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PULSED ELECTROCHEMICAL DEPOSITION OF Ag DOPED HYDROXYAPATITE BIOACTIVE COATINGS ON Ti6Al4V FOR MEDICAL PURPOSES

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The aim of this study is to develop bioactive-antibacterial coatings on Ti6Al4V using pulsed electrochemical technique. The deposition was carried out in a three electrode set-up within an electrolyte prepared by dissolving $Ca(NO_3)_2{\cdot}4H_2O$, $NH_4H_2PO_4$ *and* $Ag(NO_3)$ *in ultra-pure water. The paper aims to evaluate the effect of Ag addition on morphology, elemental and phase composition of hydroxyapatite coatings.*

The hydroxyapatite morphology has changed after silver doping, revealing a surface with agglomeration of spherical particles. Phase composition has confirmed the hydroxyapatite formation and, by adding Ag, the peaks have slightly shifted towards left, indicating that Ag is substituting the Ca present in the hydroxyapatite lattice.

Keywords: pulsed electrochemical deposition, coatings, silver doped hydroxyapatite, bioactive

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1. Introduction

The increase of geriatric population, high prevalence of dental, orthopedic, cardiovascular and neurological disorders are factors which have led to a higher awareness regarding the advantages of biomaterials and production of implantable devices, all caused by the least decades advancements in the medical field.

Titanium and its alloys have been broadly employed as implantation materials due to their favourable properties such as lower modulus, good tensile strength, excellent biocompatibility and enhanced corrosion resistance compared to 316L SS and Co-Cr alloys. However, they have a bio-inert character and cannot bond with bone directly and actively stimulate the initialization of bone formation on the surface at an early stage of implantation [1], leading to implant dislocation and premature loosening [2]. Beside optimization of mechanical and chemical compatibilities, another important aspect of implant materials is the establishment of a suitable surface state in terms of a tailored surface topography and chemistry that stimulates bone cell growth and activates an optimum bone osseointegration [3]. To achieve a successful fixation, it is important to create a stable implant-bone interface [4]. To overcome these problems, the main inorganic component in natural bone – calcium phosphate (CaP) - is widely used as bioactive coating material. Thus, Ti based implants must be able to demonstrate excellent osseointegration at the bone-implant interface, since this is a prerequisite condition for successful implantation.

The nowadays trends are directed towards activation of the bio-inert surface through coating the metallic biomaterials used for implantable devices in order to prevent bacterial adhesion, to improve core functionality and to provide bioactivity and biodegradation along with biocompatibility of the device.

Among the bioactive ceramic materials, synthetic hydroxyapatite [HAp, chemical formula $Ca_{10}(PO_4)_6(OH)_2$] has raised great attention due to its resemblance to the natural HAp found in bones [5]. Over the years, HAp has been used as scaffolds for bone substitute in small defects [6], release of active substances in drug delivery applications [7–9] and recently as coating material due to its behavior in the human body [6,7].

As coating, HAp transforms the bioinert surface [10] into an active one, offering so improved features, such as biological fixation, chemical compatibility and high osseointegration for implantable devices [11,12]. Studies have shown that HAp based coated metallic devices improve the healing duration and the body acceptance level.

Because of its structure, HAp properties can be easily adjusted by addition of elements with complementary properties such as antibacterial ones [12]. The use of antibacterial materials/elements which are delivered locally should be considered mandatory and a prerequisite, giving the actual status such as hospital bacterial infections which are very hard to fight against.

Among the elements with antibacterial properties, silver (Ag) [13–16], copper (Cu) [17] and zinc (Zn) can be mentioned [18]. Silver has the highest efficiency rate in terms of antibacterial properties and is also biocompatible with the human body [19]. Studies have showed that the HAp is an ideal biomaterial to embed silver because the Ca^{2+} ions can be easily substituted by Ag^{+} ions, creating a material with high biocompatibility and antibacterial properties [13,20]. Any change in the crystal structure of a constituent material can affect the final properties of ceramics. Materials containing silver present antibacterial properties, as silver can prevent biofilm growth and bacterial colonization on various surfaces [21,22].

Coatings with specific features can be deposited on metallic substrate through several techniques such as plasma spray [16], vapor deposition [23], sol-gel method [24], magnetron sputtering [25], pulsed laser ablation [26], dynamic mixing [27], dip coating [28], electrophoretic and electrochemical deposition [29], biomimetic coating [30], ion-beam-assisted deposition [31], hot isostatic pressing [32], polymeric route [33]. Among the aforementioned techniques, electrochemical deposition (ED) is a versatile technique, easy to use, cost effective, which allows a good control of the development of materials with properties [34]. Also it can be used to cover complex shape geometry, offering the possibility to obtain complex coatings in a single step deposition.

However, the more advanced electrochemical methods for depositing bioactive coatings with control of phase and composition generally involve reaction conditions comprising elevated temperatures (> 37°C) and special techniques such as pulsed electrochemical deposition (PED) [35].

The aim of the present study is to dope hydroxyapatite with Ag in order to develop bioactive and antibacterial coatings on titanium alloy, Ti6Al4V, using a pulsed electrochemical technique. The effect of Ag addition on morphology, elemental and phase composition of hydroxyapatite coatings is investigated. The developed surfaces are intended to be used for medical purposes as orthopedic or dental implants.

2. Materials and Methods

2.1. Sample preparation

As substrate for the pulsed electrochemical deposition (PED), a Ti6Al4V – ELI bar (Bibus Metals AG, Germany) of 20 mm diameter was used. Samples were obtained by cutting the bar as discs with a height of approximately 3 mm.

Prior to PED, the Ti6Al4V discs were metallographically prepared on SiC abrasive paper (300-1200 grit), after which the samples have been cleaned in distilled water, sonicated in acetone to remove the impurities, and subsequently dried in air.

The pulsed electrochemical deposition process was carried out in a standard three electrode electrochemical cell composed of a working electrode - Ti6Al4V substrate, a Pt foil as counter electrode and a saturated KCl electrode (SCE) as reference electrode. The electrodes have been immersed in the electrolyte solution which was prepared by dissolving $Ca(NO_3)_2·4H_2O$, $NH_4H_2PO_4$ and $Ag(NO_3)$ in ultra-pure water (ASTM I) at 75 °C, in different concentrations indicated in Table 1. The reagents concentration in the electrolytic solution was chosen in order to maintain the atomic ratios (Ca+Ag)/P fixed at 1.67.

The deposition was performed with a potentiostat/galvanostat (Parstat MC, PMC 2000, Princeton Applied Research, USA) by pulsing the potential for 2 h: deposition time of 100 s, with an applied potential of -2 V vs E_{ref}, followed by a break-time of 100 s (E = 0 V vs E_{ref}).

Table 1

Samples codification and chemical composition of the electrolyte

Sample codification	$Ca(NO_3)_2·4H_2O$ mM	$NH_4H_2PO_4$ mM	$AgNO_3$ mM	pH
HAp/Ti6Al4V	5.00	3	-	4 (adjusted with 1M HNO_3)
HAp-Ag/Ti6Al4V	4.50	3	0.5	

A schematic illustration of the electrochemical deposition cycles and the samples aspect are presented in Fig. 1.

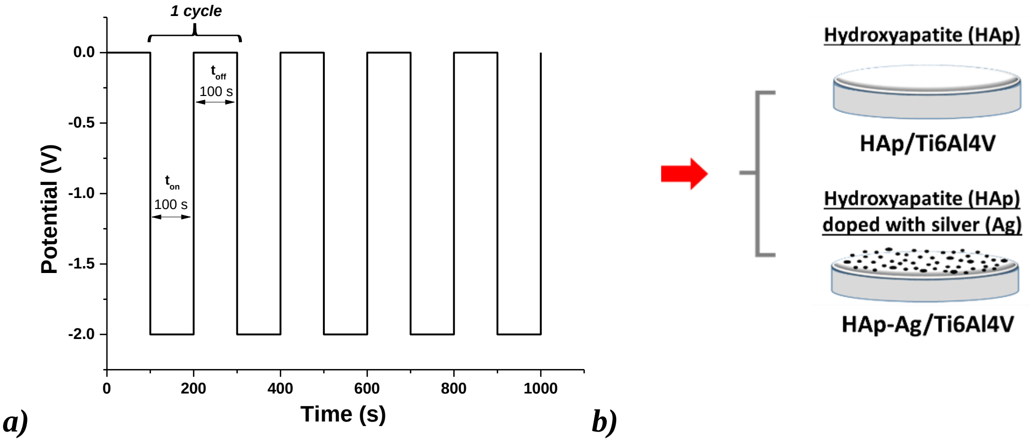


Fig. 1. Schematic illustration of the a) applied pulsed electrochemical deposition cycles and b) samples aspect and codification

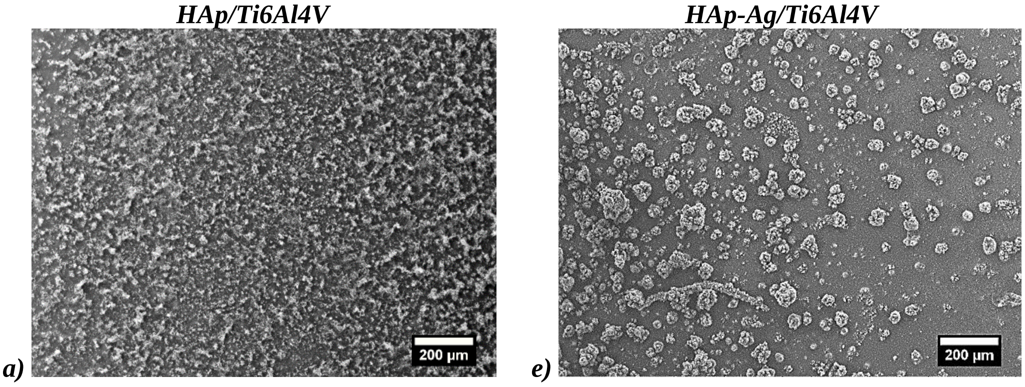
Morphology and elemental composition of the obtained samples were investigated using a scanning electron microscope (SEM, TableTop 3030Plus, Hitachi, Japan) equipped with an energy dispersive X-Ray (EDX) system (Quantax70, Bruker, USA).

The phase composition of the coatings was studied by a X-Ray diffractometer (SmartLab XRD, Rigaku, Japan) with CuKα radiation ($\lambda = 1.5405$ Å). Grazing incidence measurements were performed in the range of 20-80° with a 0.01° step, at an incidence angle of 0.2°. For this purpose, a medium resolution parallel beam optical system was used.

3. Results and discussions

3.1. Morphology and elemental composition

Fig. 2 indicates the SEM/EDS analysis on the HAp/Ti6Al4V (Fig. 2 a-d) and HAp-Ag/Ti6Al4V (Fig. 2, e-h) coatings obtained by pulsed electrochemical deposition method. As it can be seen in Fig. 2 a-c, the undoped HAp coating presents a morphology consisting of needle-like crystals which create a porous matrix that covers uniformly the Ti6Al4V substrate. At higher magnification some areas with a preferential distribution, as agglomerations can be observed. Silver addition has led to changes in the coatings morphology (Fig. 2, e-g). The surface is still uniformly covered, and areas of agglomerated white particles can be observed. At a higher magnification (Fig. 2, g), the needle-like morphology characteristic for HAp is embedded with agglomeration of white spherical particles, of Ag.



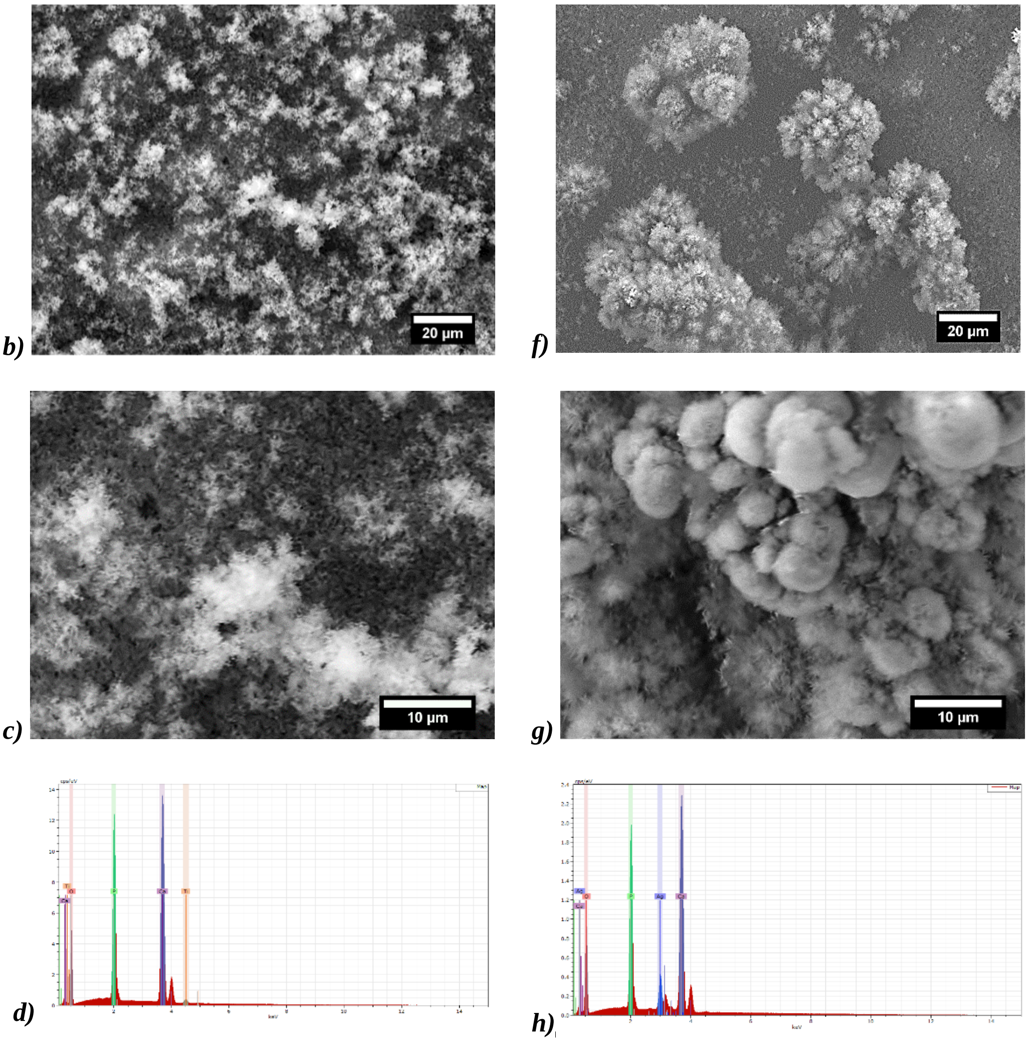


Fig. 2. Morphology and elemental composition for HAp/Ti6Al4V (a-d) and HAp-Ag/Ti6Al4V (e-g) coatings obtained by pulsed electrochemical deposition

The elemental composition obtained by the energy dispersive spectroscopy (EDS) of the developed coatings is presented in Table 2, while in Fig. 3 the elements distribution in the coatings can be observed.

Table 2

Elemental composition of the obtained coatings

Sample	**HAp/Ti6Al4V**				**HAp-Ag/Ti6Al4V**			
Elemental composition	**Area 1**		**Area 2**		**Area 1**		**Area 2**	
	% wt	**% at**	**% wt**	**% at**	**% wt**	**% at**	**% wt**	**% at**
Ca	38.04	21.80	38.03	21.69	34.55	21.19	33.31	19.40
P	15.77	11.70	15.29	11.29	14.86	11.79	14.53	10.95
O	42.14	60.51	42.59	60.86	39.53	60.72	42.97	62.70
Ti	1.23	0.59	1.13	0.54	-	-	-	-

C	2.82	5.39	2.95	5.62	2.87	4.25	2.87	5.58
Ag	-	-	-	-	8.98	2.05	6.32	1.37
Ca/P ratio	***1.86***		***1.92***		***1.97***		***1.90***	

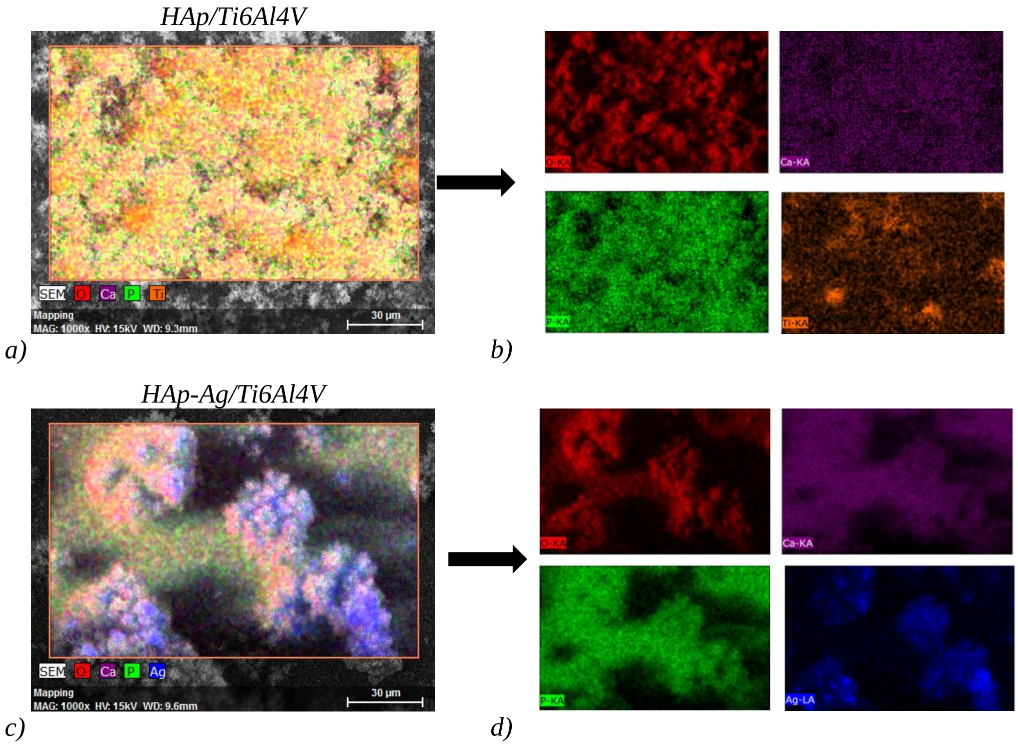


Fig. 3. SEM images of elements distribution for the obtained coatings HAp/Ti6Al4V (a, b) and HAp-Ag/Ti6Al4V (c, d)

The elemental composition has revealed the presence of the characteristic elements (Ca, P, O, Ti) of hydroxyapatite and Ti6Al4V substrate. As it can be seen in Table 2, Ti have registered small values fact which can be attributed to a significant thickness of the obtained coatings.

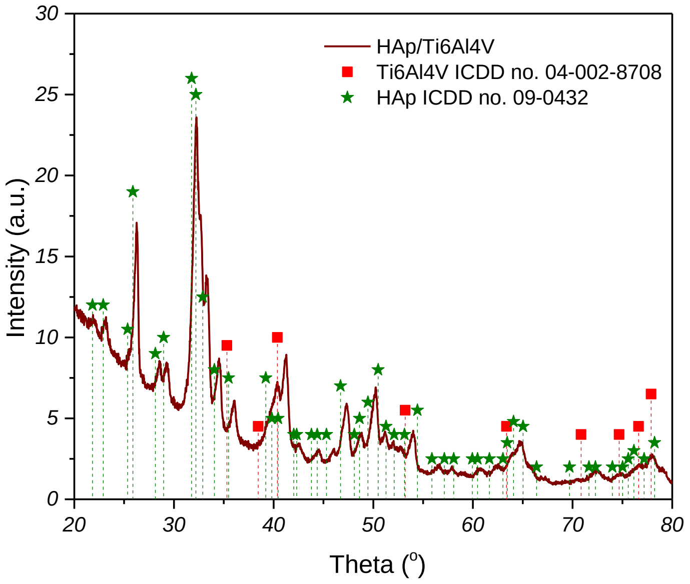
3.2. Phase composition

X-Ray diffraction (XRD) analysis was employed to determine the changes in the crystalline structure and phase composition. Fig. 4 presents all the XRD patterns indexed with respect to the specific plan, which are matched to JCPDS card no. 09-0432 of HAp [36].

As it can be seen, both developed coatings exhibit the HAp characteristic peaks, indicating that the major phase present is HAp. Among HAp peaks, reflections of the Ti6Al4V substrate were also detected. The most pronounced HAp reflection is found at ~ 26°, which indicates a (002) preferred orientation of the deposited HAp crystals just as reported in other studies [37–40].

In the case of Ag doped HAp, the corresponding diffraction peaks of Ag according to ICDD no. 01-077-6577, have been noted. It can be observed that the appearance of Ag diffraction peaks did not lead to major alterations in the crystalline structure of HAp. However, shifts towards smaller angles after Ag addition were noted, and can be explained by the substitution of Ca ions with Ag [41].

It can be seen that the coatings deposited by the electrochemical method have a crystalline structure, and the Ag doped HAp was successfully achieved without inducing major alterations in the structure of HAp. However, special attention must be given to parameters such as pH, temperature, potential, electrolyte composition, all of these can influence and/or affect the properties of coatings developed by the electrochemical deposition techniques.



a)

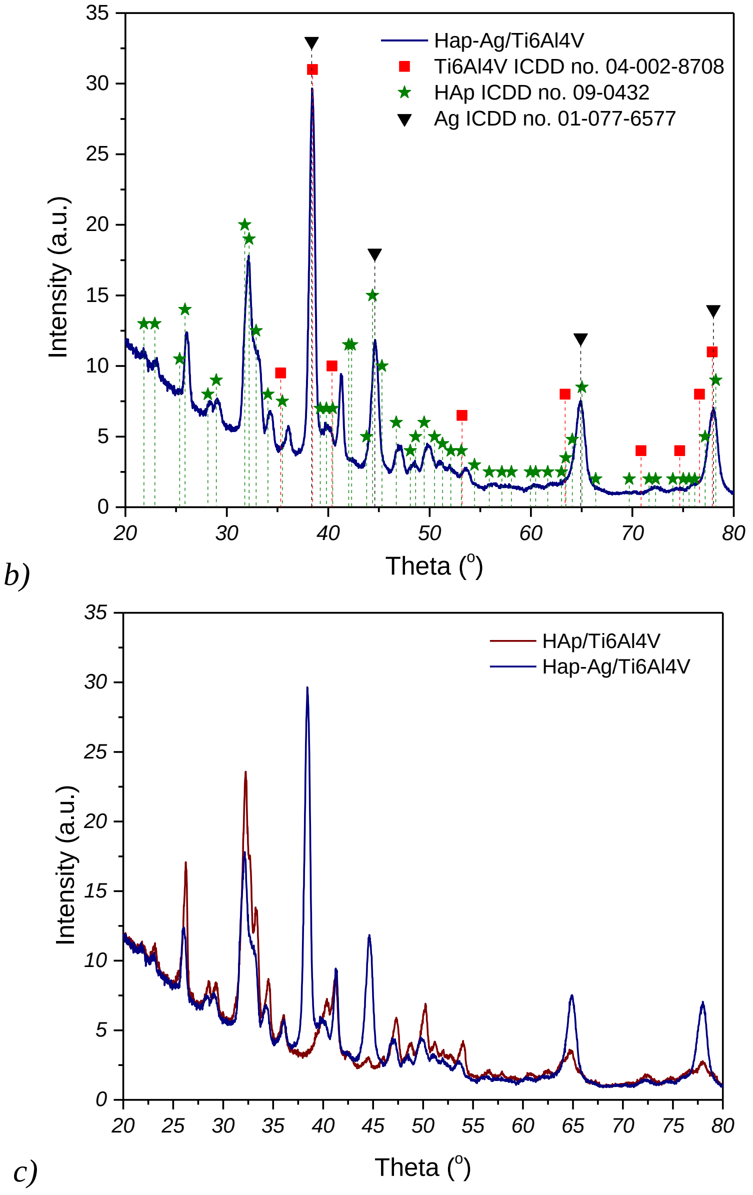


Fig. 4. XRD pattern of the obtained coatings a) HAp/Ti6Al4V and b) HAp-Ag/Ti6Al4V and c) their overlay

4. Conclusions

Coating the Ti6Al4V alloy with Ag doped HAp has been successfully achieved by the pulsed electrochemical deposition (PED) and confirmed by SEM-EDS and XRD analysis, revealing that PED is an effective method for preparing

Ag doped HAp coatings without affecting the chemical and structural characteristics of hydroxyapatite.

HAp morphology has changed after silver doping, revealing a surface with agglomeration of spherical Ag particles. Phase composition has confirmed the hydroxyapatite formation and, by adding Ag, the peaks have slightly shifted towards left, indicating that Ag is substituting the Ca present in the HAp lattice.

The pulsed electrochemical deposition is a novel technique with advantages such as co-deposition of elements from the same electrolyte in order to develop enhanced and complex coatings with prefigured properties, suitable for medical purposes.

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