Surface Modifications of Materials by Electrochemical Methods to Improve the Properties for Industrial and Medical Applications

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Abstract. There are two applied electrochemical methods in our group in order to obtain advanced functional surfaces on materials: (i) direct electrochemical synthesis by electrodeposition process and (ii) anodization of materials to form nanoporous oxide layers followed by electrodeposition of hydroxyapatite or other bioactive molecules and compounds into porous film. Electrodeposition is a process of low energy consumption, and therefore very convenient for the surface modification of various types of materials. Electrodeposition is a powerful method compared with other methods, which led her to be adopted and spread rapidly in nanotechnology to obtain nanostructured layers and films. Nanoporous thin oxide layers on titanium alloys as support for hydroxyapatite or other biomolecules electrodeposition in view of biomedical applications could be obtained by electrochemical methods. For surface modification of titanium or titanium alloys to improve the biocompatibility or osseointegration, the two steps must be fulfilled; the first is controlled growth of oxide layer followed by second being biomolecule electrodeposition into nanoporous formed titanium oxide layer.

1. Introduction

The recent developments in technological processes and the increasing interest in the trivalent interrelationship of processing parameters, the structural and functional properties of materials and protective coatings have contributed to a substantial increase in the use of these coatings materials in the industry as well as in biomedical applications [1-20].

This increasing growth has also been stimulated as a response to the needs of advanced technology for better materials. Particularly in the field of surface technologies, the evolution of so-called "high tech" coatings is evident due to the development of more and more performing surface modification technologies such as ionic implants, plasma deposition, vacuum, composite electrodeposition, etc. An important reason to introduce materials with corrosion protection (protective coatings) in different areas is first of all the economic one [3].

Materials with coatings and or protective layers or films can have a much longer lifetime compared to the substrate and so it is possible to capitalize materials as a substrate with low prices. The economic impulse to use the coatings in corrosion control is obvious, if corrosion damage can be slowed or even stopped, the cost of the material is reduced [3].
The definition of surface functionalization has several variants, but can simply be considered as a method used to introduce new properties to a particular material in order to meet certain specific requirements [3].

A functional surface comprises new and/or chemically modified groups and/or morphological features that determine environmental interaction and subsequent specific behavior.

At present, advances in surface, nanotechnology, and nanomaterial engineering allow materials to be manipulated "up to the molecular scale", paving the way for new Hi-Tech functional materials.

Functional coatings (organic, inorganic or hybrid) are a class of materials that can be adapted for many applications where they should be able to perform well-defined functions. There are many functional coatings in many applications that are part of our everyday life.

In recent years, the development of nanotechnology and nanomaterials has promoted an explosion of new functional coatings and this trend will continue to grow in the coming years. Functional and smart coatings are undoubtedly a class of materials of enormous technological interest [3].

This paper aims to discuss and present the results of two applied electrochemical methods in the CC-ITES research center in order to obtain advanced functional surfaces on materials: (i) direct electrochemical synthesis by electro-codeposition process and (ii) anodization of materials to form nanoporous oxide layers followed by electrodeposition of hydroxyapatite or other bioactive molecules and compounds into porous film.

The two electrochemical methods are applied and perfected for surface functionalization, each with specific applications, but both with the potential to improve corrosion resistance and degradation of surfaces in specific working environments.

Electrochemical depositions of metals, alloys and hybrid layers, nanostructures and nanocomposites.

Controlled growth of oxide films on the surface of metals and alloys by electrochemical techniques, respectively the top-down nanotechnology method.

Both electrochemical methods for surface functionalization are associated with one or more of the material characterization methods in order to appreciate the obtained surface properties correlated with application field.

2. Electrodeposition
The deposition of layers by the electrochemical method, or in short electrodeposition, electro-crystallization, electroreduction, has been and is a long-time method used to fight corrosion of materials or for many other applications.

Electrochemical deposition (ELD) or electrodeposition is the process of depositing a coating (layer, film) of a metal or a composite on the surface of another metal to modify its surface morphology, structure and properties. ELD is a method of obtaining adherent layers to the surface of the material that is the essential aspect of a protective coating.

How, by definition, "corrosion" is the physico-chemical interaction between a metal and its environment of use, which leads to changes in the properties of the metal and can often lead to the deterioration of the metal, the environment, or the technical system to which they belong" (ISO 8044-1986), then if the integrity of the material is affected by the external action of the environment, it is necessary to protect it against this harmful action.

By making it possible to obtain the matter in the arbitrary geometry of the three dimensions, electrodeposition is a powerful method compared to other methods, which has made it adopted and spread rapidly in nanotechnology. Nanocomposites manufactured using electrodeposition include the magnetic and non-magnetic alternating layers, each of only a few nanometers thick to micrometric thick layer for industrial or biomedical applications [3].

A challenge for the process of electro-crystallization of metals and alloys is the electrodeposition of hybrid and composite layers [3].

In the last two decades, composite layers obtained by electrodeposition have also been developed in the field of advanced materials. The subject is particularly recent, given that lately the demands of
Composite materials have become larger and their electrochemical deposition can bring many advantages compared to other processes.

Composite coatings (AC) are part of the composite materials category, which are defined as systems composed of two or more materials in order to improve their properties compared to the separate attributes of components [3].

Composites are bi- or polyphase compacted materials formed by natural processes or artificially created by man, where there are boundaries of separation between the isolated components. The MATRIX is a continuous bonding element, which may be in the solid crystalline or amorphous state. The DISPERSED phase consists of one or more dispersed phases in the matrix, in any aggregation state. It may be present as dispersed particles, being discontinuous or fiber in this case, thus being continuous.

The manufacture of these composite coatings has begun to be investigated since 1972 by the electrolysis of a suspension [10]. This method generally employs a standard electrolyte in which the dispersed particles are uniformly held in solution by suitable stirring. In most cases, the codeposition of dispersed particles with metals requires the development of new electrolytes with different compositions relative to pure metal electrodeposition.

The new method of obtaining composite coatings realizes a principle known in nature, which essentially consists in the fact that the cumulative action of various materials gives an equivalent effect to the creation of a new material, the properties of which differ from the properties of each of the component materials.

The amount of incorporated particles is the essential parameter for composite production and property improvements, such as wear resistance, corrosion and oxidation. In addition, uniform distribution of the codeposited particles in the metal matrix has proven to be another essential parameter. However, it should be mentioned that both the morphological and structural characteristics of the metal matrix are strongly affected by the presence of the particles. Codeposition with a sufficient amount of particles should result in harder and more resistant coatings [3, 8, 13].

Schematically, the electro-codeposition process is shown in Figure 1 for examples of two microsized (micro ZrO _2 - 10 mm mean diameter, UHMWPE - 10 mm mean diameter) and two nanosized particles (nano-CeO _2 - 10 nm mean diameter, nano TiO _2 - 10 nm mean diameter) and a variety of electrolyte corresponding to the metal matrix [3, 11-20]. UHMWPE is a biocompatible polymer called ultrahigh molecular weight polyethylene.

**Figure 1.** Schematic presentation of the electro-codeposition process of dispersed particles into metal matrix to obtain micro and nanocomposite and hybrid layers.
The schematic drawn of electro-codeposition process from Figure 1 includes: (a) - electrochemical equipment; (b) - electrochemical cell with the working electrodes (WE), the counter electrode (CE), the reference electrode (RE), the electrolyte and the dispersed particles held in a homogeneous suspension by means of a stirring system; (c) - nanometer and micrometric dispersed particle types; (d) SEM micrograph of Co / micro-ZrO₂ composite layer; (e) SEM micrograph of Co / micro-UHMWPE microparticles; (f) - SEM micrograph of Co / nano-CeO₂ nanocomposite layer; (g) - SEM micrograph of Ni / nano-TiO₂ nanocomposite layer.

The variety of micro and nano-composite systems that can be obtained by electro-codeposition also provides various applications for these films and layers, from industrial applications to biomedical applications.

Although there are studies and proposals in the literature, a generally valid mechanism of electro-codeposition of dispersed particles with metals has not been achieved. The electro-codeposition mechanism can generally be considered to be characterized by the following steps [3, 9, 12]:

• At the time of introduction into the electrolyte, a layer of adsorbed ionic species is formed at the surface of the dispersed particles forming the double diffuse layer around each particle.
• The particles are transported by stirring and under the influence of electric field, they will flow to the surface of the cathode.
• When the adsorbed ionic species are reduced, the particles are embedded in the composite layer (in the metal matrix).

These ionic species can not directly pass through a charge transfer stage, so the first step in depositing a metal must be its chemical transformation into an electroactive species. This stage takes place during the diffusion transport of the ionic species to the surface of the electrode that takes place inside the hydrodynamic boundary layer or in some cases in the double electric layer [3, 12].

These layers, films and composite coatings can improve the corrosion resistance of various materials in specific environments [16-20]. For example, as the content of TiO₂ nanoparticles increases in the nickel layer, the corrosion current decreases and the corrosion potential passes to more positive values [20], a passive layer is formed, but the HNO₃ solution accelerates the degradation of the passive layer. A better corrosion resistance of Ni/nano-Al₂O₃ composite layers compared to pure nickel layer was obtained in experimental data by potentiodynamic polarization and electrochemical impedance spectroscopy [21].

Hybrid composite layers obtained by the codeposition of polymeric dispersed particles with metals can confer corrosion resistance in different specific environments, from industrial to biomedical (biological fluids) [15-22].

Thus, in Figure 2, are shown the micrograph of the Co / UHMWPE (b) hybrid layer (a) and cobalt (b) produced by the electro-codeposition of high molecular weight polyethylene micrometric particles (UHMWPE), special for biomedical applications [3].

![Figure 2](image_url)

**Figure 2.** SEM micrographs of electrodeposited layers: (a) - pure cobalt; (b) - Co / UHMWPE hybrid coating obtained by electro-codeposition of UHMWPE (50 g / L) with cobalt.
Such hybrid composite layers have demonstrated better corrosion resistance and biocompatibility at their immersion in biological fluids, Figure 3 (a, b).

Figure 3. Corrosion resistance of Co / UHMWPE composite layers and pure cobalt layer immersed in Hank's biological solution after 168 hours: (a) Nyquist representation of electrochemical impedance spectroscopy data; (b) increasing the corrosion resistance of cobalt layers by increasing codeposited dispersed UHMWPE particles.

Figure 3 show the increase in polarization resistance, thus increasing the corrosion resistance, with the increase of the concentration of polymeric UHMWPE dispersed in the electrolyte. Hank's solution simulates the most aggressive fluids in the human body. An increase in polarization resistance is observed, thus decreasing the corrosion rate, with the increase of the UHMWPE polymeric particles in the cobalt electrolyte [15].

Ceramic oxide (CeO₂) nanoparticles, which are in turn biocompatible, can give also to cobalt matrix a higher corrosion resistance by codeposition with cobalt.

In Figure 4 the surface morphology of Co / nano-CeO₂ nanocomposite layer (a) and its uniform distribution in the nanocomposite layer (b) [16] is observed. The inclusion of cerium oxide (CeO₂) nanoparticles can be determined by chemical analysis or X-ray dispersion analysis on SEM provided with an X-ray analyzer, Figure 4 (c).

Figure 4. SEM-EDX analysis of Co/ nano-CeO₂ nanocomposite layers: (a) SEM surface micrograph; (b) SEM-EDX mapping for cerium (Ce); (c) SEM-EDX spectrum of the Co / nano-CeO₂ nanocomposite layer, with the peaks characteristic of the cerium element.

Figure 4 gives an EDX analysis spectrum for the Co / nano-CeO₂ nanocomposite layer, which confirms the inclusion of cerium oxide nanoparticles through the peaks characteristic of the cerium element (Ce).

The increase in the corrosion resistance in biological fluids (Hank's solution) of Co / nano-CeO₂ nanocomposite layers compared to pure cobalt layers is shown in Figure 5 [16]. Figure 5 shows both
the morphological changes induced by the cerium oxide dispersed nanoparticles and their effects on corrosion resistance in specific biological environments. Corrosion resistance increases with increasing cerium oxide concentration.

Figure 5. Increased corrosion resistance based on the percentage of dispersed phase embedded in the Co / nano-CeO$_2$ nanocomposite layer.

The effect of including dispersed nanoparticles into metallic matrices on their crystalline structure can be evidenced by X-ray diffraction. For example, inclusion of 10 nm titanium oxide (TiO$_2$) nanoparticles in the nickel matrix causes changes in the nickel crystallinity as seen in Figure 6 (a) [7, 8]. These structural changes confer also to Ni / nano-TiO$_2$ nanocomposite layers an improved corrosion resistance, Figure 6 (b) [3]. The inclusion of TiO$_2$ nanoparticles in the nickel matrix determines not only structural changes, but also determines an improvement in the corrosion resistance of Ni / nano-TiO$_2$ nanocomposite layers in NaCl solution, as can be seen in Figure 6 (b) [3, 8].

Figure 6. Ni / nano-TiO$_2$ nanocomposite layers; (a) X-Ray diffraction patterns and (b) increasing the corrosion resistance with increasing the content of dispersed particles in the electrolyte.

Ceramic carbides or oxide nanoparticles included in nanocomposite layers offer both corrosion resistance, but also improve wear resistance, resulting in better tribocorrosion resistance [3, 5, 15].

Electrodeposition can be combined with self assembled templates to prepare nanomaterials with exciting properties. Traditional applications of electrodeposition will continue, while new applications will emerge rapidly, especially in the areas of nanoelectronics, biotechnology, nanobiocorrosion, biomedicine, nanostrats, biosciences, and energy engineering. Electrodeposition of non-metallic materials will become more important, and the combination of electrodeposition with other processes will lead to a whole class of nanostructured materials.
3. Controlled growth of oxide films
Controlled growth of oxide layers or anodic oxidation is an electrochemical method for producing an oxide film on a metal substrate. It removes the electrons from a substance and oxidizes the anode. Anodic oxidation increases the corrosion resistance and wear resistance, and provides better adhesion to primers for further paints or primer than does base metal.

Anodic films can also be used for a range of cosmetic effects, either with thick, porous layers that can absorb dyes or thin, transparent layers, which add interference to reflected light [3].

Anodic oxidation is an accelerated electrochemical oxidation process, which is intensified by the natural metal oxide film. This involves applying an electrical voltage to relatively low currents while the substrate is immersed in an acidic solution. The oxide films obtained can be very dense and stable with a variety of microstructure features. Normally, anodic oxidation is carried out in an electrochemical cell containing various aqueous solutions such as sulfuric acid, hydrogen peroxide and phosphoric acid. For example, anodic oxidation is used to modify the surfaces and properties of titanium and its alloys or aluminum and its alloys due to: the resulting mechanical properties, non-biotoxicity, biocompatibility properties and corrosion resistance.

3.1. Modification of titanium and titanium alloys by anodic oxidation
Implantology has made significant progress since the osteointegration of titanium implants and its alloys has been demonstrated to achieve remarkable therapeutic results. For the subjects who have suffered various traumas, those with malformations or other diseases of the skeleton, prosthetic restorations with implants proved to be particularly effective, their superior qualities being both functional and psychological [3].

In the area of implants, surface modification has become essential. At present, more emphasis is placed on alternative solutions, such as coatings with functional layers, to solve problems from the implant-tissue interface. Changes to surface properties can be made in two ways:

a) Mechanical, physical and chemical methods change the degree of smoothing of the material, the structure and the chemical composition (polishing, thermal treatments, thermochemical treatments, electrodeposition etc.).

b) By coatings. The implant is totally or locally coated with different compositional materials (plasma deposition, sol gel, electrodeposition, etc.).

The roughness of the surface of a biomaterial increases with an increase in the oxide film on its surface. Rough surfaces can adsorb a greater amount of fibronectin compared to smooth surfaces. Also, rough surfaces can provide better bone fixation than smooth surfaces and promote macro-phase attraction. Improving surface roughness and decreasing ion release can maximize the corrosion resistance of materials for medical implants [23]. The structural and chemical properties of anodic oxide may vary widely in changing process parameters such as the potential difference between the cathode and the anode and the current density required to achieve this potential difference value, pH of the electrolyte and temperature [23-25]. In Figure 7 is schematically presented the anodic oxidation process used for the modification of titanium and titanium alloy surfaces. Prior to anodic oxidation, titanium alloy samples, e.g. titanium alloy Ti-6Al-4V, are cut into 25 x 25 x 2 mm (or other dimensions depending on the electrochemical cell), an electrical contact is provided with copper wire. The non active surfaces are insulated with resin, thus the sample remains with a well-defined active surface of 625 mm² and subsequently polished successively with impermeable abrasive paper with a grain size of 320-4000 μm with a diamond paste size of 3 and 1 μm and a suspension of SiO₂ (particle size of 0.04 μm) resulting in a mirror surface.

The natural oxide layer possesses a low level of electronic conductivity and its thickness has been estimated to be in the order of several nanometers. This natural oxide layer for the Ti-6Al-4V alloy is composed of titanium oxide in various oxidation states (TiO₂, Ti₃O₇ and TiO) and oxides of aluminum (Al₂O₃) and vanadium, which are thermodynamically stable at the physiologically pH, thus leading to excellent localized biocompatibility [26]. However, in their native form, TiO₂ films that cover titanium and its alloys have poor mechanical properties and can easily deteriorate under wear or slip conditions.
Therefore, oxide films must be intentionally formed with the help of different surface modification techniques.

![Figure 7](image)

Figure 7. Schematic of the anodic oxidation process of titanium and titanium alloys: (a) the electrochemical cell with the appropriate electrodes and the anodic oxidation electrolyte connected to an adjustable voltage current source; (b) schematic representation of a porous oxide film in cross-section; (c) schematic representation of a porous oxide film on the surface; (d) the SEM micrograph of a nanoporous titanium oxide film obtained on the Ti-6Al-4V alloy by anodic oxidation.

By the anodic oxidation process, the metal to be treated is covered with a porous film beyond which the oxygen ions diffuse and oxidize the substrate thereby increasing the thickness of the film. This treatment aims to form a film which is hard (resistant to abrasion), which is chemically stable (to withstand corrosion), which reduces the release of ions and increases the adhesion and fixation properties on the surfaces of biomaterials.

Measuring the surface roughness parameters of an implant is very important because its value influences the adhesion, adsorption and differentiation of the cells. The most common roughness parameter used for implanted materials is the mean roughness $R_a$, which represents the mean arithmetic of the deviations of a rough 2D profile relative to the median line of the profile over the entire measured length [26], or $S_a$ corresponding to a surface 3D.

In the literature, there are numerous reports that have demonstrated that the surface roughness of a titanium implant affects the rate of bone integration and biomechanical fixation [3, 26]. These reports have shown that titanium implants with rough surfaces have bone attachment larger than titanium implants with smooth surfaces.

Therefore, starting from a mirror surface with a roughness value corresponding to the 3D profile of 23.06 nm, by anodic oxidation at 100 V, higher values of the roughness profile corresponding to the 3D profile, e.g. equal to 123.35 nm was obtained [3, 26, 27].

Using Fusayama Meyer's artificial saliva solution as a biological medium, corrosion resistance tests of the untreated Ti-6Al-4V alloy and the nanoporous titanium oxide film obtained by the electrochemical treatment of this alloy were performed. Electrochemical methods for corrosion tests included open circuit potential (OCP), potentiodynamic polarization (PD) and electrochemical impedance spectroscopy (EIS).

The data from the electrochemical impedance records at the corrosion potential (open circuit potential), applying a sinusoidal signal of 10 mV, with the frequency sweep between $10^5$ and $10^{-2}$ Hz, corresponding to the two types of Ti-6Al-4V alloy surfaces have been processed in the form of diagrams in Nyquist representations (the imaginary component of impedance versus on the real
component). These Nyquist representations are used to deduce the polarization resistance that is equivalent to corrosion resistance, from the diameters of the semicircles obtained by simulation [3, 26-28]. By fitting and simulating the results, the polarization resistance can be determined.

Since most implant materials are subjected not only to an aggressive environment but are in motion, tribocorrosion tests (corrosion and wear) are more appropriate in their characterization. Thus, the influence of the nanoporous oxide film formed on the Ti-6Al-4V alloy is well emphasized on all the steps of measuring the electrochemical impedance spectroscopy diagrams, respectively before applying a force and applying the friction, during friction as well as after friction stopping, so as can be seen in Figure 8 (a, b).

![Figure 8](image)

**Figure 8.** Electrochemical impedance spectroscopy measured in saliva solution before friction (1) and during friction (2) for: (A) untreated Ti-6Al-4V alloy and (B) nanoporous TiO₂ layer formed anodically on Ti-6Al-4V alloy; (2) Ti-6Al-4V alloy. Layer a is drawn on entire EIS spectra, layer (b) represent the zoom of high frequency EIS spectra.

Figure 8 shows the beneficial effect of the nanoporous TiO₂ film on the alloy on the polarization resistance, especially during friction, which indicates a much better resistance of this oxide film during the friction or movement in an environment corrosive of the human body. For other titanium alloys, the electrochemical method of controlled oxide film formation can lead to improved corrosion resistance in specific biological use environments [3, 29-31]. As can be seen from Figures 8 (A, B), the polarization resistance of the untreated surface of the Ti-6Al-4V alloy decreases dramatically during the friction test (bidirectional fretting) compared with that obtained before friction. For the nanoporous titanium oxide layer, the polarization resistance value increases during friction compared to the measured value before friction, proving a better stability under tribocorrosion conditions.

Tribi-electrochemical characterization in simulated physiological fluid (Fusayama Meyer's saliva) showed that in their native form, TiO₂ films have poor tribological properties and are easily fractured under tribocorrosion conditions. The tribocorrosion performances of nanoporous TiO₂ films obtained by anodizing are better than untreated alloy surfaces under similar experimental conditions.

Under friction conditions the polarization resistance \( R_p \) of the untreated alloy dropped to 460 \( \Omega \cdot \text{cm}^2 \) from the saliva immersion value without application of the friction force when \( R_p \) had the value of 1180 \( \Omega \cdot \text{cm}^2 \). This is due to the removal of the oxide film in the friction area. For the surface of nanoporous titanium oxide film, the polarization resistance measured during friction was greater having the value of 2200 \( \Omega \cdot \text{cm}^2 \) compared to the value obtained by saliva immersion prior to application of the friction force and which was of \( R_p = 1200 \Omega \cdot \text{cm}^2 \). Higher polarization resistance of nanoporous TiO₂ layer formed by anodization under friction and corrosion conditions in physiological solution is due to the superior titanium oxide insulation properties as well as the variation in roughness, thickness and morphological characteristics of its surface.
4. Conclusions
Electrochemical techniques are powerful tools for surface modifications and nanostructuration of materials as well as for their characterization in specific environments.

Electrodeposition and the combination of electrodeposition with other electrochemical processes (controlled oxide growth by anodization) can lead to the entire class of hybrid, composite coatings and nanostructured layers (films) on different support materials and structures necessary for a future based on nanotechnology and nanomaterials.

By electrochemical modifications the results show improved surface properties for corrosion and tribocorrosion resistance in specific environments for industrial as well as for biomedical applications.

Functionalizing the surface of materials and biomaterials is the way to reduces or by-pass degradation by corrosion and tribocorrosion and increases the life time.

5. References
[1] Plieth W 2011 J. Solid State Electrochem. 15 1417
[2] Galus Z 2011 J. Solid State Electrochem. 15 1777
[3] Benea L 2017 Corrosion and Corrosion protection – from theory to practice, Editura Academica Galati p 1
[4] Gurrappa I, Binder L 2008 Sci. Technol. Adv. Mater. 9 1
[5] Danaila E, Benea L, Caron N, Raquet O 2016 Met. Mater. Int. 22 924
[6] Benea L, Celis J P 2016 Materials 9 269
[7] Pavlov A I, Benea L, Celis J-P, Vasquez L 2013 Dig. J. Nanomater. Biostruct. 8 1043
[8] Benea L, Danaila E, Celis-J-P 2014 Mater. Sci. Eng. A 61 106
[9] Benea L, Bonora P L, Borello A, Martelli S, Wenger F, Ponthiaux P, Galland J 2001 J. Electrochem. Soc. 148 C461
[10] Guglielmi N 1972 J. Electrochem. Soc. 119 1009
[11] Benea L 2015 Solid State Phenom. 227 243
[12] Benea L, Danaila E 2016 J. Electrochem. Soc. 163 D655
[13] Benea L, Basa S B, Danaila E, Caron E, Raquet O, Ponthiaux P, Celis J-P 2015 Mater. Design. 65 550
[14] Benea L 2009 J. Appl. Electrochem. 39 1671
[15] Danaila E, Benea L, Bounegru I 2015 Solid State Phenom. 227 507
[16] Benea L 2013 Metall. Mater. Trans. A 44 1114
[17] Benea L, Ciubotariu A, Sand W 2013 Int. J. Mater. Res. 104 489
[18] Benea L, Ponthiaux P, Wenger F 2011 Surf. Coat. Technol. 205 5379
[19] Ciubotariu A, Benea L, Mitoseriu O, Ponthiaux P, Wenger F 2009 J. Optoelectron. Adv. M. 11 892
[20] Baghery P, Farzam M, Mousavi A B, Hosseini M 2010 Surf. Coat. Technol. 204 3804
[21] Ciubotariu A C, Benea L, Lakatos-Varsanyi M, Dragan V 2008 Electrochim. Acta 53 4557
[22] Ciubotariu A, Benea L, Sand W 2011 An. Univ. "Dunarea Jos" Galati, Fasc. IX 1 51
[23] Hossain M M, Gao W 2008 Trends Biomater. Artif. Organs 22 144
[24] Liu X, Chu P K, Ding C 2004 Mater. Sci. Eng. R Rep. 47 49
[25] Diamanti M V, Pedefeferri M P 2007 Corros. Sci. 49 939
[26] Benea L, Danaila E, Ponthiaux P 2015 Corros. Sci. 91 262
[27] Benea L, Mardare-Danaila E, Celis J P 2014 Tribol. Int. 78 168
[28] Benea L, Mardare E, Mardare M, Celis J P 2014 Corros. Sci. 80 331
[29] Mardare E, Benea L, Celis J P 2012 Dig. J. Nanomater. Biostruct. 3 933
[30] Benea L, Danaila E, Ponthiaux P 2017 IOP Conf. Ser.: Mater. Sci. Eng. 174 012044
[31] Benea L, Danaila E, Dumitrascu V M, Ponthiaux P 2015 E-Health and Bioengineering Conference (EHB) 2015 1