Mg-Containing Hydroxyapatite Coatings Produced by Plasma Electrolytic Oxidation of Titanium

César Augusto Antônio*, Elidiane Cipriano Rangel*, Steven Frederick Durrant*, Adriana de Oliveira Delgado-Silva*, Manfredo H. Tabacnik*, Nilson Cristina da Cruz*

*Laboratory of Technological Plasmas, Sorocaba Institute of Science and Technology, Paulista State University - UNESP, Sorocaba, SP, Brazil
**Sorocaba College of Technology, Sorocaba, SP, Brazil.
†Federal University of São Carlos, Sorocaba, SP, Brazil.
&Institute of Physics, University of São Paulo - USP, São Paulo, SP, Brazil.

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1. Introduction

Owing to high biocompatibility, good corrosion and wear resistance, good mechanical properties, low density and chemical inertness, titanium and its alloys are widely used in the production of dental and orthopedic implants.

Although titanium is biocompatible, its intrinsic bioinertness does not stimulate spontaneous bone-implant integration. To expand the successful applications as dental and orthopedic implants several methods are used to modify the titanium surface with the objective of improving its bioactivity. In this context, great improvement in biological properties, consequently reducing the rejection of implants, has been achieved with calcium phosphate coatings.

Hydroxyapatite \((\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)\) (HA) is a calcium phosphate that constitutes about 70% in weight of human bones. HA is a natural mineral that has excellent biological properties. When it is synthetically produced on the surface of titanium, it can promote bioactivity and improve the connection with bone tissue. Nowadays it is possible to produce synthetic HA with similar characteristics to those of human bone, including bioactivity and biocompatibility, that can be used in biomedical applications.

Over the last decade, various methods for producing HA coatings on titanium and its alloys have been developed. These include plasma spray, sputtering, electrophoretic deposition, immersion in simulated body fluid (SBF), biomimetic techniques, sol-gel procedures, and laser ablation. There are, however, some problems related to the hydroxyapatite coatings, such as poor control of the chemical composition and structure and poor coating adhesion to the substrate. Therefore, there is still a demand for methods to produce HA with greater bioactivity and similarity to human bone combined with good mechanical properties.

The absorption of nutrients and the growth of bone are improved by the presence of ions such as \(\text{Zn}^{2+}, \text{Mg}^{2+}, \text{Na}^+, \text{CO}_3^{2-}\) and \(\text{F}\) in non-stoichiometric compounds of low crystallinity. Owing to that, improvements in the biological properties and greater similarity to human bone can be achieved by the incorporation of ionic elements into synthetic HA. Magnesium is the fourth most abundant ion present in the human body, where it helps to inhibit crystallization, to reduce crystal size, to decrease the proliferation and activities of osteoblast-like cells. Therefore, magnesium deficiency can affect bone metabolism and growth, reducing osteoplastic activity and resulting in fragile bones.

Plasma Electrolytic Oxidation (PEO) combines the effects of conventional electrolysis with micro-arc discharges that appear on the sample surface. When the voltage applied...
between two electrodes immersed in electrolytic solutions exceeds several hundred volts, the dielectric barrier of the oxide coating produced on the metal surface at the anode is broken down mostly by impact ionizations. Consequently, many high energy micro-arcs able to melt the oxide coating arise on the surface of the sample. In this condition, chemical elements present in the electrolytic solution can be incorporated into the coating. Also, the high thermal energy from the micro-arcs can produce ceramic coatings with complex structures. This method has been successfully used to produce ceramic coatings on light weight metals such as Ti, Al, Nb, Ta and Mg.

Recent studies have shown that HA can be produced by PEO of titanium and its alloys. Usually, however, long process times (>20 min) or two-step procedures are required and the HA produced is of low crystallinity. In titanium oxidation using PEO other structures such as anatase, rutile, and phosphates are also produced. Results of X-ray diffraction (XRD) studies have shown that the proportion of HA is generally low, i.e., anatase and rutile phases are predominant. To our best knowledge there were no studies of the production of HA by PEO with Mg incorporation into the coating for improved bioactivity of the synthetic HA. Thus, this study aims to produce a coating on Grade 4 titanium with a high concentration of Mg-doped HA with very short treatment time.

2. Experimental description

The HA coatings were deposited on grade 4 titanium disks 8 mm in diameter and 2 mm thick. After machining and polishing, the substrates were ultrasonically cleaned and stored. Figure 1 shows schematically the treatment system. The treatments have been performed using a two liter stainless steel tank, enclosed in a cooling system that keeps the temperature of the solution constant. The substrate was connected to the positive terminal of a pulsed bipolar voltage supply and the tank itself served as the cathode. The electrolytic solution used for the treatment was prepared by diluting 0.2 M of calcium acetate and 0.02 M of sodium glycerophosphate in deionized water. The variable process parameter was the amount \( C_M \) of magnesium acetate (MgA) added in concentrations of 0.0, 0.02, 0.04, 0.06 and 0.08 M to the electrolytic solution. The samples have been biased with positive pulses of 480 V with frequency and duty cycle of 100 Hz and 60 %, respectively. The substrates were treated for 120 s in the potentiostatic mode. After PEO treatment, the samples were cleaned with distilled water and dried.

A previous study by the authors concluded that a treatment time of 120 s was sufficient to produce a coating with a high HA content. Therefore, based on that study, all the other process parameters were maintained; only a different amount of MgA in the electrolytic solution was used.

![Figure 1. Schematic representation of the treatment cell.](image)

After metallographic preparation of cross-sectioned samples, coating thickness was measured using scanning electron microscopy (SEM). Roughness was investigated using profilometry and surface morphology was examined by SEM.

The chemical composition of the samples was analyzed using Rutherford backscattering spectrometry (RBS). A He beam, from a Pelletron-tandem accelerator produced by National Electrostatic Corporation (NEC) model 5SDH, was directed onto the samples in a vacuum chamber at 7° incidence and 170° scattering angles. The energy of the ions was 3.29 MeV and the beam charge was 10 µC. Chemical composition and elemental depth profiles were determined by computer simulations using RUMP and SIMNRA softwares.

Analysis of the coating crystalline structure was based on X-ray diffraction data obtained using a Panalytical X-Pert Powder diffractometer in theta-2 theta geometry, which employed Cu-K\(_\alpha\) radiation (\( \lambda = 1.54 \) Å). Data acquisition was performed at diffraction angles of between 20 and 60°, using a step-size of 0.02° at 5 s per step. The Rietveld Refinement technique was employed to determine the proportion of each phase as well as hydroxyapatite cell parameters. The refinement was performed using X’Pert HighScorePlus software with the structural model (ISCD database) listed in Table 1. The quantity of each phase was calculated, but the cell parameters were determined only for the HA phase, the main object of study in this research. The electric current through the electrolytic cell was measured with a digital amperimeter every 2 s during the treatment. Three measurements were performed for each treatment condition.

3. Results and Discussion

3.1. Current density characteristics.

Figure 2 (a) shows the current density during the treatment and the average current density after 7 s of treatment, when the voltage reached 480 V, is presented in Figure 2 (b).
Table 1. Structural model (ICSD database) of the possible phases present in the PEO coating.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>ICSD code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>TiO₂</td>
<td>200392</td>
</tr>
<tr>
<td>Rutile</td>
<td>TiO₂</td>
<td>36413</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>43614</td>
</tr>
<tr>
<td>Calcium Phosphate</td>
<td>Ca₅P₈</td>
<td>74854</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>Ca₅(PO₄)₃(HO)₂</td>
<td>203027</td>
</tr>
<tr>
<td>Magnesium Phosphide</td>
<td>Mg₃P₂</td>
<td>24489</td>
</tr>
</tbody>
</table>

In a general way, the addition of MgA to the electrolytic solutions increased the current density due to the increment of ion densities in solution. The maximum value was observed for treatments with C_M = 0.06 M. The current density in these treatment conditions was 0.99 (± 0.012) A cm⁻², which is 24% higher than the current density measured during treatments with C_M = 0.0 M.

Inspection of Figure 2 (b) reveals some variations in the current density, which were caused by instabilities generated by micro-arc discharges produced when the ion density was increased. The amount of MgA increased linearly but the micro-arcs occur in thermodynamic non-equilibrium and the electrolysis does not occur according to the usual electrochemical laws. Consequently, detailed explanations of the observed variations in the current densities are not available.

3.2. Thickness and roughness

The coating thicknesses were measured from MEV images of sample cross-sections prepared by metallography. Averages and standard deviations determined from measurements of the thicknesses of three samples are given. Figures 3 (left and right) show the thicknesses as a functions of C_M and typical cross-sections of samples treated by PEO. The addition of magnesium acetate to the electrolytic solutions did not change significantly the coating thickness. Samples treated in solutions with C_M up to 0.06 M had thicknesses of around 10 µm but samples treated at a C_M of 0.08 M had thicknesses of around 8.0 µm. It was also was observed that dispersion of the thickness measurements decreases when the C_M was 0.06 M. Therefore, the results show that this condition (C_M = 0.06 M) produced a more uniform coating because the process combined the best parameters of current density, voltage, composition of the electrolytic solution and treatment time.

As it can be noticed in Figure 4, which shows the Ra roughness as a function of C_M, the roughness decreases with the increasing of C_M up to 0.06 M and then grows to reach 6.5 ± 1.17 µm when C_M = 0.08 M. This result reflects the modification of the intensities of the micro-arc as the proportion of magnesium acetate is modified.

3.3. Coating Morphology

Figure 5 presents SEM micrographs of surfaces produced in solutions with various C_M. It can be pointed out the presence of clusters of granular structures on the surface of all the samples produced with C_M < 0.08 M. As previously reported, such structures are mostly composed of hydroxyapatite. Therefore, the decrease of the density of such clusters in Figure 5 suggests that the higher C_M the lower the proportion of HA.
3.4. Chemical compositions

As previously noted, the samples present porous irregular surfaces. As can be observed in Figure 6, which shows typical simulated and experimental RBS spectra, such rough morphology makes rather difficult the theoretical adjustment of the measured RBS spectra. Therefore, to ensure a good agreement between theoretical and experimental values, the simulations were restricted to the outermost 100 nm thick layer of all the samples. It is important to mention that the complexities of the simulations imposed by the irregular surface introduced an estimated error of about 5%.

Figure 6. RBS spectrum (measured and simulated) of the sample treated by PEO with $C_{M} = 0.06$ M.

The average proportions of Ca, P, Mg, and Ti in a 100 nm thick superficial layer can be observed in Figure 7. The proportions of carbon (nearly 32%) and oxygen (approximately 47%) have been omitted since they do not provide any useful information to the discussions that follow. According to the results, the addition of MgA to the electrolytes caused the Ca concentration to decrease from 12.2 to 8.9 at%, independently of $C_{M}$. On the other hand, the concentration of phosphorous remained constant at 8.4 at% and decreased when MgA was added in proportions larger than 0.04 M reaching 1.2 at% when $C_{M} = 0.08$ M. This strong decrease can be attributed to the low boiling point of P (553.6 K), which can easily evaporate from sample surface. It has been observed the intensification of the light emitted by the micro-arcs as magnesium acetate is added to the solution. This observation associated to the higher current observed in Figure 2 indicates the enhancement of the energy transferred to the sample when MgA is added to the solution, which may cause the heating of the coating. The heating near the surface of the sample makes impedes the deposition of low melting point elements and also increases the diffusion of species to inner coating regions. Both mechanisms contribute to the observed depletion of phosphorous. In addition, the Mg concentration in the coating increased with the increasing of the proportion of magnesium acetate added to the solution, reaching about 3.6 at% on samples treated with $C_{M} = 0.08$ M. Less than 1.0% of titanium has been detected in all the samples indicating that the electrophoretic deposition rather than the re-deposition of the quenched metal after melting by the micro-arc is the predominant mechanism of coating growth. Accordingly to the RBS analyses, the surfaces produced in this work are very promising for implants since they are mostly composed by Ca, P, and Mg.

X-ray energy dispersive spectroscopy (EDS) has been employed to evaluate the coating composition in bulk regions deeper that those probed by RBS. As can be seen in Figure 8 the concentrations are significantly different from those determine near the surface. In disagreement with what is observed near the surface, the average concentrations of Ca, P and Ti in the bulk are nearly independent of the amount of magnesium acetate added up to $C_{M} = 0.04$ M. Larger $C_{M}$ caused the proportions of Ca and P to decrease. When $C_{M} = 0.08$ M the proportion of Ca is 35% smaller than that measured without the addition of Mg acetate while the proportion of titanium increases fourfold with the same variation of $C_{M}$.

It is interesting to mention that the proportions of calcium and phosphorous in all the conditions are roughly the same as was detected by RBS on the superficial layer of the samples produced without the addition of magnesium. This observation corroborates the supposition of the enhancement of the diffusion of species to deeper regions as a consequence of the increase of the heating caused by larger currents when the amount of MgA in the solution is increased. Moreover, larger current densities can produce micro-arcs intense enough to reach the substrate beneath the coating resulting in the ejection of molten titanium towards the liquid. The quenching of the metal by the electrolyte explains the high amount of Ti in the bulk of coatings as thick as 8 µm.

3.4. X-ray Diffraction and Rietveld Refinement.

Figure 9 shows X-ray diffraction spectra of the coatings produced with various $C_{M}$. From this figure it is possible...
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Figure 8. Atomic proportions determined by EDS in the bulk of samples treated with different $C_M$.

Figure 9. XRD patterns of coatings produced by PEO with different $C_M$, where the letters stand for: H - Hydroxyapatite; P - Calcium Phosphate, R - Rutile, M - Magnesium phosphide, A - Anatase, and T - titanium.

Figure 10. Phases proportion calculated by Rietveld refinement of samples treated by PEO as a function of $C_M$. The letters stand for: H - Hydroxyapatite, R - Rutile, M - Magnesium phosphide, and A - Anatase.

Figure 11. Rietveld refinement of sample treated by PEO with different $C_M$. The letters stand for: H - Hydroxyapatite, R - Rutile, M - Magnesium phosphide, A - Anatase, C - Calcium phosphide, and T - titanium.

The phase composition of the samples can be better evaluated from the results of Rietveld refinement presented in Figure 10. The coating produced without the addition of MgA is composed by 83.5% HA, 15.9% rutile and 0.9% calcium phosphate. Samples treated with $C_M = 0.02$, $0.04$, and $0.06$ M are composed of around 50% hydroxyapatite. The reduction in the amount of HA can be attributed to the greater incorporation of Mg and the reduction of the proportion of phosphorous in the coatings, as shown in Figure 8. In addition, the same amount of P was bound as magnesium phosphide (Mg$_3$P$_2$).

The greatest amount of magnesium phosphide was observed in samples produced in electrolytic solutions with $C_M = 0.06$ M. Therefore, this condition produced an ideal coating for biological applications because the composition of crystalline phases combines significant amounts of hydroxyapatite, magnesium phosphide and TiO$_2$ (rutile). On the other hand, the samples produced with $C_M = 0.08$ M were predominately composed by titanium (4.5%) and titanium dioxide (65.3% rutile, 28.8% anatase). No HA was formed under that condition because of the deficiency of phosphorous.

Some authors have reported that Mg$^{2+}$ ions can be incorporated into the crystalline structure of hydroxyapatite, replacing Ca$^{2+}$ ions. The Mg$^{2+}$ ions have ionic radius of 0.069 nm that is smaller than radius of Ca$^{2+}$ ions (0.099 nm). Thus Mg$^{2+}$ can easily replace Ca$^{2+}$ in the crystalline structure. This effect can also reduce the lattice parameters $a$ and $c$ of the hexagonal crystalline structure of the HA. In the present study, it may be observed from Figure 11 that those lattice parameters did decrease when the samples were treated with $C_M = 0.02$ M and $0.04$ M in comparison with samples treated without addition of MgA to the electrolyte. This effect is attributed to the replacement of Ca$^{2+}$ by Mg$^{2+}$ ions in the hydroxyapatite crystalline structure. The sample treated with $C_M = 0.06$ M presents the lattice parameters closer to the lattice parameters of samples treated without addition of MgA.

The results of Rietveld refinement revealed that this coating contains 17.4% magnesium phosphide, the largest proportion of this phase found in this study. Therefore, most of the magnesium incorporated is present as magnesium phosphide, thus explaining why the hydroxyapatite crystalline structure is similar to the crystalline structure of the hydroxyapatite produced with $C_M = 0$.

4. Conclusion

In the present work the efficacy of PEO to produce Mg-doped HA was studied. The addition of magnesium acetate to the electrolytic solution of calcium acetate and sodium glycerophosphate allowed the production of coatings with up

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to 50% of Mg-containing HA. Results of Rietveld refinement have shown the decrease of the lattice parameters $a$ and $c$ of HA crystalline structures in coatings produced in solutions with $C_M = 0.02$ and 0.04 M. Such characteristics suggest the replacement of Ca by Mg ions in the HA structure, confirming the production of Mg-doped HA. The treatment with the electrolyte containing 0.06 M MgA was effective in producing HA with a crystalline structure similar to that of HA produced with $C_M = 0.0$ M. In that case, the coating produced contained around 17% of magnesium phosphide. In conclusion, this work demonstrated the versatility of PEO with various $C_M$.

5. Acknowledgment

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6. References


