA·cm⁻² and deposition time of 30 min the layers have a thickness of 30.13 μ m for Co/nano-ZrO₂ (0 g·L⁻¹) and 36.63 μ m for Co/nano-ZrO₂ (10 g·L⁻¹). The increase in the layer thickness for this current density with the increase in the dispersed phase concentration, in this case, is 6.5 μ m.



Figure 5. Optical microscopy micrographs of the layer thicknesses of the electrodeposited layers at the current density of 72 mA·cm⁻² and the time of 30 min for: (**a**) Co/nano-ZrO₂ (0 g·L⁻¹ nanoparticles in the cobalt electrolyte), (**b**) Co/nano-ZrO₂ (10 g·L⁻¹) nanoparticles in the cobalt electrolyte.

If at the current density of 23 mA·cm⁻² the thickness of the pure cobalt layers is 13.05 and 13.46 µm for Co/nano-ZrO₂ (10 g·L⁻¹), at the current density of 72 mA·cm⁻² and the deposition time of 30 min the layers have a thickness of 30.13 µm for Co/nano-ZrO₂ (0 g·L⁻¹) and 36.63 µm for Co/nano-ZrO₂ (10 g·L⁻¹). The increase in the thickness of the layers between the lowest current density and the highest current density studied at a constant deposition time of 30 min is 17.08 µm for the layer without the addition of nanoparticles and 23.17 µm for the layer with the addition of ZrO₂ nanoparticles.

Figure 6 shows the thickness of the cross-sectional layers obtained by optical microscopy for the Co/nano-ZrO₂ (0 g·L⁻¹) and Co/nano-ZrO₂ (10 g·L⁻¹) layers obtained at a current density of 23 mA·cm⁻² and deposition time of 60 min.



Figure 6. Optical microscopy micrographs of the layer thicknesses of the electrodeposited layers at the current density of 23 mA·cm⁻² and the time of 60 min for: (a) Co/nano-ZrO₂ (0 g·L⁻¹ nanoparticles in the cobalt electrolyte), (b) Co/nano-ZrO₂ (10 g·L⁻¹) nanoparticles in the cobalt electrolyte.

Figure 6 shows an increase in the thickness of the layers with the increase in the electrodeposition time and with the added dispersed phase of ZrO_2 .

If at the current density of $23 \text{ mA} \cdot \text{cm}^{-2}$ and the deposition time of 30 min, Figure 3a, the thickness of the layers is $13.05 \text{ }\mu\text{m}$ for the pure cobalt layer and $13.46 \text{ }\mu\text{m}$ for the layer

in which 10 g·L⁻¹ of ZrO₂ nanoparticles were added in the plating electrolyte, increasing the time to 60 min, Figure 6a, there is practically a doubling of the layer thickness in the case of Co/nano-ZrO₂ (0 g·L⁻¹) and Co/nano-ZrO₂ (10 g·L⁻¹) systems compared to the studied time of 30 min. At the same time, in this case also, at the deposition time of 60 min, there is a difference in the layer thickness for pure cobalt, which is 23.58 µm and the layer thickness of the nanocomposite layer, Co/nano-ZrO₂ that is 24.03 µm.

The layer thicknesses obtained at the time of 90 min and the same current density of $23 \text{ mA} \cdot \text{cm}^{-2}$ are shown in Figure 7.



Figure 7. Optical microscopy micrographs of the layer thicknesses of the electrodeposited layers at the current density of 23 mA·cm⁻² and the time of 90 min for: (a) Co/nano-ZrO₂ (0 g·L⁻¹ nanoparticles in the cobalt electrolyte), (b) Co/nano-ZrO₂ (10 g·L⁻¹) nanoparticles in the cobalt electrolyte.

With the increase in the deposition time to 90 min, a tripling of the layer thickness is observed for both studied systems compared to the current density of 23 mA·cm⁻² and the time of 30 min. The increase in layer thickness at 90 min for Co/nano-ZrO₂ (10 g·L⁻¹) compared to the pure Co layer is 2.74 μ m, thus demonstrating that by including nanoparticles in the cobalt matrix the electrodeposition efficiency is improved by charge transfer of cobalt ions adsorbed on nanoparticles.

The images obtained by optical microscopy on the cross-sectional layers confirm that the nanocomposite and cobalt layers without the addition of ZrO₂ nanoparticles have very good adhesion to the substrate, so we can conclude that the electrodeposition process is a very good process to obtain functional surfaces, with multiple uses in industry and medicine.

3.2. Dispersed Phase Distribution into Nanocomposite Layers—SEM-EDX Analysis on Cross Section of Layers

SEM-EDX analyzes are performed in cross-sections for the electrodeposited layers to highlight the inclusion and distribution of the dispersed phase in the electrodeposited nanocomposite layer, Figures 8 and 9. SEM-EDX analyzes are performed punctually at different points to highlight the presence of the zirconium element as well as on the entire micrograph surface of the layer in order to observe the degree of inclusion of zirconium oxide nanoparticles in the deposited layer. These spectra show the presence of zirconium oxide nanoparticles embedded in the cobalt metal matrix.

In Figure 8a it can be seen the SEM micrograph of the electrodeposited layer of pure cobalt or Co/nano-ZrO₂ (0 g·L⁻¹) while in Figure 8b is the EDX spectrum as the general analysis on the selected layer. It is observed that the electrodeposited layer is pure Co.



Figure 8. SEM-EDX in cross-section of pure cobalt layer obtained: (**a**) SEM micrograph of pure cobalt layer showing Co layer thickness; (**b**) EDX spectra for general analysis on pure cobalt layer.

SEM micrograph, general and point EDX analysis of a Co/nano-ZrO₂ nanocomposite layer (10 g·L⁻¹) is shown in Figure 9a–c.



Figure 9. SEM-EDX in cross-section of nanocomposite layer Co/nano-ZrO₂ (10 g·L⁻¹) obtained: (a) SEM micrograph of nanocomposite layer showing layer thickness; (b) EDX spectra for general analysis showing a 4.60 wt. % of nano-ZrO₂ embedded into cobalt matrix; (c) EDX spectra for punctual analysis (P1 as dark phase on SEM micrograph).

In Figure 9a it is observed the good adhesion of the nanocomposite layer to the 304L steel support as well as the uniformity of Co/nano-ZrO₂ (10 g·L⁻¹) layer thickness.

The EDX general analysis on the nanocomposite layer, in Figure 9b, shows an embedded percent of nano- ZrO_2 dispersed phase of 4.60 wt. %, while the point analysis, P1 from Figure 9a, confirms the inclusion of zirconium oxide into the cobalt matrix as the dark phase with a wt. % of zirconium element of 9.42, calculating as nano- ZrO_2 at 12.72 wt. %. (Figure 9c).

3.3. Distribution of Nano-ZrO₂ Particles inside Cobalt Matrix—EDX Elements Mapping in Cross Section of Layers

The presence of the dispersed phase of zirconium oxide inside the cobalt matrix as well as its uniform distribution is also highlighted by the distribution map of the elements (Co, Zr) on the SEM micrographs in cross section as can be seen in Figure 10.



Figure 10. SEM-EDX analysis in cross section of Co/nano-ZrO₂ layer (10 g·L⁻¹): (**a**) SEM micrograph; (**b**) cobalt element mapping; (**c**) Zr element mapping.

From the analysis of Figure 10, we can say that the element Zr is uniformly distributed over the entire surface of the studied nanocomposite layer, which confirms a homogeneous distribution of the dispersed phase of nano- ZrO_2 in the cobalt matrix.

3.4. The Efficiency of the Electrodeposition Process

The influence of the current density on the efficiency of the current or the process efficiency, η [%], of the electrodeposition process in the case of the layers made of pure cobalt and Co/nano-ZrO₂ (10 g·L⁻¹) is shown in Figure 11. The calculation methodology for determining the current efficiency is mentioned in the chapter Materials and Methods.



Figure 11. The influence of current density on the current efficiency of the electrodeposition process: (1)—Co/nano-ZrO₂ (0 g·L⁻¹) layers, (2)—Co/nano-ZrO₂ (10 g·L⁻¹) layers.

In Figure 11 it is observed that in the range of applied current densities of 23–72 mA·cm⁻² the current efficiency for the nanocomposite layers is superior, having approximate values of over 90%, for the Co/nano-ZrO₂ system (10 g·L⁻¹) at the highest current density compared to the current efficiency for obtaining pure cobalt layers, which is about 88%.

It is found that the current density does not have a significant influence on the current efficiency of the electrodeposition process. The addition of the dispersed phase in the electrolyte solution, namely the nanoparticles of zirconium oxide, determines the increase in the efficiency in the process of the electrodeposition of nanocomposite layers.

This can be explained by the adsorption of cobalt ions on ZrO_2 nanoparticles, their transport to the cathode and the faster transfer of electric charge for transformation into a cobalt metallic matrix, following the Equation (2) and schematically shown in Figure 12.



Figure 12. Schematic drown of cobalt ions adsorbed on nano-ZrO₂ and reduced during electro crystallization to form metallic cobalt matrix with embedded ZrO₂ dispersed phase.

The increase in the current efficiency with the addition of a dispersed phase in the plating electrolyte of metal electrodeposition depending on the current density is also reported in the literature by other authors [1-4].

Regarding the current efficiency for the electrodeposited layers as a function of the electrodeposition time, in Figure 13, the values are approximately equal to those reported for the influence of current density on the electrodeposited layers.



Figure 13. The influence of the time applied to the electrodeposition process on the current efficiency when obtaining the electrodeposited layers at the current density of 23 mA·cm⁻²: (1) Co/nano-ZrO₂ (0 g·L⁻¹), (2) Co/nano-ZrO₂ (10 g·L⁻¹).

It is observed that the current efficiency for the electrodeposited layers is higher for Co/nano-ZrO₂ (10 g·L⁻¹), compared to the pure cobalt layers, obtained at the same value of the electrodeposition time. The current efficiency value for the nanocomposite layer is over 90%, compared to that of pure cobalt layers, which is about 84%, which confirms the inclusion of particles in the nanocomposite layer and their contribution to the real mass of the electrodeposited layer. The increase in the current efficiency with the addition of the dispersed phase in the plating electrolyte and the time imposed on the electrodeposition process is also observed in the specialized literature by other authors [4].

3.5. The Degree of Inclusion of Nano-ZrO₂ in the Cobalt Matrix

The influence of current density is also observed on the effect of embedding zirconium oxide nanoparticles in the cobalt metal matrix. The literature shows that the degree of inclusion of particles decreases with increasing current density [4,5]. Reaching a maximum degree of incorporation depends considerably on the current density due to the effect it has on the current–potential relationship [5]. In the field of low current densities, the increase in the current density produces an increase in the degree of incorporation of the particles in the metallic matrix for the Co-SiC [17], Ni-Al₂O₃, [27–29], Co/nano-CeO₂ systems [4]. In the case of nano-ZrO₂ codeposition, the dispersed phase content included in the cobalt metallic matrix decreases as the current density increases from 23 to 72 mA·cm⁻², for the obtained nanocomposite layers, Figure 14.

Figure 14 shows a decrease in the degree of inclusion of ZrO_2 nanoparticles with increasing current density. The highest degree of incorporation, 10.44% (mass percentage), is obtained at the current density of 23 mA·cm⁻², while the lowest value of the degree of inclusion of ZrO_2 nanoparticles is obtained at the current density of 72 mA·cm⁻², respectively, 4.06% (mass percentages).

The Co/nano-ZrO₂ layers obtained by the electrochemical codeposition process show an increase in the number of particles incorporated in the metallic matrix as a function of the decrease in current density. This behavior can be explained based on the adsorption model proposed by Guglielmi in 1972, which describes quantitatively the influence of the content of particles in the electrolyte and the current density on the incorporation of particles in the metallic matrix [30]. In the first phase, the particles become poorly adsorbed on the electrode surface and remain in equilibrium with the particles in the solution [30,31].



Figure 14. The degree of inclusion of nano- ZrO_2 in the cobalt matrix depending on the current density applied to obtain the nanocomposite layers for Co/nano- ZrO_2 (10 g L⁻¹).

In the second phase, the shield of the adsorbed ions is broken by the electric field at the interface, followed by strong adsorption of the particles at the electrode and thus the nanoparticles are incorporated into the metallic matrix [30,31]. The influence of the deposition time is also observed on the degree of embedding of the zirconium oxide nanoparticles in the cobalt metallic matrix. The content of the dispersed phase included in the metallic matrix increases with the increase in the deposition time from 30 to 90 min, for the obtained nanocomposite layers, Figure 15.



Figure 15. The degree of inclusion of nano- ZrO_2 in the cobalt matrix as a function of deposition time for Co/nano- ZrO_2 nanocomposite layers (10 g·L⁻¹) at constant current density of 23 mA·cm⁻².

For the Co/nano-ZrO₂ (10 g·L⁻¹) nanocomposite layer the highest degree of incorporation, of 13.03 wt. % is obtained at a deposition time of 90 min. For the deposition time of 60 min, the degree of inclusion is 12.75 wt. % while for the time of 30 min the degree of inclusion of nano-ZrO₂ is 10.44 wt. %. The Co/nano-ZrO₂ layers obtained by the electrodeposition process show an increase in the number of particles incorporated in the metal matrix depending on the increase in the deposition time, a phenomenon also observed by other authors [4].

4. Conclusions

The study highlights the influence of deposition parameters such as time, current density, and the addition of ZrO_2 nanoparticles on the obtained layer thickness, current efficiency and the degree of inclusion of the nanoparticles in the Co-nano- ZrO_2 nanocomposite layer. The analysis of the layer thickness in cross-section with the help of optical microscopy confirms the increase in the layer thickness with the increase in the electrode-position time, of the current density and of the addition of the dispersed phase for the nanocomposite layers.

The analysis of the current efficiency as a function of current density and time concludes the beneficial effect of the inclusion of nanoparticles in increasing the current efficiency for the studied nanocomposite layer compared to the Co/nano-ZrO₂ layer (0 g·L⁻¹).

From the SEM-EDX analyses, with which the degree of inclusion is calculated, the inclusion of zirconium oxide nanoparticles in the cobalt metallic matrix is confirmed along with the decrease in the current density and the increase in the electrodeposition time.

Through the SEM micrographs in cross-section, the presence of the dispersed phase of zirconium oxide is also highlighted by the distribution map of the elements, observing a uniform distribution of the zirconium oxide nanoparticles inside the nanocomposite layer.

The study confirms the possibility of obtaining nanocomposite layers in a cobalt matrix with a dispersed phase consisting of zirconia nanoparticles with good adhesion to the metal support, with different layer thicknesses and different degrees of inclusion of the dispersed phase in the metallic matrix, aspects that offer different improved properties to these layers, which can be used from biomedical applications to industrial applications.

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