Biomimetic coating on titanium: evaluation of bioactivity and corrosion

Mariny Fabiéle Cabral Coelho1, Luciola Lucena de Sousa1, Carolina Cruz Ferreira1, Brenda Fernanda Gaspar de Souza1, Eliana Cristina da Silva Rigo1 and Neide Aparecida Mariano1

1 Federal University of Alfenas - UNIFAL-MG, Rodovia José Aurélio Vilela, 11.999, Cidade Universitária, Km 533, 37.715–400, Poços de Caldas, MG, Brazil
2 University of São Paulo-USP, Avenida Duque de Caxias Norte 225, Jardim Elite, 13.635–970, Pirassununga, SP, Brazil

E-mail: luciolalucena@yahoo.com.br

Keywords: Titanium, biomimetic method, corrosion, biomaterial, hydroxyapatite

Abstract

In this work, the effect of coating by the biomimetic method on a titanium substrate was studied, consisting of the immersion of the substrate in a synthetic SBF (Simulated Body Fluid) solution, with composition, pH and temperature similar to blood plasma. The coating was efficient for obtaining hydroxyapatite, which was confirmed by the techniques of scanning electron microscopy (SEM), x-ray diffraction (XRD) and infrared. The bioactivity assay revealed that the samples which received the coating with 1.5 SBF presented bioactive characteristic by the formation and development of the carbonated hydroxyapatite on the surface, in a superior way to the samples without coating, thus suggesting a fast osseointegration of the bone with the implant. The polarization curves showed that the titanium without coating presented a higher resistance to corrosion compared to the titanium with coating.

1. Introduction

Currently, titanium (Ti) and its alloys are among the main metal biomaterials used as implants, due to characteristics such as low density, high mechanical resistance and elevated chemical stability, because of the formation of a titanium oxide layer in its surface [1–5].

Ti surface can be physically or chemically modified to enhance biomaterial-tissue integration. Thus, several studies have been performed with the purpose of improving the interaction of the metal alloys, which have a great mechanical resistance associated to the biological system by techniques for coating of the metal material surface [9–16]. Hydroxyapatite (HA), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is one of the coatings which have been investigated, for presenting similar properties to those of natural bone [17–23]. Actually, the adherence of the HA layer to the biocompatible alloy depends, among other factors, on the nature and porosity of the oxide that covers it; therefore, it becomes interesting to combine the studies of growth of these oxides to those of hydroxyapatite deposition [24, 25].

Hydroxyapatite, which is in the group of bioactive and bioreabsorbable ceramics, presents an excellent biocompatibility and chemically binds to the bone without interposition from any other type of tissue [26]. It results from the fact that HA is a compound formed by the same ions that form the mineralized phase of natural bone (Ca, P, O), and can participate in calcium/phosphate equilibrium in the organism.

Thus, these ceramics associated to the metals as coating have been widely used as regenerative bone grafts, orthopedic and dental implants, percutaneous access devices and maxillofacial reconstruction [27].

The biomimetic method is one of the methods of coating with calcium phosphate that have been studied in the last years, proposed by Abe et al (1990). This method simulates the conditions of hydroxyapatite precipitation in the human body, aiming at coating the substrates of varied nature with a layer of biological hydroxyapatite [28]. The use of Ti as substrate consists of its interaction with an alkaline aqueous solution, for the
formation of an alkaline titanate hydrogel layer, with subsequent heat treatment, followed by immersion in 1.5 SBF (simulated body fluid) to compose the apatite layer.

The methods for the formation of oxides and decomposition of calcium phosphate layers aim at modifying the surface of titanium and its alloys, combining the properties of the bioinert material with the bioactivity of the calcium phosphates, in order to thus enhance the osseointegration process [29–31]. Regarding the electrochemical properties of the alloys, the adherence of the HA layer to the biocompatible alloy depends on the nature and porosity of the oxide that covers it; therefore, it is necessary to combine the studies of growth of these oxides to those of hydroxyapatite deposition.

This work aimed at studying hydroxyapatite coating on commercially pure titanium (Ti c.p.) by the biomimetic method and to evaluate the effect of this coating on the bioactivity and resistance to corrosion of these materials.

### 2. Experimental

As substrate, commercially pure titanium grade 1 was used, in the form of discs with 8 mm diameter and 3 mm thickness. The chemical composition of the samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

The microstructural characterization of Ti c.p. was performed by optical microscope (OM) and scanning electron microscopy coupled to an energy dispersive x-ray spectrometer (SEM-EDS), according to the norm ASTM E3–95 [32], and to reveal the microstructure, a Kroll solution (3% of nitric acid, 10% of hydrofluoric acid and 85% in volume of distilled water) was used. X-ray diffraction analyses were also conducted, with Cu Kα radiation, in a range of 20 of 10° to 90°, with a step of 0.02° per 2 s/step.

For the biomimetic coating, the samples were initially sanded with a 180-mesh abrasive paper, to promote a rough surface, generating the increase in the specific area and surface energy. According to Vercik [33], this characteristic is necessary to favor apatite precipitation. The substrates were then immersed in an aqueous solution of 5 M NaOH at 60 °C and maintained in this condition for 24 h to produce active sites on the metal surface to favor hydroxyapatite precipitation [33–36].

Subsequently, the substrates were heat treated at 600 °C for one hour, following cooling at room temperature, to eliminate the hydrated phase and form a stable layer. The samples were submitted to the nucleation stage, which consists in the immersion in a sodium silicate solution at 36.5 °C for seven days. Then, the samples were immersed in a 1.5 SBF solution at 36.5 °C for seven days for the process of apatite deposition which enables a slower and more organized nucleation of the apatite to be deposited. The solution was changed every 48 h to favor the supersaturation conditions of the solution and induce coating formation [37, 38].

The bioactivity assay was performed according to norm ISO 23317:2012 [39], for Ti c.p. covered with hydroxyapatite and for the Ti c.p. without coating, with further infrared analysis.

The corrosion assays were performed using the open circuit polarization technique (OCP) and potentiodynamic polarization. In the assay, an electrochemical cell was used, composed of a saturated calomel reference electrode (SCE), a platinum counter electrode and the work electrode. The electrolytic solution employed was SBF solution at pH 7.4, at room temperature and 36.5 °C. The polarization curves were obtained with a scanning speed with a potential of 0.001 V s⁻¹, varying the potential (E) from −1 V (SCE) to 2 V (SCE).

### 3. Results and discussion

Table 1 shows the chemical composition of Ti c.p. Degree 1, which is according to the specification of norm ASTM F67–06 [40].

| Sample            | N    | C    | H    | Fe   | O    | Ti   |
|-------------------|------|------|------|------|------|------|
| ASTM F67–06       | 0.03 max | 0.10 max | 0.015 max | 0.20 max | 0.18 max | balance |
| Ti c.p.           | 0.006 | 0.09 | 0.013 | 0.11 | 0.14 | balance |

Optical micrograph of Ti c.p. is presented in figure 1(a) and it is observed that the grains have homogeneous morphology with an equiaxial granular structure, distributed along the matrix, characteristic of phase α. This phase can be confirmed by the x-ray diffractogram, shown in figure 1(b).

The alkaline treatment with NaOH is necessary to produce active sites on the metal surface and favor hydroxyapatite precipitation, since on titanium surface, a very stable layer of titanium oxide, TiO₂, is...
spontaneously formed, which makes the metal little reactive to apatite deposition, as reported by Coelho [2] and Vercik [33]. The reaction between TiO₂ and NaOH forms a titanate hydrogel. During thermal treatment (600 °C for one hour), the titanate hydrogel layer dehydrates and stabilizes in a partially crystalized form of sodium titanate (Na₂Ti₅O₁₁). Therefore, substrate immersion in a NaOH solution will enable the increase in the number of active sites on the surface of Ti c.p.

Figure 2(a) shows Ti c.p. micrograph after the alkaline treatment with NaOH and thermal treatment at 600 °C, and a structure is observed with the appearance of a microporous layer with scattered and homogeneously distributed needles on the surface of Ti c.p., figures 2(b) and (c) show EDS at points A and B, which confirm the presence of the elements Na and O originated from the alkaline treatment.
Figure 3 (a) shows Ti c.p. surface after immersion in 1.5 SBF; (b) EDS spectrum at point A.

Figure 4. SEM micrographs of Ti c.p. covered with 1.5 SBF, after the bioactivity assay. (a) First week. (b) Second week. (c) Third week. (d) Fourth week. (e) EDS spectrum at point A of the fourth week.

Figure 3 (a) shows Ti c.p. surface after the immersion in 1.5 SBF for seven days, and homogeneous layers of carbonated hydroxyapatite are observed, which are formed by small and compact globules without porosity. In figure 3(b), the qualitative analysis by EDS is presented at point A, in which the presence of the elements Ca, P and O is evidenced, characteristic of the carbonated hydroxyapatite layer.

Figures 4(a)–(d) present the evolution of Ti c.p. surface covered with 1.5 SBF along four weeks of the bioactivity assay, after coating with 1.5 SBF. It is observed that in the four weeks, there is a great amount of carbonated hydroxyapatite (CHA) layers, and as layer overlap occurs, it is observed that the coating structure has a globular shape, of the have diameter smaller than 3 μm, nevertheless, from the first week of bioactivity assay, it is possible to observe the formation of an overlapping CHA layer, than the previous layer, indicating that as overlap occurs, the layer that forms subsequently limits the growth of the previous layer.

Figure 4(e) shows the spectrum obtained in the microanalysis by EDS, at point A, indicates the presence of the chemical elements phosphorus (P), calcium (Ca) and oxygen (O), present in the hydroxyapatite structure.
The presence of the chemical elements magnesium (Mg) is associated with the reagents used in the alkaline treatment and in the constitution of the simulated body fluid.

Hydroxyapatite, when used as a coating of metallic materials, has the ability to increase both surface area and surface porosity, which are relevant factors in osteointegration, as it enhances the bioactivity and proliferation of bone cells around the implant [41–43].

And several clinical and experimental studies report that the increased surface area of the implanted material favors the formation of bonds with host tissues, besides providing greater osteoconduction and cell adhesion, demonstrating the efficacy of HA in the regenerative process of bone defects and in the application bone grafting [44–46].

Costa et al, 2015 observed that hydroxyapatite showed good osteointegration and support for bone neoformation due to the cellular conduction of osteoblasts and precursors in order to promote tissue growth at the injured site, also observed by ROLIM et al, 2018; SOUZA et al, 2018 [47–49].

Figures 5(a)–(d) present micrographs of Ti c.p. without coating as a control of the bioactivity assay. The formation of small CHA globules is observed, from the second week, still being possible to observe the titanium surface, which does not happen on the third week, where the formation of a second CHA layer is observed. The globules of the first layer of figure 5(c) present pores among them, while in the fourth week shown in figure 5(d), a reduction in pores is observed between HA globules.

Figure 5(e) shows the spectrum obtained in the microanalysis by EDS, at point A of the fourth week, and indicates the presence of the chemical elements phosphorus (P), calcium (Ca) and oxygen (O), present in the hydroxyapatite structure. The presence of the chemical elements magnesium (Mg), sodium (Na) and chlorine (Cl), are associated with the reagents used in the alkaline treatment and in the constitution of the simulated body fluid.

Figure 6(a) shows the change of the infrared bands along the bioactivity assay for Ti covered with 1.5 SBF. It is possible to identify the characteristic bands at 561, 601, 963 and 1019 cm\(^{-1}\), which are attributed to the PO\(_4\)\(^{3-}\) group; at 1658 cm\(^{-1}\), a characteristic H\(_2\)O band was formed and between 3000–3500 cm\(^{-1}\), there is a large band which can be attributed to the presence of hydroxyl and incorporated water.

It is also possible to observe bands at 873 and 1461 cm\(^{-1}\) referring to the binding of CO\(_3\)\(^{2-}\) type B, whereas CO\(_3\)\(^{2-}\) type A ligation was observed at 1455 cm\(^{-1}\), characterizing a CHA of the type AB. These bands appear in the four weeks of bioactivity assay and is in accordance with figures 4(a)–(d), where the formation of characteristic CHA globules is observed on the substrate surface in the four weeks of assay.
The infrared spectrum for the bioactivity assay of Ti c.p. without coating is presented in figure 6(b). On the first week, there are no bands related to the ligations $\text{CO}_3^{2-}$, $\text{PO}_4^{3-}$, $\text{OH}^{-}$ corresponding to the carbonated hydroxyapatite, which is consistent with figure 5(a), where no CHA structure was observed on the surface of the substrate. From the second week, it is possible to identify bands of the group $\text{PO}_4^{3-}$ in 563, 603, 950 and 1025 cm$^{-1}$, of the group $\text{OH}^{-}$ at 3350 cm$^{-1}$. $\text{CO}_3^{2-}$ ligations of type B are observed by the bands at 874 cm$^{-1}$ and at 1417 cm$^{-1}$ and $\text{CO}_3^{2-}$ of type A at 1455 cm$^{-1}$.

The appearance of the bands from the second week is consistent with Fig. from 5b to 5d, where it is possible to observe CHA globules on the surface.

Comparing the bioactivity assay for titanium with and without 1.5 SBF coating, it is possible to observe that the presence of coating provides a higher growth of carbonated hydroxyapatite on the surface, suggesting a rapid osseointegration of the bone with the implant.

In the corrosion assays, the open circuit potentials (OCP) for Ti c.p. without and with coating, in SBF solution with pH 7.4, in the temperatures 25 °C (room temperature) and 36.5 °C (body temperature), are presented in figures 7(a) and (b), respectively.

The open circuit potential for Ti c.p. without coating at temperatures 25 °C and 36.5 °C revealed a rise in the potential with time, indicating the formation of a passive film ($\text{TiO}_2$) in the surface of the substrates. Conversely, for these same temperatures, for Ti c.p. with coating the potential remained constant, providing the stability and adherence of the coating, a result also observed by Talha et al [50]. Moreover, the substrate that did not receive CHA coating had higher potentials than the substrate that received the CHA coating, indicating that the formation of passive film ($\text{TiO}_2$), tends to protect the substrate, for both temperatures (25 °C and 36.5 °C).
By the potentiodynamic polarization curves of Ti c.p. without and with coating in SBF solution with pH 7.4 at 25 °C and at 36.5 °C, presented in figures 8(a) and 8(b) respectively, it was possible to determine the electrochemical parameters: corrosion potential ($E_{corr}$), current density ($I_{corr}$) and passivation current density ($I_{pass}$), as observed in Table 2.

It was observed that the corrosion potential for Ti c.p. without and with coating in both temperatures, obtained by the polarization curves, were lower than the values determined in open circuit. This behavior may occur because potential scanning started in more negative potentials than the corrosion potential, which might have partially removed the passive film and/or the coating.

The Ti c.p. without coating presented a more positive ($−0.2518$ V and $−0.3091$ V) corrosion potential ($E_{corr}$) compared to the coating ($−0.4811$ V and $−0.4627$ V), respectively, at the temperatures 25 °C and 36.5 °C, as observed by Mariano [51]. The corrosion potential of Ti c.p. without coating was higher than with coating, a result which indicates that the titanium oxide formed is more stable, adherent and homogeneous than CHA coating.

No significant variation was observed in the corrosion current density ($I_{corr}$), at 25 °C and at 36.5 °C, for the Ti c.p. without coating ($8.72 \times 10^{-8}$ A/cm² and $1.47 \times 10^{-7}$ A/cm²), respectively, and for the Ti c.p. with coating ($1.43 \times 10^{-7}$ A/cm² and $2.56 \times 10^{-7}$ A/cm²), respectively.

The polarization curves obtained for this substrate, in all conditions studied, revealed a clear passive region and the passivation current density was determined ($I_{pass}$). The current density in this region was constant in a broad range of potentials, indicating the formation of a passive and compact titanium oxide (TiO₂) film on the surface of Ti c.p. without coating, as observed by Robin [52] and Sasikumar [53]. On the other hand, it is suggested that for Ti c.p. with coating, the carbonated hydroxyapatite layer on the surface was protective and did not present porosity, as observed by Mittal [54].

4. Conclusions

The alkali and heat treatments and the nucleation step were efficient for the formation of carbonated hydroxyapatite on the substrates, demonstrating that the biomimetic method was efficient in the acquisition and formation of hydroxyapatite.
The bioactivity assay revealed the formation and development of CHA on the substrates with and without coating. Nevertheless, it is observed that in the substrates covered with HA, the growth of CHA started in the first week, whereas in the substrates without coating, CHA growth started in the second week. A thicker layer was also observed at the end of the fourth week on the substrates covered with HA.

The open circuit potential revealed a rise in the potential with time, indicating the formation of a passive film in the surface of the substrates for Ti cp. without coating at the temperatures 25 °C and 36.5 °C. Conversely, for these same temperatures, the potential remained constant in the substrates that received coating, providing the stability and adherence of the coating. The electrochemical parameters: corrosion potential (E_{corr}), corrosion current density (I_{corr}) and passivation current density (I_{pass}) at temperatures 25 °C and 36.5 °C, obtained from the polarization curves, were higher for Ti cp without coating (used as a control), promoting higher stability and homogeneity, relative to Ti cp with coating.

Acknowledgments

The authors thank Brazilian research funding agencies FAPEMIG, CNPq, FINEP and CAPES for financial support.

ORCID iDs

Mariny Fabiêla Cabral Coelho  https://orcid.org/0000-0003-3310-4095
Luciola Lucena de Sousa  https://orcid.org/0000-0001-7494-052X
Carolina Cruz Ferreira  https://orcid.org/0000-0002-1345-4904
Brenda Fernanda Gaspar de Souza  https://orcid.org/0000-0003-2830-341X
Eliana Cristina da Silva Rigo  https://orcid.org/0000-0003-3368-5707
Neide Aparecida Mariano  https://orcid.org/0000-0001-8345-1808

References

[1] Wang Y, Yu H, Chen C and Zhao Z 2015 Review of the biocompatibility of micro-arc oxidation coated titanium alloys Mater. Des. 85 640–52
[2] Coelho M F C, Cronemberger M E R, Pereira I N, Nakamatsu S, Maestrelli S C, Rigo E C S and Mariano N A 2014 A comparative study of biomimetic coatings on titanium and stainless steel Mater. Sci. Forum 802 440–5
[3] Fomin A, Dorozhkina S, Fomina M, Kshoburov V, Rodoniov I, Zakharievich A, Petrova N and Skaptsov A 2016 Composition, structure and mechanical properties of the titanium surface after induction heat treatment followed by modification with hydroxyapatite nanoparticles Ceram. Int. 42 10838–46
[4] Mumjitha M and Raj V 2015 Fabrication of TiO2–SiO2 bioceramic coatings on Ti alloy and its synergetic effect on biocompatibility and corrosion resistance J. Mech. Behav. Biomater. Mater. 46 205–21
[5] Zhou J, Li B, Han Y and Zhao L 2016 The osteogenic capacity of biomimetic hierarchical micropore/nanorod-patterned Sr–HA coatings with different interrodspacings Nanomol. Nanotechnol. Biol. Med. 12 1161–73
[6] He D, Liu P, Liu X, Ma F, Chen X, Li W, Du J, Wang P and Zhao J 2016 Characterization of hydroxyapatite coatings deposited by hydrothermal electrochemical method on NaOH immersed Ti6Al4V J. Alloys Compd. 672 336–43
[7] Liu Y-T, Long T, Tang S, Sun J-L, Zhu Z-A and Guo Y-P 2014 Biomimetic fabrication and biocompatibility of hydroxyapatite/chitosan nanohybrid coatings on porous carbon fiber felts Mater. Lett. 128 31–4
[8] Tang S, Tian B, Guo Y-J, Zhu Z-A and Guo Y-P 2014 Chitosan/carbonated hydroxyapatite composite coatings: fabrication, structure and biocompatibility Surface & Coatings Technology 251 210–6
[9] Best S M, Porter A E, Thian E S and Huang J I 2008 Bioceramics: past, present and for the future J. Eur. Ceram. Soc. 28 1319–27
[10] Shahi F A, Trobos M, Thomsen P and Palmquist, A 2016 Commercially pure titanium (cp– Ti) versus titanium alloy (Ti6Al4V) materials as bone anchored implants — Is one truly better than the other? Materials Science and Engineering C 62 960–6
[11] Geetha M, Singh A K, Aokamani R and Gogia A K 2009 Ti based biomaterials, the ultimate choice for orthopaedic implants—a review Prog. Mater. Sci. 54 397–425
[12] Rautray T R, Narayanan R and Kim K-H 2011 Ion implantation of titanium based biomaterials Prog. Mater. Sci. 56 1137–77
[13] Hung K-Y, Lo S-C, Shih C-S, Yang Y-C, Feng H-P and Lin Y-C 2013 Titanium surface by hydroxyapatite coating for dental implants Surface & Coatings Technology 231 337–45
[14] Fukuda A and al Bone bonding bioactivity of Ti metal and Ti–Zr–Nb–Ta alloys with Ca ions incorporated on their surfaces by simple chemical and heat treatments Actu Biomater. 7 2011 1379–86
[15] Yamaguchi S, Takadama H, Matsushita T, Nakamura T and Kokubo T 2011 Preparation of bioactive Ti–15Zr–4Nb–4Ta alloy from HCl and heat treatments after an NaOH treatment J. Biomed. Mater. Res. Part A 97A 135–44
[16] Mariano N A, Oliveira R G, Fernandes M A and Rigo E C S 2009 Corrosion behavior of purê titanium in artificial saliva solution Revista Matéria 14 878–80
[17] Guastaldi M and Aparecida A H 2010 Fosfatos de cálcio de interesse biológico: importância como biomateriais, propriedade e métodos de obtenção de recobrimentos Química Nova 33 1352–8
[18] Dinçer M, Teker D, Sağ CP and Öztürk K 2013 Enhanced bonding of biomimetic apatite coatings on surface modified titanium substrates by hydrothermal pretreatment Surface & Coatings Technology 226 27–35
Abe Y, Kokubo T and Yamamuro T 1990 Apatite coating on ceramics, metals and polymers utilizing a biological process Mater. Lett. 63 2659–61

Kawai T, Takemoto M, Fujibayashi S, Neo M, Akiyama H, Yamaguchi S, Pattanayak D K, Matsushita T, Nakamura T and Kokubo T 2012 Bone-bonding properties of Ti metal subjected to acid and heat treatments J. Mater., Sci., Mater. Med. 23 2981–92

Kawai T, Takemoto M, Fujibayashi S, Tanaka M, Akiyama H, Nakamura T and Matsuda S 2015 Comparison between alkali heat treatment and sprayed hydroxyapatite coating on thermally-sprayed rough Ti surface in rabbit model: effects of bone-bonding ability and osteoconductivity J. Biomed. Mater. Res. Part B 103B 1069–81

Sasikumar Y and Rajendran N 2013 In vitro assessment of zinc apatite coatings on titanium surfaces Ceram. Int. 40 15300–10

Chen Y J, Feng B, Zhu Y P, Weng J, Wang J X and Lu X 2009 Fabrication of porous titanium implants with biomechanical compatibility Mater. Lett. 63 2659–61

Mittal M, Nath S K and Prakash S 2011 Characterization of plasma sprayed hydroxyapatite coatings on AISI 316L SS and titanium substrate and their corrosion behavior in simulated body fluid J. Mater. Sci., Mater. Med. 22 3911–18

Kulpetchdara K, Limpichaipanit A, Rujijanagul G, Randorn C and Chokethawai K 2016 In vitro assessment of zinc apatite coating in simulated body fluid J. Mech. Behav. Biomater. 42 57–93

Abe Y, Kokubo T and Yamamuro T 1990 Apatite coating on ceramics, metals and polymers utilizing a biological process J. Mater. Sci., Mater. Med. 1 233–8

Kokubo T and Yamaguchi S 2016 Novel bioactive materials developed by simulated body fluid evaluation: surface-modified Ti metal and its alloys Acta Biomaterialia 44 16–30

Zhang E, Zou C and Yu G 2009 Surface microstructure and cell biocompatibility of silicon-substituted hydroxyapatite coating on titanium substrate prepared by a biomimetic process Materials Science and Engineering: C 29 399–405

Lim P N, Chang L and Thian E S 2015 Development of nano-sized silver-substituted apatite for biomedical applications: a review Nanomaterials 5 1–33

ASTM Standard E3, 1995, —— Standard Practice for Preparation of Metallurgical Specimens, ASTM International, West Conshohocken, PA 1995 (https://doi.org/10.1505/0003-95@astm.org)

De O. Vercik L C, de Assis C M, Fook M V L, dos Santos M L and Guastaldi A C 2003 Recobrimento de apatitas e hidroxiapatitas com pré-tratamento álcali-térmico sobre aços inoxidáveis austeníticos Revista Brasileira de Engenharia Biomédica 23 117–22

Fraga A F, de E, Filho A, Fraga A F, Bini R A and Guastaldi A C 2011 Bioactive coating on titanium implants modified by Nd:YVO4 laser Surfa. Sci. 576 1–10

Fraga A F, Hsu Y-S, Lin S-H and Sun J-S 2002 The effect of Ca concentration and temperature of simulated body fluid on the growth of hydroxyapatite coating on alkali-treated 316L stainless steel Biomaterials 23 4029–38

Mittal M, Nath S K and Prakash S 2011 Characterization of plasma sprayed hydroxyapatite coatings on AISI 316L SS and titanium substrate and their corrosion behavior in simulated body fluid Journal of Minerals & Materials Characterization & Engineering 10 1041–9