



ELECTROCHEMICAL DEPOSITION AND SEM SURFACE MORPHOLOGY OF Co AND UHMWPE/Co COMPOSITE LAYERS

Lidia BENE¹, Marilena MARDARE-PRALEA^{1,2}, Paula COJOARU³

¹Dunarea de Jos University of Galati, Faculty of Metallurgy and Materials Sciences, Research Center Interfaces – Tribocorrosion and Electrochemical Systems (CC-ITES). Romania

²LBR Laboratory, Arcelor-Mittal Steel Galati, Romania

³Dipartimento di Chimica, Materiali, Giulio Nata Politecnico di Milano, Italy
email: Lidia.Benea@ugal.ro, Marilena.Mardare@ugal.ro

ABSTRACT

The work aims at obtaining composite coatings in cobalt matrix with dispersed phase UHMWPE (ultra high molecular weight polyethylene) and at characterizing the surface morphology analyse by SEM, the thickness of the deposited layers and the microhardness of Co and Co/UHMWPE composite coatings. All coatings were obtained on stainless steel plates (304L). The electro-deposition of these metal and composite layers is a process consisting of inclusion of UHMWPE (ultra high molecular weight polyethylene) particles in the cobalt matrix during electroplating process. The dispersed particles were suspended in a sulphate cobalt plating electrolyte within the metal which electro-crystallizes and forms the metal matrix. By means of the potentiostat a number of five current densities were applied during deposition as follow: 23 mA/cm², 48 mA/cm², 72mA/cm², 96mA/cm² and 120mA/cm². Keeping particles in suspension was ensured by magnetically stirring at a rotation speed of 300 rotations per minute. After processing the results, it has been noticed that with increasing current density there is an increase in the pure Co layer thickness too as well as in the UHMWPE/Co layers thickness. Adding particles UHMWPE particles in the electrolyte solution, the composite layers thickness is greater as compared with the thickness of pure Co layer obtained under the same electrodeposition conditions. UHMWPE was selected as surface modifier element, due to its high biocompatibility and excellent wear behaviour being used in many biomedical applications. Cobalt is already used in many cobalt alloys as biomedical implants as cobalt – chromium alloys. UHMWPE is also used as bio-polymer in many implants. The metal-matrix composites are materials in which the properties of a metallic host material are modified with addition of a second phase (ceramics, polymers, etc.) by electrodeposition process.

KEYWORDS: Electrodeposition, UHMWPE, cobalt, composite coatings, thickness.

1. Introduction

Obtaining new super-performant materials led to the development of a class of products known as composite materials.

To protect ferrous metals (steel, cast iron) against corrosion, Co coatings are widely used in particular those obtained by electrolytic processes.

The process of metal and composite layers electrodeposition essentially consists in the inclusion of solid particles suspended in an electrodeposition bath into the electrocrystallizing metal which is in fact the metal matrix. These particles are generally

considered insoluble [1].

Objectives are for example: increase in strength of conducting materials while maintaining the high conductivity, improvement in low temperature creep resistance (reactionless materials), improvement of burnout behavior (switching contact), improvement of wear behavior (sliding contact), increase in operating time of spot welding electrodes by reduction of burn outs, production of layer composite materials for electronic components, production of ductile composite superconductors, production of magnetic materials with special properties. For other applications different development objectives are

given, which differ from those mentioned before. For example, in medical technology, mechanical properties, like extreme corrosion resistance and low degradation as well as biocompatibility are expected [2].

A major condition that any coating should meet is the electrochemical relationship between the metal coating and metal base. The metal coating must have a negative potential more negative than that of the base metal (the object being coated). In this case, the galvanic pair which is formed in the coating pores will gradually destroy the protection metal, and not the base one. In the iron-zinc pair, the latter is more electronegative, thus forming a good iron protection against corrosion [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 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.

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. 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 [11].

Biomaterial application is an interdisciplinary field of research (Fig. 1) and can use all classes of materials from metals, ceramics, polymers to composites [12].

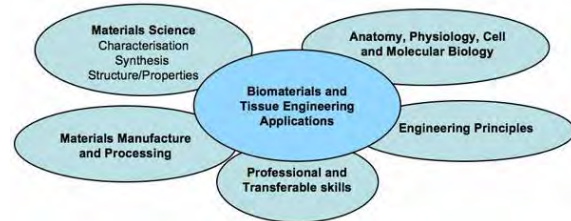


Fig. 1. *Interdisciplinarity of biomedical materials applications*

The biomaterials could be divided roughly into three user types. These are:

- (i) inert or relatively inert with minimal host response,
- (ii) bioactive which actually stimulates bonding to the surrounding tissue and (iii) biodegradable which resorbs in the body over a period of time.

Metals are generally chosen for their inert qualities whereas ceramics and polymers may offer bioactivity or resorption.

Composites could combine the properties of metals with ceramics or metals with polymers.

Our work combines polymer and metals (cobalt) by electrodeposition process to obtain a new biocompatible material (coating). UHMWPE was selected as surface modifier element, due to its high biocompatibility and excellent wear behaviour being used in many biomedical applications. Cobalt is already used in many cobalt alloys as biomedical implants as cobalt – chromium alloys. UHMWPE is also used as bio-polymer in many implants. The metal-matrix composites are materials in which the properties of a metallic host material are modified with addition of a second phase (ceramics, polymers, etc.) by electrodeposition process.

2. Experimental research

The electro-deposition of these metal and composite layers is a process consisting of 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 within the metal which electro-crystallizes and forms the metal

matrix, shown in Fig 2. Co plate of 99.9% purity was used as anode. As cathode we used stainless steel plates (chemical composition and mechanical properties are presented in Table 2). The cathode samples were degreased, immersed in HCl 1:1 and afterwards washed with distilled water, before electrodeposition.

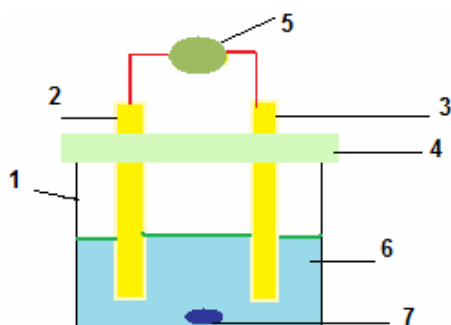


Fig. 2. Cell for electrodeposition
1. Electrolytic cell, 2. Anode (Co), 3. Cathode (stainless steel), 4. Electrical contact copper, 5. Potentiometer, 6. Electrolyte and suspension of disperse phase, 7. Stirrer.

The UHMWPE particles were provided by TICONA Germany at 20 μm mean diameter and the SEM image of shape is presented in Fig. 3.

By means of the potentiostat a number of five current densities were applied during deposition as follows: 23 mA/cm^2 , 48 mA/cm^2 , 72 mA/cm^2 , 96 mA/cm^2 and 120 mA/cm^2 .

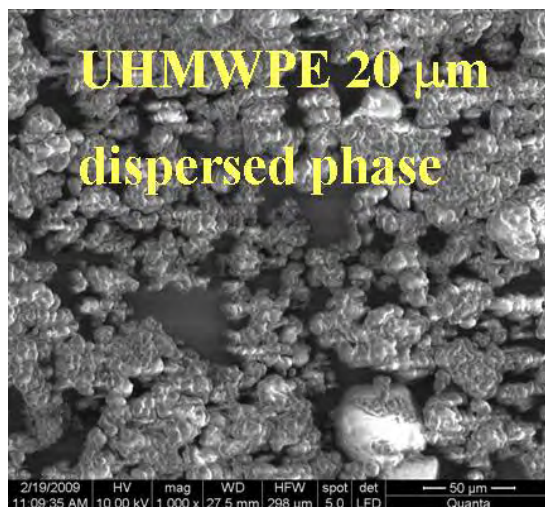


Fig. 3. SEM image of UHMWPE particles

By means of the potentiostat a number of five current densities were applied during deposition as follow: 23 mA/cm^2 , 48 mA/cm^2 , 72 mA/cm^2 , 96 mA/cm^2 and 120 mA/cm^2 .

Obtaining these layers of pure Co and UHMWPE/Co (ultra high molecular weight polyethylene) was done in a sulphate cobalt electrolyte solution. For depositing UHMWPE/Co composite coating UHMWPE particles were added to electrolyte in two concentrations of 20 g/L and 30 g/L.

Table 2. Chemical composition and mechanical properties of stainless steel

Stainless steel	Chemical composition												
	C	Mn	Si	P	S	Co	Cr	Ni	V	Al	Mo	Ti	Nb
%	0,05	0,86	0,23	0,034	0,010	0,05	17,5	0,14	0,037	0,008	0,001	0,011	0,02

Keeping particles in Co electrolyte suspension, UHMWPE was provided by magnetic stirring at a rotation speed of 300 rpm.

The deposition time was 30 min, and 60 min. respectively.

Electrodeposition experiments were performed at room temperature.

3. Results and discussions

After processing the results, it was noticed that by increasing current density and maintaining the deposition time more, from 15 minutes, 30 minutes to 60 minutes, the thickness of the deposited layers increases too.

The coating thickness of pure cobalt and composite based on cobalt with UHMWPE (30 g/L dispersed in the electrolyte) determined by XRF is presented in Figure 4 (a, b).

The coating thicknesses determined by weighting the cathode before and after deposition or co-deposition re presented in the Figures 5 and 6. There are shown the increases of thicknesses with increasing the current density for pure cobalt as well as for UHMWPE / Co composite coatings at both concentrations of dispersed particles in the electrolyte 20 and 30 g/L. The increasing of thicknesses with current density increasing are within in the same range values for composite coatings compared with pure cobalt coatings.

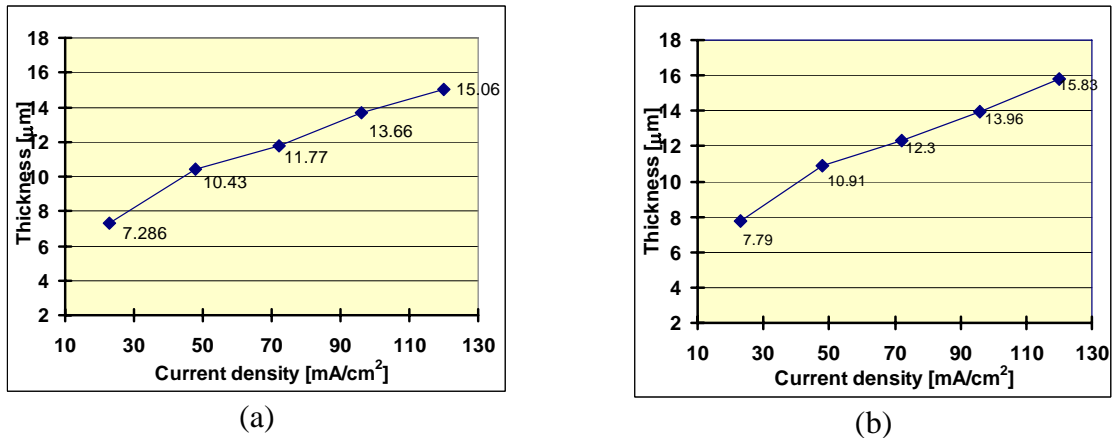


Fig. 4. Coating thickness versus current density at deposition time of 15 minutes, determined by XRF: (a) Pure cobalt coatings, (b) UHMWPE/Co composite coatings

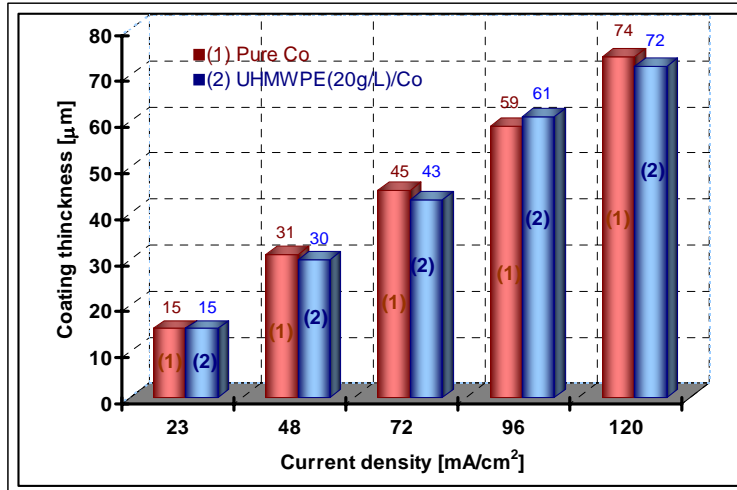


Fig. 5. Coating thickness versus current density, at deposition time of 30 min: (■) (1) Pure Co coatings; (■) (2) UHMWPE/Co (20 g/L) composite coatings

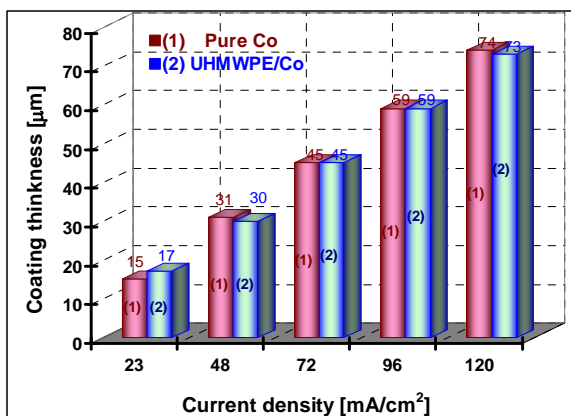


Fig. 6. Coating thickness versus current density, at deposition time of 30 min: (■) (1) Pure Co coatings; (■) (2) UHMWPE/Co (30 g/L) composite coatings

The SEM images of pure Co and UHMWPE/Co 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, Figures 7-8. 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^oC 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. 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. Our results regarding Co and UHMWPE/Co composite electrodeposition from sulphate electrolyte seem 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.

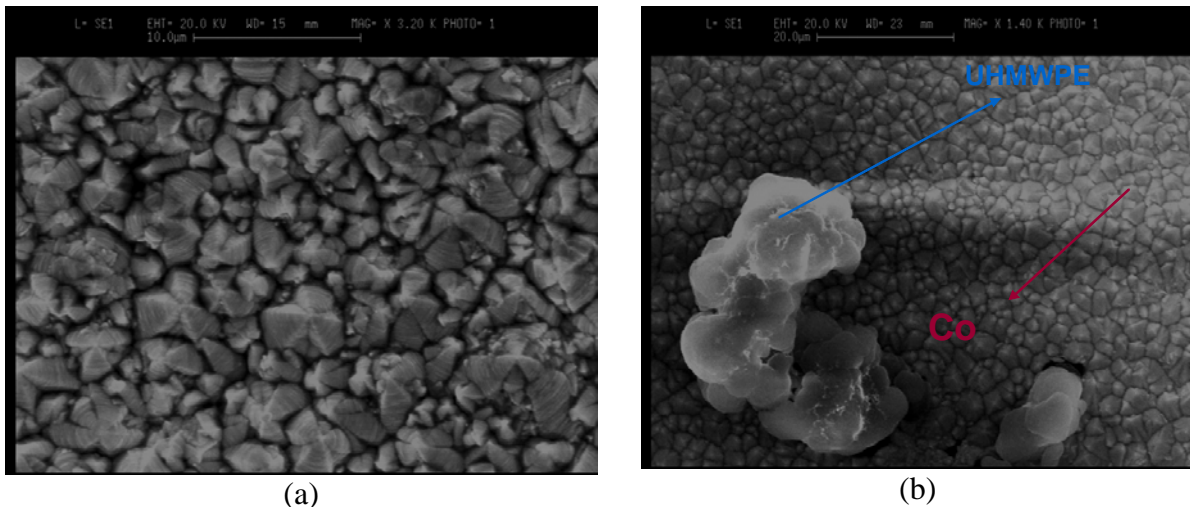


Fig. 7. SEM surface micrographics of:
(a) Pure Co Coatings, obtained at current density of 96 mA/cm^2 and deposition time of 30 min;
(b) UHMWPE / Co Composite Coatings with 30g/L UHMWPE obtained with a current density of 96 mA/cm^2 and deposition time of 30 min

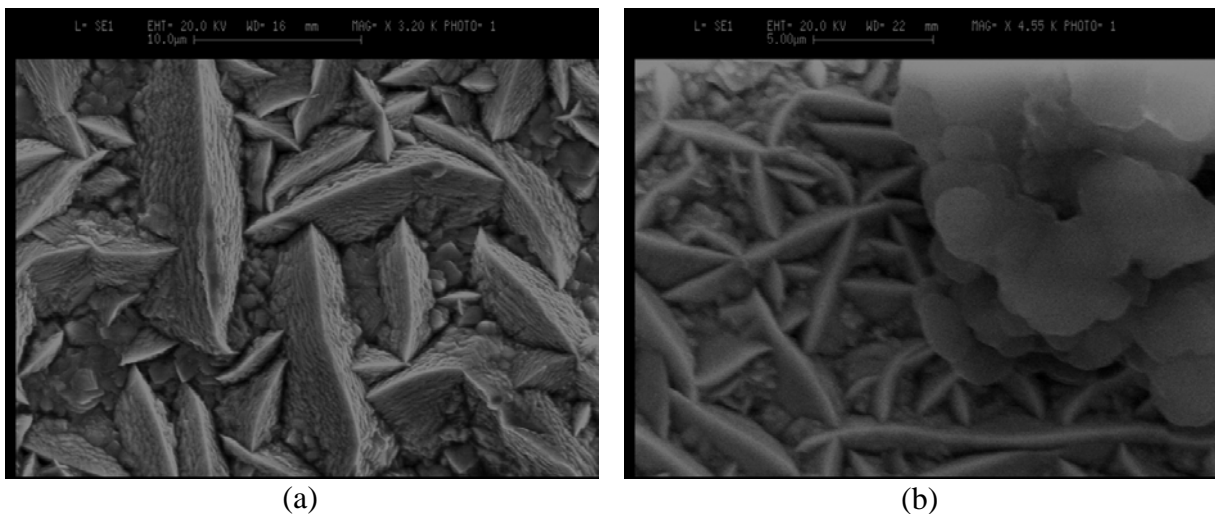


Fig. 8. SEM surface micrographics of:
(a) Pure Co Coatings, obtained at current density of 96 mA/cm^2 and deposition time of 30 min;
(b) UHMWPE / Co Composite Coatings with 30g/L UHMWPE obtained with a current density of 23 mA/cm^2 and deposition time of 30 min

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.

Studying the UHMWPE particles distribution in the cobalt matrix on surface of coatings, Figure 9 by SEM image and EDX element distribution (C) it is shown a good dispersion phase inside cobalt and a good adhesion and uniformity of UHMWPE/Co

composite coatings on stainless steel support.

The carbon content of UHMWPE / Co composite Coatings obtained with 30g/L UHMWPE was found at 14 % C in the Co matrix (for a composite coating obtained at 52 mA/cm^2 current density).

The SEM - EDX images of UHMWPE/Co composite coatings on stainless steel, show the presence of dispersed phase UHMWPE in the cobalt matrix.

The SEM studies of UHMWPE/Co composite coatings on stainless steel show also the changing in surface morphologies compared with pure cobalt coating obtained in the same conditions of electrodeposition.

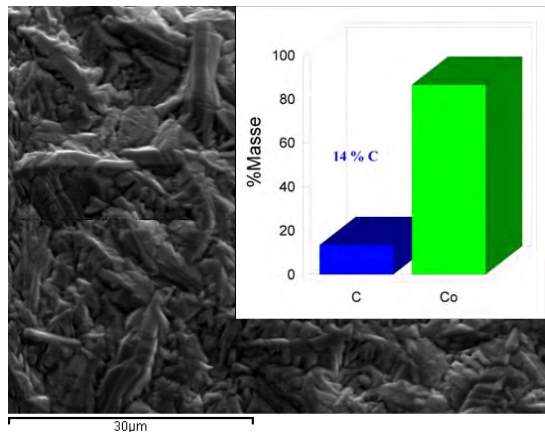


Fig. 9. SEM-EDX image and content of C in UHMWPE/Co composite coatings ($52\text{mA}/\text{cm}^2$)

The roughness of both pure cobalt and UHMWPE/Co composite coatings increases with increasing the current density, observing a higher increasing of roughness for composite coatings compared with pure cobalt coatings, Figure 10.

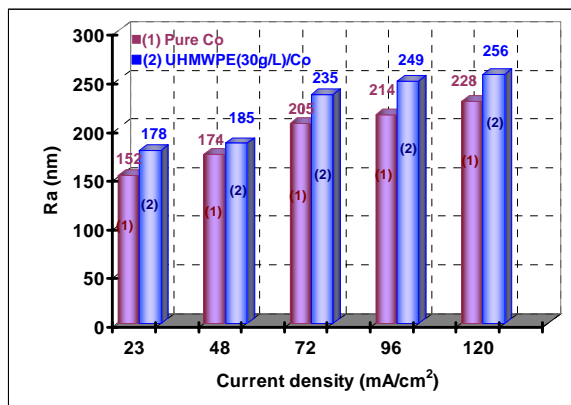


Fig. 10. Roughness versus current density:
(■)(1) Pure Co coatings; (■)(2) UHMWPE (30g/L)/Co composite coatings

The future work will be done on the following directions: Modelling the mechanism of co-deposition and electroplating parameters; Correlation of coating thickness with electrodeposition parameters; The mechanical behavior of the modified materials; Electrochemical Corrosion in Simulating Body Fluids (SBF); Tribocorrosion studies in SBF; Biocompatibility tests and Bacteria attachment and biofilm growth.

4. Conclusions

It is feasible to prepare UHMWPE/Co composite coating by properly incorporating the UHMWPE microparticulates to be co-deposited in the Co plating bath from a sulphate cobalt electrolyte.

Coatings thickness increases with the increasing of current density; the composite layer is almost equal to or a little bit smaller than that of the cobalt matrix at the same current density.

Moreover, the incorporation of the UHMWPE micro-particulates in the plating bath leads to changes in the morphology of the composite coatings as compared to the pure Co coatings evidenced by SEM studies.

The surface morphology of composite coatings layers is different compared with pure cobalt coated.

The regular crystal structure characteristic of electroplated cobalt coatings was disturbed by UHMWPE particles in cobalt electrolyte for electrodeposition.

The amount of UHMWPE particles embedded in the cobalt matrix has to be determined by a method easy to use which will be established.

The adhesion and uniformity of UHMWPE/Co composite coatings were analyzed by SEM showing good results.

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References

- [1]. Lidia Benea - *Electrodepuneri compozite în teorie și practică*, p.65, 1998
- [2]. K. K. Chawla - *Composite Materials: Science and Engineering*, Springer-Verlag, New York, 1998
- [3]. Xuli Xia, Igor Zhitomirsky, Joseph R. McDermid* - *Electrodeposition of zinc and composite zinc-yttria stabilized zirconia coatings*, Journal of materials processing technology 209 (2009) 2632–2640, 2008
- [4]. B.D. Rantner, A.S. Hoffman, F.J. Schoen, J.E. Lemons - *Biomaterials Science: An Introduction to Materials in Medicine*, Academic Press, 1996.
- [5]. T. Tsuruta, A. Nakajima (Eds.) - *Multiphase Biomedical Materials*, V.S.P., Utrecht, The Netherlands, 1989.
- [6]. K. Ishihara, S. Tanaka, N. Furukawa, K. Kurita, N. Nakabayashi - *Improved blood compatibility of segmented polyurethanes by polymeric additives having phospholipid polar groups. I. Molecular design of polymeric additives and their functions*, J. Biomed. Mater. Res. 32, 1996, 391–399.



[7]. **K. Ishihara, K. Fukumoto, Y. Iwasaki, N. Nakabayashi** - *Modification of polysulfone with phospholipid polymer for improvement of the blood compatibility. Part 1. Surface characterization*, *Biomaterials* 20, 1999, 1545–1551.

[8]. **C.E. Kinley, A.E. Marble** - *Compliance: a continuing problem with vascular grafts*, *J. Cardiovasc. Surg.* 21, 1980, 163–170.

[9]. **W.M. Abbott, J. Megerman, J.E. Hasson, G. L'Italien, D.F. Warnock** - *Effect of compliance mismatch on vascular graft patency*, *J. Vasc. Surg.* 5, 1987, 376–382.

[10]. **S.F. Stewart, D.J. Lyman** - *Effects of a vascular graft/natural artery compliance mismatch on pulsatile flow*, *J. Biomech.* 25, 1992, 297–310.

[11]. **Yanjerappa Arthoba Naik, Thimmappa Venkatarangaiah Venkatesha, Perdur Vasudeva Nayak** - *Electrodeposition of Zinc from Chloride Solution*, *Turk J Chem*, 2002, Volume 26, p. 725 – 733.

[12]. **Lidia Benea, Pierre Ponthiaux, Marilena Mardare, Jean Pierre Celis** - *Alternative materials – Cobalt / UHMWPE composite coatings*: Conference presented at COST 533 Action on Materials for Improved Wear Resistance of Total Artificial Joints final meeting, 2nd Workshop on Biotribology - Bridging Engineering and Medicine 25 - 27 May 2009, Guimarães Portugal.

[13]. **A. Vincenzo, P.L. Cavallotti** - *Electrochim. Acta* 49, 2004, 4079-4089.