Preparation of Laser-Modified Ti-15Mo Surfaces With Multiphase Calcium Phosphate Coatings

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Multiphasic bioceramic scaffolds have been enhanced for dental and orthopedic applications. In this perspective, the laser surface texturing of metallic surfaces combined to bioactive calcium phosphate coatings have shown to be promising and economically feasible for biomaterial clinical applications. Ti-15Mo alloy samples were irradiated by pulsed Yb: YAG laser beam. The formation of HA and other calcium phosphates phases by biomimetic method should occur in the presence of Ca$^{2+}$, PO$_4^{3-}$, Mg$^{2+}$, HCO$_3^-$, K$^+$ and Na$^+$. The modified surfaces were submitted to thermal treatment at 380 and 580°C. The results showed the processes of fusion and fast solidification from the laser beam irradiation, inducing the formation of stoichiometric α-Ti, TiO$_2$ and non-stoichiometric titanium oxides, Ti$_3$O and Ti$_6$O with different oxide percentages depending on applied fluency (fluency of 0.023, 0.033, 0.040 and 0.048 J/mm$^2$).

The morphological and physicochemical properties have indicated the formation of a multiphase bioceramic coatings. It was observed the formation of amorphous calcium phosphate (ACP), octacalcium phosphate (OCP), and magnesium phosphate (Mg$_3$(PO$_4$)$_2$) phases at 380°C, whereas β-TCP (tricalcium phosphate), OCP, and substituted β-TCP with Ca$_{2.589}$Mg$_{0.41}$(PO$_4$)$_2$ were obtained at 580°C. Therefore, the multiphasic bioceramic modified Ti-15Mo surface could enhance osteointegration for bone regeneration.

Keywords: Ti-15Mo alloy, biomimetic coatings, calcium phosphates, laser ablation.

1. Introduction

Calcium phosphates have been used in a variety of applications for the treatment of the bone system, since insulated material that surface coating of metallic implants$^{1-7}$. The clinical limitations of the use of hydroxyapatite (HA) phase, due to its slow biodegradation, has aroused the interest in the others calcium phosphates phases, including amorphous calcium phosphate (ACP), octacalcium phosphate (OCP), and magnesium phosphate (Mg$_3$(PO$_4$)$_2$)$^{8-12}$. In this context, magnesium has been considered the most important ion used in calcium substitution, promoting a change in the biological and chemical behavior of these materials$^{12-15}$.

The biomimetic coating method is based on the heterogeneous precipitation on titanium substrates and their alloys. The nucleation and growth of the calcium phosphate coating occurs after immersion in a balanced salt solution (Hank’s solution or SBF) at 37°C for several days$^{4,16}$. This process is similar to the process of bone biomineralization$^{4,17,18}$. The modified biomimetic method represented a major advance in the area of biomaterials. The growing interest in the use of other phases of calcium phosphates has resulted in more promising properties than the HA phase, new strategies have been described in bioceramic coating on metal surfaces$^{16,19}$.

In our previous work$^2$, Ti–Mo laser-activated surfaces were coated by sol-gel calcium phosphates, indicating a mixture of phases under different temperature control. As a continuation of our previous work, this study has evaluated six different simulated body fluid solutions, which were called modified SBF, in order to design a multiphase bioceramic coatings with controlled chemical deposition on metallic surface. The aim of this work was to evaluate the morphological and physicochemical properties of the surfaces of the Ti-15Mo alloy modified by Yb: YAG laser beam, as well as deposition of bioactive ceramics using the modified biomimetic method.

2. Materials and Methods

2.1 Laser-activated surface modification

Samples of Ti-15Mo alloy (4 mm length, 4 mm wide, 2mm thick) were submitted to Yb:YAG multipulse laser irradiation using a Laser OmniMark 20 F (OmniTek, São Paulo, SP, Brazil).
Paulo, Brazil) (λ = 1090 nm) at a short exposition time (1 minute). Our research group has evaluated the topography of metallic surfaces in order to relate parameters of Ti-15Mo surface, such as morphology and roughness and surface energy, depend on the formed phases. The surfaces were modified under ambient pressure and air, using the parameters (power, frequency and scan speed) with four fluency (ablation) of 0.023, 0.033, 0.040 and 0.048 J/mm² (n = 5 for each treatment), respectively (Table 1). After irradiation, the samples were treated ultrasonically and separately in solutions of ethyl alcohol, acetone and deionized water, followed by oven-drying and characterization.

2.2 Preparation of the modified SBF solution and biomimetic coating

The irradiated samples were immersed in modified SBF solution (SBFMg). This solution contained different ions in order to improve the formation of the phases of interest. The reagents used were: NaCl, K₂HPO₄, CaCl₂, H₂O, MgCl₂, H₂O and HCl supplied by J. T. Baker; Tris (hydroxymethyl) aminomethane was purchased from Mallinkrodt. Table 2 indicates the ionic concentrations of the SBFMg solution used to obtain the calcium phosphate coatings on the laser beam irradiated Ti-15Mo surfaces. The preparation of the SBFMg solution was modified from reported protocol by Aparecida (2007), in order to minimize the possibility of solution loss caused by its precipitation.

The substrates were washed sequentially with alcohol, acetone and deionized water. To obtain the calcium phosphate coatings using the SBFMg solution, all the samples were immersed in 50 mL of modified SBF solution (pH 7.4), and remained in controlled temperature condition at 37°C for 4 days. The solution was exchanged every 24 hours for the purpose of promoting the super-saturation conditions of the solution and, consequently, inducing the formation of the calcium phosphate coating. After the period to obtain the coatings, the samples were air dried and submitted to thermal treatment at 380°C and 580°C for 3 hours, without atmospheric control. The heating and cooling rate used was 5°C/minute.

2.3 Characterization

All the coated and uncoated samples were characterized by scanning electron microscopy (SEM), using a Zeiss EVO LS-15, with EDS/EBDS Oxford INCA Energy 250 system. The X-ray diffraction analysis was performed in a Siemens D5000 X-ray diffractometer, using a scan angle of 5 at 60° with a step size of 0.02 (20). Each sample was subjected to a counting time of 10s/step in a Bragg-Brentano configuration, using Cu (ka1) radiation. Quantification by Rietveld refinement was performed in a Rigaku RINT-2000 X-ray diffractometer with rotating anode, operating under the experimental conditions of 42KV, 120mA, with divergence slits, scattering angle of 0.5°, 5 mm horizontal opening of the divergence slit, 0.3 mm receiving signal, 5° Soller, copper anode, and wavelengths of kα₁ = 1.55056 Å and kα₂ = 1.5444 Å, λ/kα₁/λ/kα₂ = 0.5. The chemical bonds of the calcium phosphates coatings were characterized by vibrational infrared spectroscopy, using a Bruker Vertex 70 FTIR spectrophotometer equipped with a diffuse reflection DRIFT Collector™.

3. Results and Discussions

3.1 Morphological properties

The micrographs of the surfaces of the uncoated samples Ti-15Mo alloy submitted to laser beam using different fluencies (0.023, 0.033, 0.040 and 0.048 J/mm², respectively) are presented in Figure 1A. It can be observed the increased fluency, due to longer exposure time of the laser beam to the alloy surface, promotes typical morphologies with different surface energies. This can be explained through the formation of new structures (metal oxides) produced during the fast melt and solidification process. Figure 1B shows the morphologies of the coatings obtained in samples 1, 2, 3, and 4, using the SBFMg solution and heat treated at 380°C. It was possible to identify the formation of a coating with morphology characteristic of the ACP 2, OCP and Mg₃(PO₄)₂ phases.

The morphologies of the coatings obtained for samples 1, 2, 3 and 4, using the SBFMg solution and heat treatment treated 580°C are presented in Figure 1C. The formation of a multiphase coating was evidenced, evidenced by the presence of particles with different morphologies and size, characteristic of the phases of β-TCP, TCP replaced with magnesium - Ca₂Mg₅(OH)₅(PO₄)₂ - E OCP and Mg₃(PO₄)₂ phases. The presence of magnesium phosphate phases resulted in the absence of calcium deficient HA or HA, since these compounds present crystallization temperatures at 580°C, inhibiting the conversion of calcium phosphates to HA. According to the literature, the Mg⁺ ion inhibits HA growth, since it complexes more easily with PO₄³⁻ ions than Ca²⁺ ions.

3.2 XRD Rietveld refinement

Figure 2 shows the diffractograms of samples (0.023, 0.033, 0.040 and 0.048 J/mm²), respectively. It was possible to produce the formation of stoichiometric and non-stoichiometric oxides as predicted by the fluency equation. X-ray diffraction spectra revealed the oxide phases percentage obtained by Rietveld refinement, corresponding to laser beam-irradiated Ti-15Mo surfaces. It can be observed the fusion and solidification process under ambient air, inducing the

| Table 1. Fluency obtained by irradiation of the laser beam. |
|---|---|---|---|---|
| Samples | Am1 | Am2 | Am3 | Am4 |
| Fluency (J/mm²) | 0.023 | 0.033 | 0.040 | 0.048 |

| Table 2. The ionic concentrations of the solution SBFMg (nmol.mm⁻³) |
|---|---|---|---|---|---|---|
| | Na⁺ | K⁺ | Mg²⁺ | Ca²⁺ | Cl⁻ | HPO₄²⁻ |
| SBFMg | 45,30 | - | 0,32 | 1,00 | 46,09 | 0,60 |
| SO₄²⁻ | HCO₃⁻ | - | - | - | - | - |
Table 3. Percentage of phases composed of Ti and O after refinement by Rietveld

| Phases (%) | Fluency (J/mm²) |
|------------|-----------------|
|            | 0.023 | 0.033 | 0.040 | 0.048 |
| α-Ti       | Am1   | Am2   | Am3   | Am4   |
| Ti₂O       | 23.00 | 29.57 | 38.36 | 32.26 |
| Ti₅O       | 23.84 | 23.19 | 29.61 | 31.26 |
| TiO₂       | 18.77 | 28.89 | 16.44 | 17.39 |

Figure 1. SEM of the (A) Ti-15Mo alloy submitted to laser beam using different fluences 0.023, 0.033, 0.040 and 0.048 J/mm² (Samples Am1, 2, 3 and 4, respectively). 500x; and after coating by immersion in modified SBFMg and heat treatment at (B) 380 °C and (C) 580 °C. 50.000X.
formation of titanium oxides with different degrees of oxidation by laser ablation. The oxidation mechanism of titanium is complex owing to the high solubility of oxygen in the hexagonal-close-packed (h.c.p.) structure of α-titanium. A recent study has shown there are two other potential interstitial sites (hexahedral and crowdion) in α-Ti where the oxygen can be located\(^3\). The presence of the TiO\(_2\) and Ti\(_3\)O substoichiometric phases can be explained by interstitial oxygen diffusion in the Ti lattice\(^3\).

The X-ray diffraction patterns of the bioceramic coatings, obtained using the SBFMg solution on the surfaces of the samples (1: F = 0.023 J / mm\(^2\), 2: 0.033 J / mm\(^2\), 3: 0.040 J / mm\(^2\) and 4: 0.048 J / mm\(^2\), Figure 2B). All peaks corresponding to the Ti-15Mo alloy (\#: 89-4913) were identified, formation of an ACP 2 phase mixture OCP (\#: 26-1056) and magnesium phosphate (\#: 48-1167). The formation of the ACP phase to the HA phase can occur directly from ACP1, whereas its transformation through the formation of intermediates occurs with ACP2 as another intermediate\(^2,27,34\).

The use of the SBFMg solution favors the formation of OCP (octacalcium phosphate) due to the presence of the Mg\(^{2+}\) ion which allowed the crystallization of the ACP 2 and its partial transformation to OCP and the appearance of the magnesium phosphate phase. It was observed the amount of Mg\(^{2+}\) incorporated into calcified tissues associated with the calcium phosphates phase decreases with stronger calcification, leading to changes of the bone matrix that determines the bone fragility\(^1,13,35\). Therefore Mg\(^{2+}\) ions were incorporated into calcium phosphate ceramics, it is expected the in vivo process of this synthetic materials is more similar to bone mineral, as compared to Mg free synthetic materials\(^1,36\).

Figure 2C shows the X-ray diffraction patterns of the bioceramic coatings, obtained using the SBFMg solution on the surfaces of samples 1, 2, 3 and 4. In all samples the peaks corresponding to the Ti-15Mo alloy (\#: 89-4913), the formation of a mixture of phases tricalcium phosphate (β-TCP) (\#:70-2065) TCP replaced with magnesium -Ca\(_{2.589}\)Mg\(_{0.411}\)(PO\(_4\))\(_2\) (\#:87-1582), magnesium phosphate -Mg\(_3\)(PO\(_4\))\(_2\) (\#: 48-1167) e OCP (\#: 26-1052)\(^3\). The formation process of the β-TCP and Ca\(_{3}\)Mgy(PO\(_4\))\(_2\) phases may be related to the decomposition of the non-stoichiometric hydroxyapatite phase, between 600 and 750°C, reaction below\(^1,27,37,38\):

\[
\text{Ca}_{10} (\text{PO}_4) \text{OH} \rightarrow \beta \text{-Ca}_3 (\text{PO}_4)_2 + \text{Ca}_3 (\text{PO}_4) \text{OH} \rightarrow \text{CO}_2 \uparrow
\]

The Mg\(^{2+}\) ion is one of the most abundant trace ions in biological hard tissues. In dental enamel, the concentration is 0.4%, in the 1% dentin and in the bone 0.5%. The amount of Mg\(^{2+}\) in dental enamel increases from the surface to the enamel / dentin junction area. The properties of calcium phosphates of biological interest can be affected by the presence of Mg\(^{2+}\). This ion has been reported as responsible

![Figure 2](https://example.com/figure2.png)

**Figure 2.** X-ray diffraction samples 0.023, 0.033, 0.040 and 0.048 J/mm\(^2\), before (2A) after calcium phosphate coatings obtained by immersion in SBFMg and heat treated at 380 °C (2B) and 580 °C (2C).
for the calcium phosphate crystallization disorder, especially HA, when present in the solution in quantities sufficient to compete with Ca\(^{2+}\) ions. Studies have shown that when the Mg / Ca molar ratio of the solution is greater than 0.05, formation of Mg\(^{2+}\)-substituted TCP will occur.\(^{13,37-39}\)

3.3 Fourier transform infrared spectroscopy

The spectra in the middle infrared region of the bioceramic coatings using the SBFMg solution on the surfaces of samples 1, 2, 3 and 4 are shown in Figure 3A 380 °C and 3B 580 °C.

In the Figure 3B, it can be observed that all the spectra present bands in the regions between 1240-940 and 760-720 cm\(^{-1}\) which indicate the asymmetric stretching of the P-O-P bond, and a band in the 1240 cm\(^{-1}\) region relative to the stretching of P = O.\(^{40,41}\) In all samples (1, 2, 3 and 4) the presence of the 630 and 545 cm\(^{-1}\) regions was observed, which may be associated with the OH group stretching, the PO\(^{3-}\) group vibration and the unfolding of the group PO\(^{2-}\) and refer to the probable formation of the hydroxyapatite phase.\(^{42,43}\) Bands in the region of 1733-1630 cm\(^{-1}\) are attributed to the incorporation of water molecules. The bands 1386-1455 cm\(^{-1}\) may be associated with the CO\(^{2-}\) vibration from the CO\(_2\) of the atmosphere during the processes of dissolution, agitation, reaction and calcination.\(^{24,27,41,43,44}\)

**Figure 3.** Absorption spectrum in the medium infrared (FTIR) of the samples (1, 2, 3 and 4), after coating of calcium phosphates obtained by immersion in SBFMg and heat treated at (A) 380°C and (B) 580°C.

4. Conclusion

Bioceramics coatings have been deposited on metal and its alloy surfaces by laser ablation process. Multiphasic calcium phosphates must exhibit a combination of enhanced bioactivity and mechanical stability that is difficult to obtain in single-phase materials. In the present study, it has been also demonstrated the formation of different stoichiometric and non-stoichiometric oxides, such as α-Ti, TiO, TiO\(_2\), Ti\(_2\)O, as well as the different oxide percentages depending on the applied fluency. This aspect has provide typical morphologies of the calcium phosphates phases. In this perspective, a multiphasic bioceramic coatings on Ti-15Mo surfaces could be obtained depending on the thermal treatment performed at 380 and 580°C. Therefore, the multiphasic bioceramic coatings deposited on Ti-15Mo surfaces can be further improved by providing an bio compatible and long term performance for biomedical applications, including bone regeneration in orthopaedics, oral and maxillofacial surgery.

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