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ELECTRODEPOSITION OF UHMWPE PARTICLES WITH COBALT FOR BIOMEDICAL APPLICATIONS

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UHMWPE (ultra high molecular weight polyethylene) particles (mean diameter 10 μm) have been deposited by electro-co-deposition method with cobalt on stainless steel substrate(304L) to obtain thick (15 - 80 μm), strongly adherent Co/UHMWPE composite biocoatings. UHMWPE was selected as surface modifier element, due to its high biocompatibility and low coefficient of friction being used in many biomedical applications. Cobalt is already used in biomedical implants as cobalt – chromium alloys. Electrodeposition process was carried out by dispersing UHMWPE powders in an electrolytic solution of cobalt sulphate/cobalt chloride solution to obtain Co/UHMWPE composite coating and also in pure cobalt sulphate/chloride electrolyte for UHMWPE free cobalt coating. The electro-co-deposition process of UHMWPE with cobalt was investigated by electrochemical methods such as: cathodic potentiodynamic diagrams and electrochemical impedance spectroscopy measurements at cathodic potentials. The effect of current density and time of deposition as principal factors of coating thickness were correlated. Atomic Force Microscopy and Scanning Electron Microscopy in conjunction with energy dispersive analysis were used to identify chemical composition, and surface texture/topography and roughness of the coatings. Results indicate the formation of Co/UHMWPE composite biocoatings promising to enhance the surface properties.

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1. Introduction

Thin composite layers are widely used as functional materials for different applications. The electrochemical deposition technique has been increasingly established as efficient preparation route [1, 2]. The quality and properties of Co layers could be considerably improved by the electro-co-deposition of ceramics, polymers or even metallic particles during the electroplating process. The process of composite layers electrodeposition essentially consists in the inclusion of solid particles suspended in an electrolytic bath into the electrocrystalizing metal which is in fact the metal matrix. These particles are generally considered insoluble [3]. Fundamental requirements for biomaterials used in the construction of medical devices and artificial organs are biocompatible surfaces and favourable mechanical properties [4]. Advances in medical treatment also demand substantial improvements in biomaterial properties. Conventional single-component polymer materials cannot satisfy these requirements. Therefore, multi-component polymer systems have been designed and prepared for developing new multifunctional biomaterials [5]. Many biomaterials have been prepared by the immobilization methods such as the coating, grafting, or reacting of biocompatible polymers with the surface of substrates such as segmented polyurethane, nylon, polystyrene, and polyethylene terephthalate. Other methods

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include blending of the biocompatibility polymer with the substrate [6, 7]. In the above-mentioned methods, the surface properties can be controlled although the mechanical properties are hardly changed since they retain the properties of industrial substrate that does not adapt to tissues and organs. For instance, the difference in mechanical properties between a native artery and an artificial blood vessel induces hemodynamical flow disturbance and stress concentration near the anastomoses, causing further thrombus formation and neointimal hyperplasia [8–10]. Therefore, biomaterials require mechanical properties that are matched with various regions such as soft tissue, hard tissue, and organs. To create the polymer biomaterials corresponding to the purpose and use conditions, methods that can control both the bulk properties and the surface properties are necessary. Composites could combine the properties of metals with ceramics or metals with polymers for biomedical applications.

Good deposition depends mainly on the nature of bath constituents. Generally, a plating bath contains conducting salts, buffering agents, complexing agents and metal ions. Among these the complexing agents effectively influence the deposition process, solution properties and structure of the deposit. The action of these complexing agents is specific and depends on pH, nature of anion, temperature and other ingredients of the medium [11, 12]. Too many ingredients cause difficulties in maintaining the operating parameters of the bath solution during the plating process. Some of these agents smooth the deposit over a wide current density range and the other addition agents influence the production of bright deposits [13].

The composite coatings protective properties are strictly related to the particles dispersion into the metal matrix and thus to the microstructural modifications that these may cause. Extensive work on the electrocrystallization of cobalt has been carried out by many authors [14-22] on different electrode materials from aqueous solutions. However, no work could be found on the influence of UHMWPE biopolymer particles added to cobalt electrolyte on their mechanism of electroreduction and surphace morphology of nanocomposite coatings obtained.

This paper is devoted to investigate the possibility to obtain composite coatings in cobalt matrix with dispersed phase of UHMWPE (ultra high molecular weight polyethylene) by electro-co-deposition process and properties characterisation. UHMWPE was selected as surface modifier element, due to its high biocompatibility and low coefficient of friction being used in many biomedical applications. Cobalt is already used in biomedical implants as cobalt – chromium alloys.

2. Experimental

The electro-co-deposition of Co/UHMWPE biocomposite layers was done by inclusion of UHMWPE (ultra high molecular weight polyethylene) particles in the cobalt matrix during electroplating process. The dispersed particles were suspended in an electro-deposition cell with cobalt sulphate-chloride electrolyte (pH=4.5). The cobalt electro-crystallizes and forms the metal matrix which includes the UHMWPE particles as it is shown schematically in Figure 1.

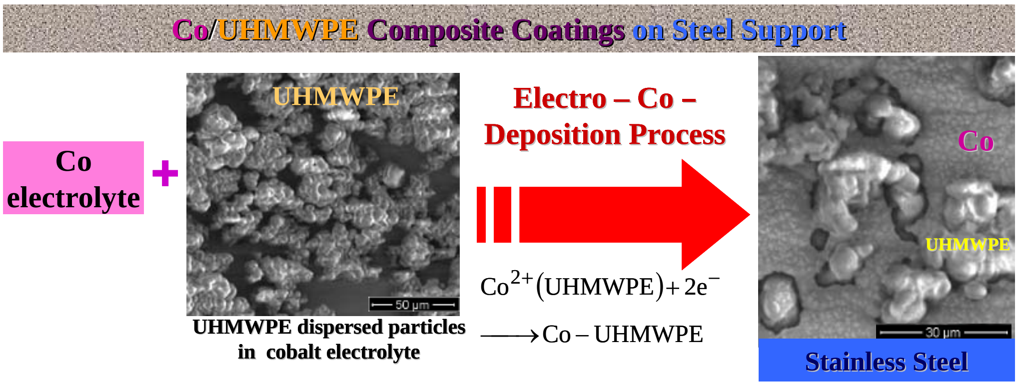

Fig. 1. Schematic representation of electro-co-depositing UHMWPE dispersed particles with cobalt to obtain Co/UHMWPE biocomposite coatings

The electrochemical setup was a standard three-electrode cell with stainless steel (304L) as a working electrode, pure cobalt foil (99.9% purity) as a counter electrode, and Hg/Hg_2SO_4, K_2SO_4(sat'd), ESS as a reference electrode. UHMWPE particles with a mean diameter of 10 µm, provided by TICONA Germany, were dispersed in cobalt sulphate – chloride electrolyte as second phase and maintained in homogenous suspension by magnetic stirring. The cathode samples were degreased, immersed in HCl 1:1 and after washed with distilled water, before electrodeposition. Electrochemical impedance spectroscopy (EIS) diagrams at cathodic potentials were performed on a potentiostat – galvanostat - frequency analyser type by means of a computer program for EIS plotting.

3. Results and discussions

3.1. Electrokinetic behaviour by EIS diagrams

In aqueous solutions, cobalt is present in the form of divalent cobaltous ion with octahedral coordination, having four equatorial and two axial coordination sites [14], each occupied by water molecules. By adding UHMWPE particles in the electrolyte some ions could be adsorbed on their surfaces. Cobalt electrodeposition studies can be categorized according to the working electrode and the type of solution systems used. Most studies have been performed with glassy carbon electrodes [15, 16–20], others being gold [19, 21], nickel [22] and copper [15, 20]. Chloride solutions have been the preferred systems for studying the electrochemistry of cobalt [17–22], rather than sulfate systems [16, 22]. Regarding the reaction mechanisms, it has been found that cobalt electrodeposition initiates predominantly via progressive nucleation, which can change to instantaneous nucleation mechanisms by enhancing mass transfer, by using ultrasound [16], or by increasing cobalt concentration [19], for example. We studied the UHMWPE concentration effect on cobalt electrocrystalisation by impedance diagrams performed at cathodic potentials. No such measurements could be found in the literature for comparison purpose and diagram interpretations are based on exiting theories about metal and alloy electrocrystallisation.

The electrochemical impedance spectroscopy (EIS) method was used at cathodic potential in the presence of UHMWPE dispersed particles at different concentration in the cobalt electrolyte. The eletrochemical impedance measurements were performed in the frequency range from 100 KHz to 5 mHz at E = -900 mV vs ESS cathodic potential with different concentrations of UHMWPE particles in the solution. The Nyquist representations of the impedance diagrams are presented in Fig. 2.

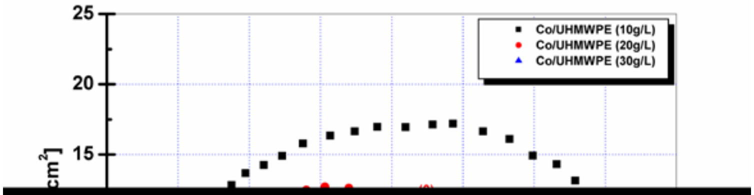

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Fig. 2. Nyquist representations of the impedance diagrams at a potential of E=-900 mV vs ESS, stirring rate of dispersion solution of 450 rpm and UHMWPE dispersed phase concentration of: (1, ■) UHMWPE - 10g/L, (2, ●) UHMWPE - 20g/L, (3, ▲) UHMWPE - 30g/L

The shape of impedance diagrams in the presence of UHMWPE particles are not changed but the charge transfer resistance decreases with increasing the UHMWPE concentration in the electrolyte. As it is shown in the Figure 2, the charge transfer resistance R_{CT} decreases from $37{,}73\ \Omega \cdot \mathrm{cm}^2$ for 10 g/L of UHMWPE in the electrolyte to $21{,}19\ \Omega \cdot \mathrm{cm}^2$ for 30 g/L of UHMWPE dispersed particles in the electrolyte. As it can be seen the impedance diagrams for the UHMWPE – cobalt composite electrodeposition have the same shape while the time constants for the intermediate steps take the same values. This could confirm that dispersed particles do not modify the metal electrocrystallisation mechanism; they only activate the charge transfer process.

The decrease of charge transfer resistance in the presence of higher concentration of UHMWPE as dispersed phase can be due to the electrically active metal species which are absorbed or formed on the particles surface to be subsequently reduced on the cathode surface. From published experimental data concerning cobalt electrodeposition, some authors found that the Co electrocrystallisation in aqueous solution is accompanied by simultaneous hydrogen evolution reaction (HER) [24, 25] which makes analysis of experimental current transients of cobalt electrodeposition very difficult. Correia et al. [26] and Gómez et al. [27] analyzed the electrocrystallization of Co on carbon and gold substrates, from chloride baths and a progressive nucleation mechanism was found. Soto et al. [28, 29] studied Co electrodeposition, using different pHs and concluded that distinct mechanisms of nucleation are involved during early stages of Co deposition. Therefore more inside studies are necessary in order to know the influence of UHMWPE particle on cobalt electro-reduction.

The complex plane impedance diagrams for UHMWPE co-deposition with cobalt allow the calculations of the equivalent circuit for the intermediate steps with electron transfer during electrodeposition and therefore the estimation of the corresponding time constants. Reaction paths for the dissolution of divalent species involving univalent intermediates must exhibit pseudo capacitance effects in transient or ac phenomena. This is due to the fact that the change in potential must be accompanied by a corresponding change in the concentration of the intermediate. This can be done only by exchanging charge with the electrode. The impedance could be described by the following equation:

$$Z = R_e + \frac{R_{CT}}{1+(j\omega\tau)^{\beta}} \quad (\text{with } 0 < \beta \ \leq 1) \tag{1}$$

Where: R_e is the electrolyte resistance between the reference electrode and the working electrode and R_{CT} is the charge transfer resistance of electrochemical reaction. The value of β determines the amplitude of the depressed impedance semi-circle and the importance of the discrepancy between the Randles' circuit model with a pure capacitor C_{dl} and the equivalent circuit with the CPE insteade of C_{dl}. The borderline case of the Randles' circuit is found if $\beta = 1$. Simple equivalent circuits fitted better the experimental impedance data and allow us to calculate the charge transfer resistance during Co/UHMWPE composite coatings elecrodeposition, Figure 3.

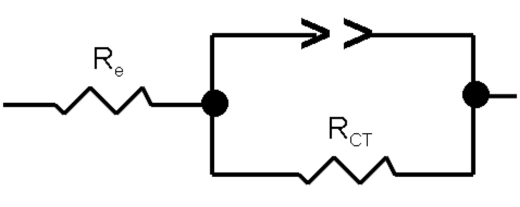


Fig. 3. Equivalent circuit proposed to fit the experimental impedance data during cathodic co-deposition of bio-UHMWPE dispersed particles with cobalt

CPE’s are constant phase elements, accounting for the fact that the centres of the capacitive arcs of the impedance circle are under the axis of real part. This feature of capacitive arcs is encountered in all electrochemical impedance studies performed on inhomogeneous surfaces and has given rise to extensive studies. CPE are not pure capacitors but components depending on frequency.

Reaction paths for the deposition of divalent species involving univalent intermediates must exhibit pseudo capacitance effects in transient or ac phenomena. This is due to the fact that the change in potential must be accompanied by a corresponding change in the concentration of the intermediate. This can be done only by exchanging charge with the electrode. In the absence of an electric field on the cathode surface there is an adsorbed layer of ion species, which includes hydrated metal ions and ions from the particles adsorption area. Particles are absorbed on the cathode surface due to the ions absorbed at their surfaces. Bivalent metal transition from ion state to metal state takes places in two steps of ion transfer which call for a lower energy barrier than only one step of two ion changing. In poor acid or neutral solutions they form chemical species with the hydroxyl ions (OH^-) of type (MOH^+) and $M(OH)_2$ which exist in enough concentration on the cathode surface to compete with the free metal ion during the mass transfer.

3.2. Coating thickness versus current density

One of the most important operating conditions in an electroplating process is the current density. Increasing the current density the thickness of the deposited layers increases too. The coating thicknesses determined by weighting the cathode before and after deposition or co-deposition are presented in the Figure 4 for 20 g/L of UHMWPE in the electrolyte and 30 minutes deposition time at different current densities. There are shown the increases of thicknesses with increasing the current density for pure cobalt as well as for Co/UHMWPE composite coatings at both concentrations of dispersed particles in the electrolyte 20 and 30 g/L. The increasing of thicknesses with current density increase is about in the same range values for composite coatings compared with pure cobalt coatings.

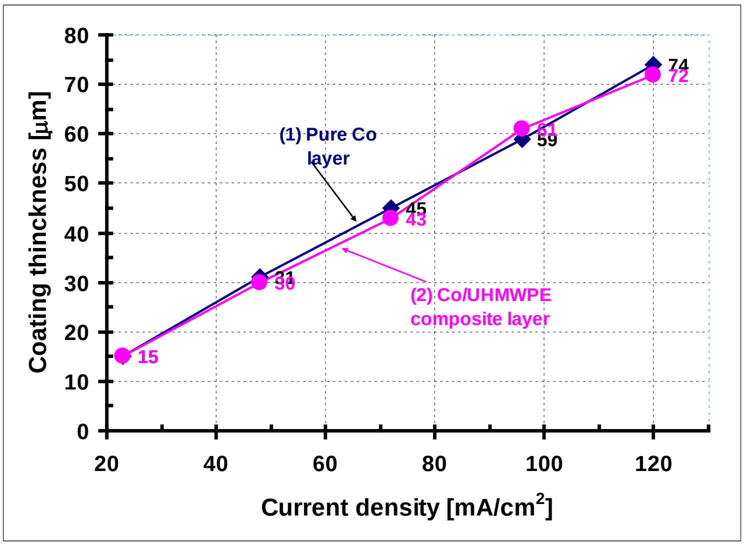
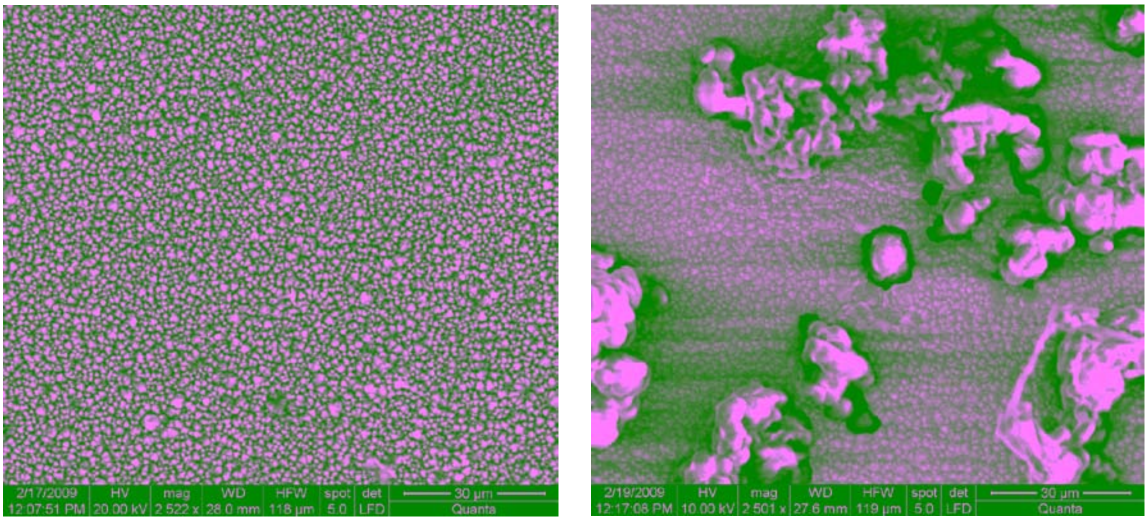


Fig. 4. Coating thicknesses versus current density at deposition time of 30 min: (1) Pure Co coating; (2) Co/UHMWPE (20 g/L) composite coating

3.3. SEM and AFM surface study

Surface morphologies of these deposits are shown in Figures 5 (a and b). The SEM images of pure Co and Co/UHMWPE composite coatings, on stainless steel, show the presence of dispersed phase UHMWPE in the cobalt matrix and differences in surface morphologies of composite coatings compared with pure cobalt coatings obtained at same current density.

The easy occurrence of preferred orientation in electrodeposited cobalt has stimulated number of investigations, without however, achieving the stage of a comprehensive view [13]. Cobalt electrocrystallisation has been far less studied compared to Ni. Electrolytic Co crystallizes with both hexagonal closed packed (hcp, α-Co) the stable allotropic modification at temperature below 417^{0}C and face centered cubic (fcc, β-Co) lattice structure, as first reported by Hull [13]. β-Co is favoured by low temperature, high current density and low pH.



(

(a) b)

Fig. 5. SEM surface morphology of coatings obtained at current density of 48 mA/cm^2 and deposition time of 30 min: (a) Pure Co; Co/UHMWPE Composite Coatings with 30g/L

With increase of pH the structure becomes completely of the α-phase and deposits texture depends mainly on solution pH and, to a minor extent, on temperature and current density [13]. Our results regarding Co and UHMWPE/Co composite electrodeposition from sulphate - chloride electrolyte seems to have two-phase composition and need more inside investigation in order to explain the changes in surface morphology of composite coatings as compared with pure cobalt layers obtained in the same electroplating conditions [30]. Advances in the comprehension of the factors and mechanism participating in Co electro crystallization are expected to contribute to a systematic understanding of the structure-properties correlation of cobalt and matrix cobalt composites.

AFM surface topography gives further support for electro-co-deposition of UHMWPE particles with cobalt to obtain biopolymer in the cobalt matrix composite layers. Comparative AFM images of the surface topography of Co layer and Co/UHMWPE composite layer on stainless steel obtained at two current densities are presented in Figures 6 (a, b) and 7 (a, b).

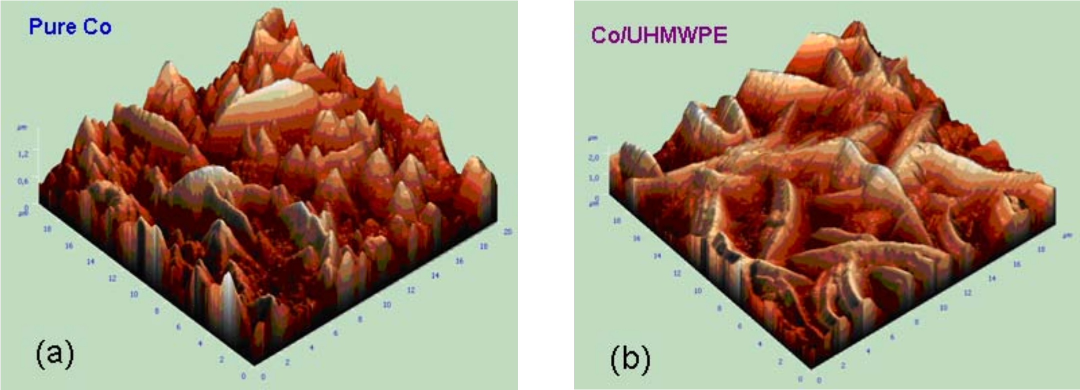


Fig. 6. AFM surface topography images of layers obtained at

current density of 23 mA/cm^2 and deposition time of 60 min: (a) Pure Co and (b) Co/UHMWPE Composite Layers with 30g/L UHMWPE in the electrolyte

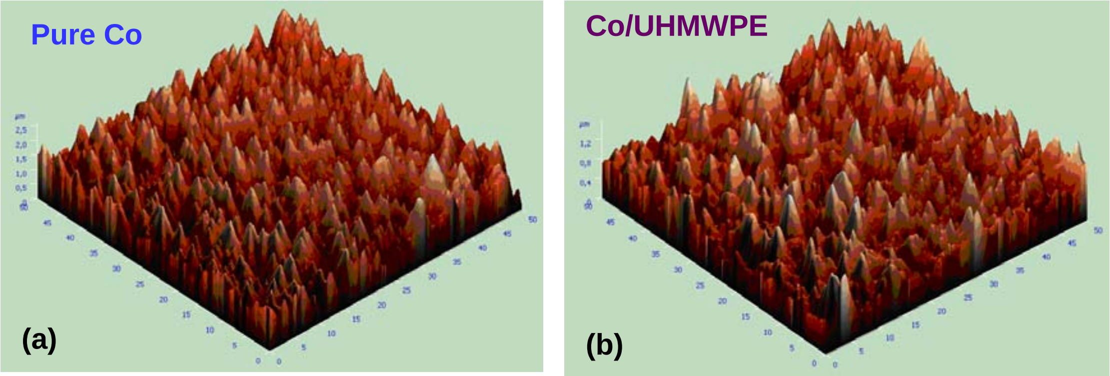


Fig. 7. AFM surface topography images of layers obtained at current density of 48 mA/cm^2 and deposition time of 30 min: (a) Pure Co and (b) Co/UHMWPE Composite Layers with 30g/L UHMWPE in the electrolyte

The roughness determined from AFM measurements of both pure cobalt and Co/UHMWPE composite coatings increases with increasing the current density, observing a higher increasing of roughness for Co/UHMWPE composite coatings compared with pure cobalt layers, Figure 8.

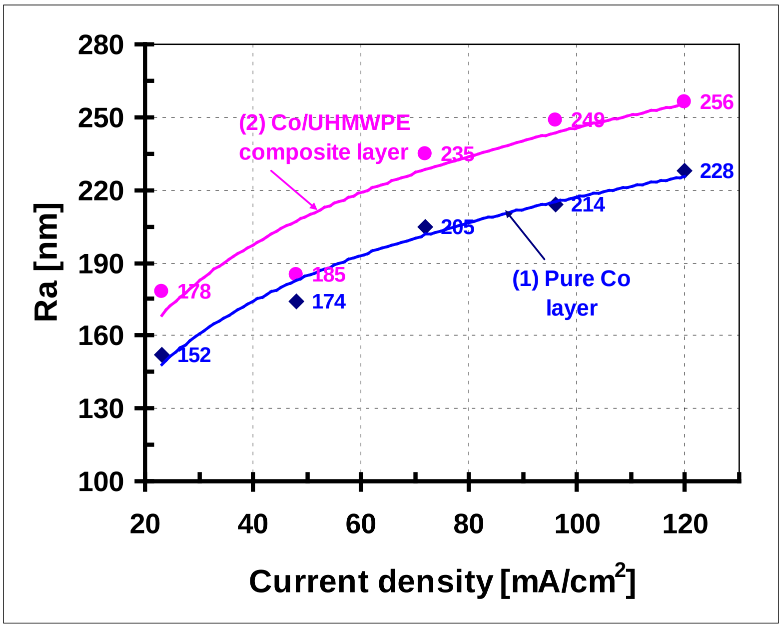


Fig. 8. Roughness versus current density: (1) pure cobalt coatings; (2) Co+UHMWPE composite coatings

3.4. Microhardness

The microhardness of electrodeposited layers has been determined by optical microscopy, using the Vickers method on a METKON type microscope on the samples surface. A load of 0.025 kg on the Vickers scale was used. The surface Vickers microhardness versus current density of electrodeposited layers of pure cobalt and Co/UHMWPE composite show about same values at smallest current density of 23 mA/cm^2, Figure 9.

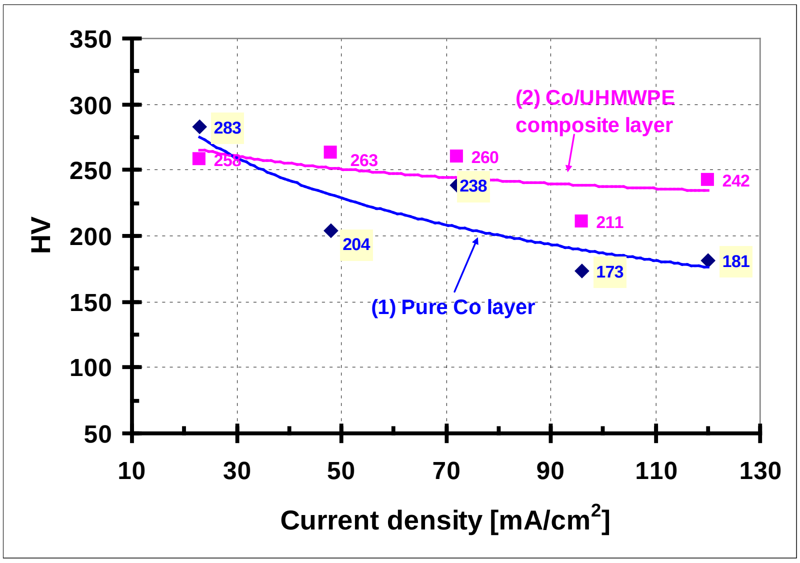


Fig. 9. Microhardness versus current density
(1) Pure Co coating; (2) Co/UHMWP Composite Coatings

By increasing the current density of electroplating process the microhardness of pure cobalt layers decrease slowly (from 283 HV to 181 HV) while the microhardness values of Co/UHMWPE composite layers remain about constant. The variation is very small from 250 HV at 23 mA/cm^2 to 242 HV at 120 mA/cm^2. Excepting the current density of 23 mA/dm^2 where the microhardness of Co/UHMWPE layer is lower (250 HV) comparatively with pure cobalt layer, at all others current densities the Co/UHMWPE composite layers exhibits higher microhardness than that of pure cobalt layer (Figure 9).

As known from classical metallurgy, hindering the dislocation movement could increase the hardness of a material by lattice distortions (grain boundaries density or small grain size). The higher hardness of metals is ascribed to smaller grain size as one of the possibility.This could be an explanation of increasing microhardness by co-depositing UHMWPE with cobalt.

Finally, we should mention, that the results described above have demonstrated the possibility to obtain UHMWPE bio polymer dispersed in a cobalt matrix as biocomposite layers with a possibility to be used further as biomaterials due to their biocompatibility as individual components.

4. Conclusions

In this electrochemical study, we identified the feasibility to prepare Co/UHMWPE composite coatings by properly incorporating the UHMWPE micro particles to be co-deposited in the Co plating bath from a sulphate-chloride cobalt electrolyte.

Adding UHMWPE particles in the electrolyte solution, the composite layers thickness are about the same compared with the thickness of pure Co layer obtained under the same electrodeposition conditions.

EIS plots in Nyquist representations of the impedance diagrams at different concentrations of UHMWPE dispersed phase in cobalt electrolyte, showed that charge transfer resistance increase with decreasing the concentration of UHMWPE dispersed particles in the electrolyte.

The SEM morphologies of electrodeposited pure cobalt and Co/UHMWPE (ultra high molecular weight polyethylene) coatings, on stainless steel, show differences due to UHMWPE polymer particles incorporation in the cobalt matrix.

The AFM images reveal the modification of topographies and the increase of roughness

with the current density. The roughness of composite coatings is a little bit higher comparatively with pure cobalt coating obtained at the same current density.
UHMWPE particles added in the Co electrolyte influence the electrodeposition process and the effect must be further investigated.

Finally, through this study, we show that new composite layers of UHMWPE dispersion in a cobalt matrix could be obtained as possible alternative of biomaterials with the observation of electrochemical impedance spectroscopy electrochemical method as a powerful way to get a better understanding of complex transformation occurring during composite electro-co-deposition.

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