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CHARACTERIZATION OF HYDROXYAPATITE COATINGS ON DIFFERENT PRETREATED Ti_6Al_7Nb ALLOY SUBSTRATES

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ABSTRACT. The aim of the present work was to characterize the influence of the surface conditioning treatment of a medical grade Ti_6Al_7Nb alloy substrate on the homogeneity, morphology and adhesion strength of hydroxyapatite coatings. The substrates were obtained by means of a Selective Laser Melting process using different laser powers.The deposition of hydroxyapatite was performed by dip-coating, followed by a heat treatment at 600°C for 30 min., in air. The morphology of the coatings was studied by means of scanning electron microscopy. Bonding strength was evaluated by pull-off tests.

Keywords: *Ti_6Al_7Nb alloy, hydroxyapatite, dip-coating, coating morphology, bonding strength*

INTRODUCTION

Titanium alloys are widely used in the medical field for hard tissue replacement, due to their favorable combination of mechanical properties, corrosion resistance, low density, and biocompatibility. Even if well tolerated by the human body, they are bio inert materials. For an improved osteointegration, the surface of the future implant could be coated with bioactive ceramics as hydroxyapatite, bio glass, etc [1].

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is often used to this aim. Techniques such as plasma spray, sputter coating, electron beam deposition, spin-coating, or dip-coating may be employed to coat the biomaterial substrate. HA coatings obtained by high temperature processes are characterized by

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good adhesion to the substrate, with bonding strengths up to 30 MPa [2]. On the other side, the high processing temperature and the rapid heating and cooling ratecould affect both the surface structure of the implant and the structure of HA [3]. Low-temperature processes such as dip-coating, which donot affect the structure of HA or of the substrate, result in low adhesion strength of the coating to the implant surface. Several mechanical and chemical surface treatments could be applied to the substrate in order to increase the surface roughness and to modify the surface chemistry for an improved adhesion of the coating [4 - 6].

In the present work, a substrate of medical grade - Ti_6Al_7Nb alloy obtained by Selective Laser Melting (SLM) technique - was coated with HA employingthe dip-coating method. Different surface pretreatments were performed on Ti6Al7Nb alloy substrate, in order to improve both HA bonding strength and morphology. The conditioning treatments aimed to increase the amount of Ti oxides on the surface, which are benefic to the HA adhesion [7].

RESULTS AND DISCUSSION

The surface roughness R_a of the Ti_6Al_7Nb alloy obtained with 120 W and 200 W was 15 μm and 7 μm, respectively. Thus, as expected, it decreased by increasing the applied laser power. The micro hardness HV0.1 was 455±11 for the substrate obtained with 120 W and 481±8 for the substrate obtained with 200 W. It is well known that the structures obtained by the SLM technique have residual stresses which may be estimated, among other methods, by micro hardness measurements. The residual stresses may contribute to the surface energy, which plays an important role in the interaction between the substrate surface and the coating. Since the micro hardness values of the Ti alloy substrates obtained with 120 W and 200 W are quite close, it could be presumed that the possible contribution of the residual stresses to the surface energy is roughly the same for the two different processed substrates.

The SEM images of the Ti_6Al_7Nb substrate surface processed with 120 W before and after dip-coating with HA are shown in Figure 1 and Figure 2, respectively. The surface of the as-processed material, Figure 1, was characterized by the presence of porosity. After dip-coating, the coverage with HA was lower than 100%, as shown in Figure 2; areas of uncoated substrate could be seen by SEM.The surface topology was not of primary importance in this study. In consequence, only the Ti_6Al_7Nb substrate obtained with a laser power of 200 W was considered for the future work. In order to facilitate the bonding strength determination, the surfaces on which the HA would be deposited were ground and polished. The polished Ti_6Al_7Nb samples were subjected to various pretreatments as specified in the Experimental section.

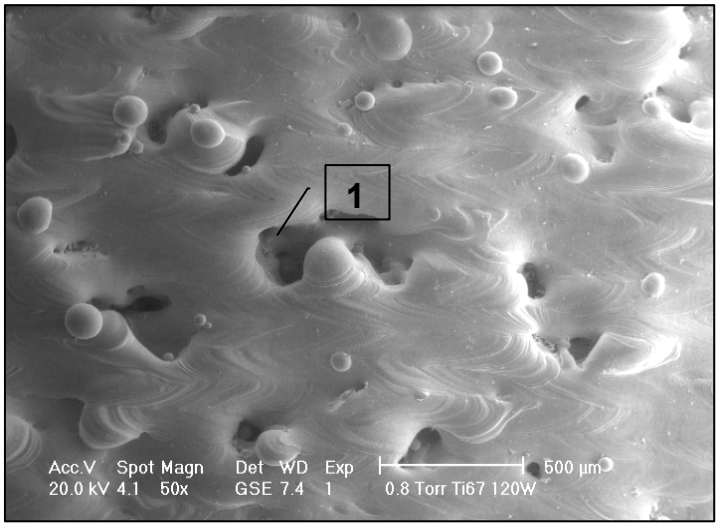

Figure 1. SEM image of the surface of the Ti_6Al_7Nb substrate processed with 120 W; 1 – pore.

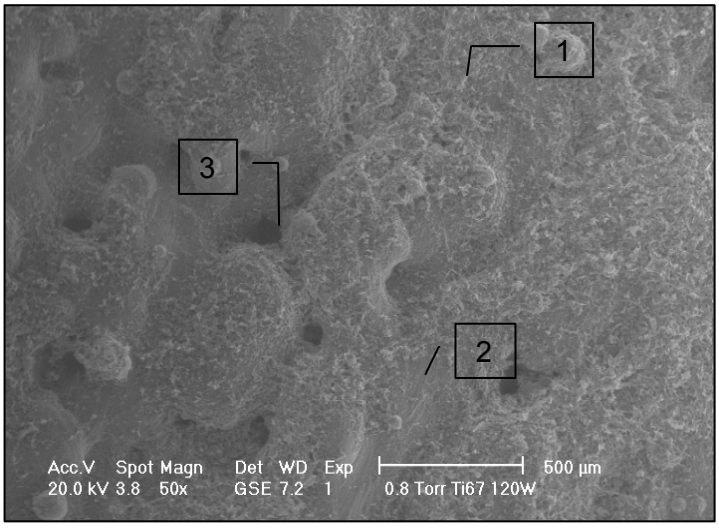

Figure 2. SEM image of the HA coated Ti_6Al_7Nb substrate processed with 120 W 1 - HA coating; 2 – substrate; 3 – pore.

The aspect of the substrate obtained with 200 W, ground and polished, is shown in Figure 3. The surface was smooth, without pores. After the alkali surface treatment in NaOH 5M and heat treatment at 600°C, the surface was characterized by the presence of micro pores, as shown in Figure 4, which are expected to enhance the coverage and bonding strength of the HA to the substrate.

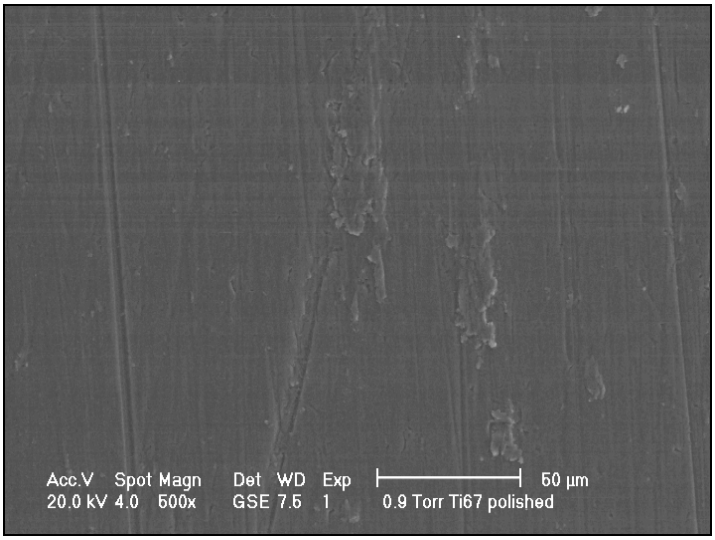

Figure 3. SEM image of the surface of Ti_6Al_7Nb substrate obtained with 200 W, ground and polished.

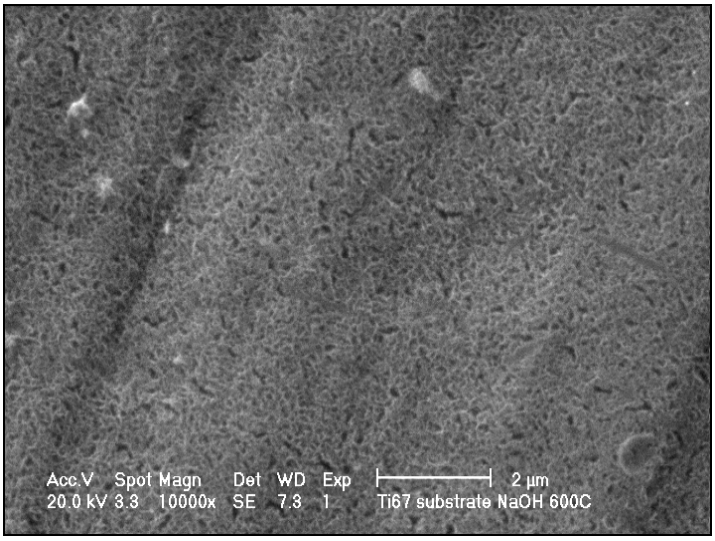

Figure 4. SEM image of the surface of Ti_6Al_7Nb substrate obtained with 200 W, ground and polished, treated in NaOH 5M.

The SEM aspect of the polished surface of Ti_6Al_7Nb after dip-coating with HA is shown in Figure 5 and Figure 6. Some uncoated areas, light colored in Figure 5, were observed. A higher magnification revealed the presence of some micro cracks in the HA coating, Figure 6.

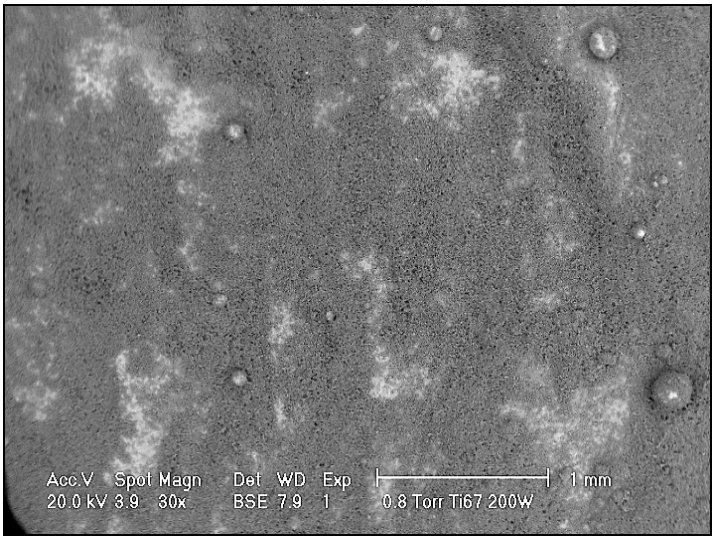

Figure 5. SEM image of the HA coating on the surface of Ti_6Al_7Nb substrate obtained with 200 W, ground and polished.

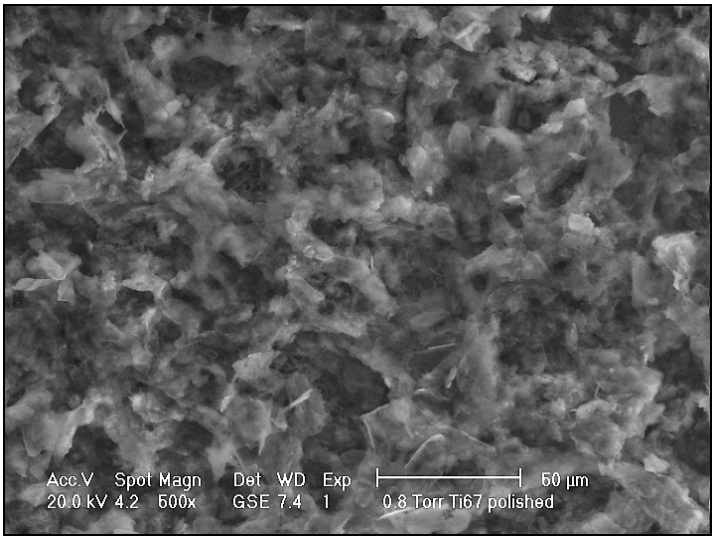

Figure 6. SEM image of the HA coating on the surface of Ti_6Al_7Nb substrate obtained with 200 W, ground and polished. Higher magnification.

A higher coverage and a better homogeneity characterized the HA coated on the alkali-treated substrate surface (Figure 7), even though at a high magnification the SEM analyses evidenced some uncoated substrate, as shown in Figure 8.

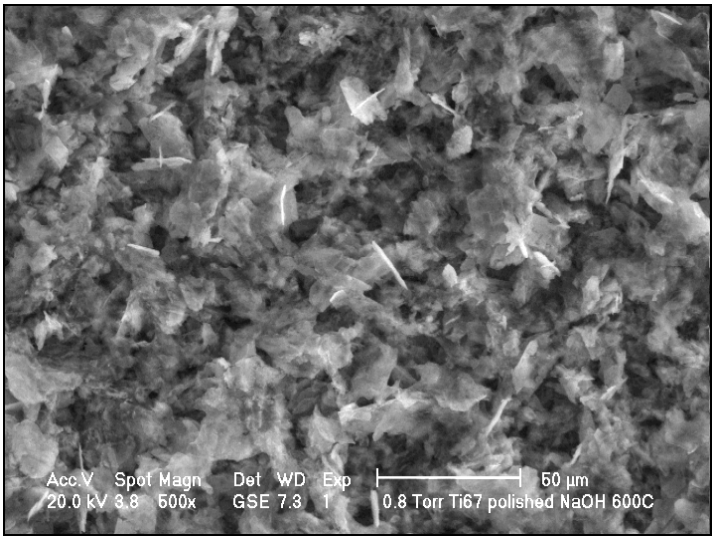

Figure 7. SEM image of the HA coating on the surface of Ti_6Al_7Nb substrate obtained with 200 W, ground and polished, then alkali treated in NaOH 5M.

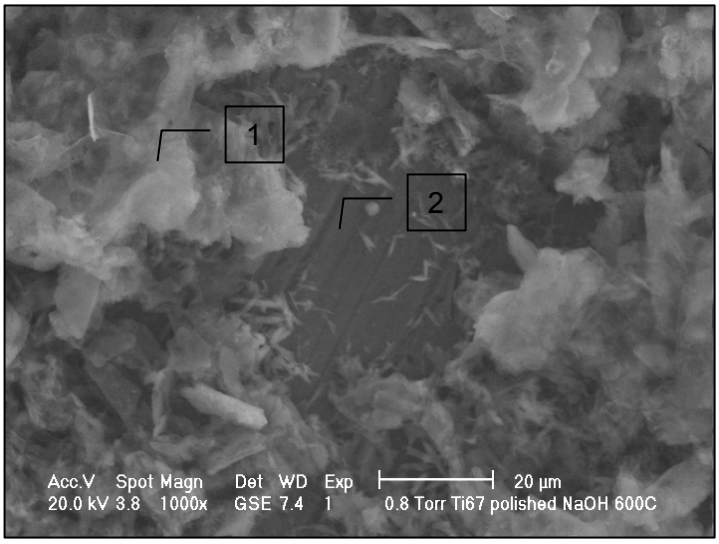

Figure 8. SEM image of the HA coating on the surface of Ti_6Al_7Nb substrate obtained with 200 W, ground and polished, then alkali-treated in NaOH 5M. Higher magnification. 1-HA; 2-substrate.

A small number of small micro cracks, as indicated by the arrow in Figure 10, appeared in the structure of HA coatings deposited on the alkali treated substrate.

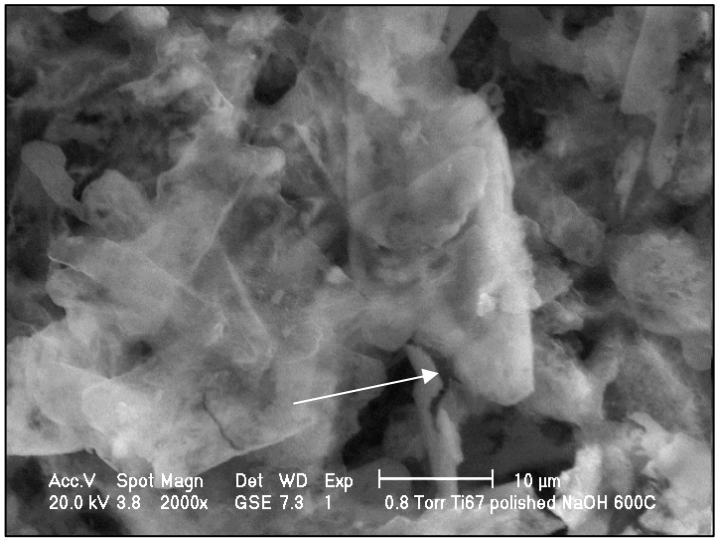

Figure 10. SEM image of the HA coating on the surface of Ti_6Al_7Nb substrate obtained with 200 W, ground and polished, then alkali treated in NaOH 5M. Micro crack indicated by the arrow.

The most affected HA coating with regard to the micro cracking occurrence was that deposited on the surface of the substrate heat treated at 400°C, whose morphology is shown in Figure 11 and in Figure 12.

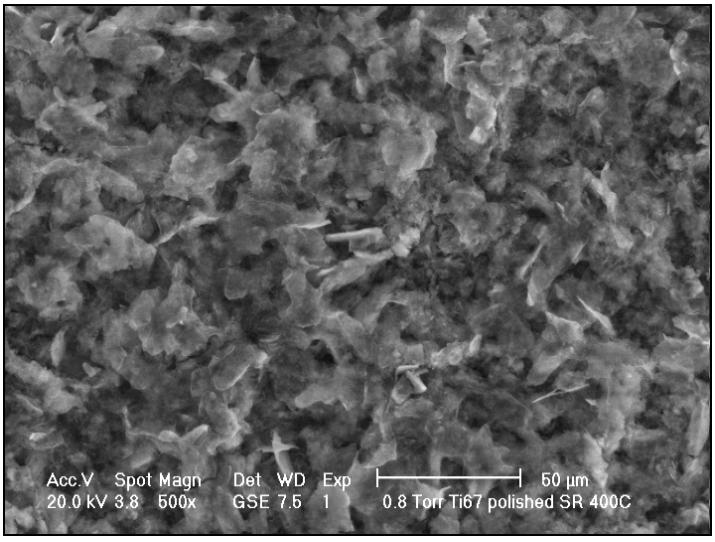

Figure 11. SEM image of the HA coating on the surface of Ti_6Al_7Nb substrate obtained with 200 W, ground and polished, then heat treated in air at 400°C.

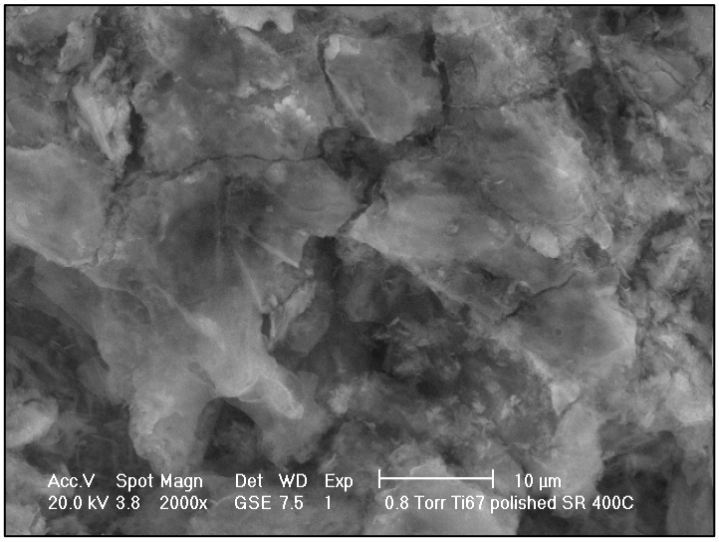

Figure 12. SEM image of the HA coating on the surface of Ti_6Al_7Nb substrate obtained with 200 W, ground and polished, then heat treated in air at 400°C. Presence of micro cracks.

The EDS analyses performed on the HA coatings on different pre-treated substrates revealed the presence of Ca, P, O; the ratio Ca/P was between, 1.78 and 1.90. As an example, Figure 13 shows the EDS spectrum corresponding to the HA coating on the polished Ti_6Al_7Nb.

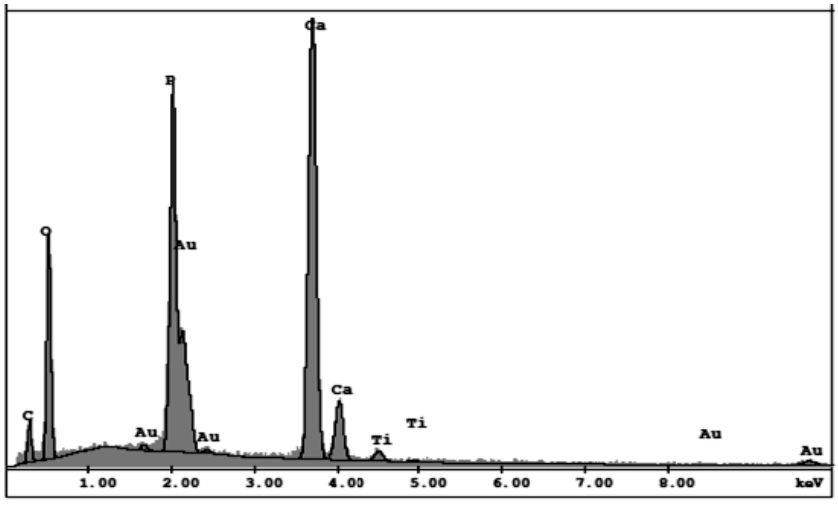

Figure 13. EDS analysis of the HA coating on the surface of Ti_6Al_7Nb substrate obtained with 200 W, ground and polished.

The formation of the micro cracks in the HA coatings could be attributed to an improper heating rate during the final heat treatment at 600°C. For the future experiments, the heating rate will be lowered in order to minimize the micro cracking occurrence in the structure of the HA coatings.

The bonding strength and failure mode of the HA coating on the different pre-treated Ti_6Al_7Nb substrates are given in Table 1. The values are in good agreement with those reported by the literature [4, 8, 9]. The highest bonding strength was displayed by the HA coating on the alkali treated Ti_6Al_7Nb substrate.

Table 1. Bonding strength and failure mode of HA coatings on different treated Ti_6Al_7Nb substrates

Substrate surface condition	Bonding strength MPa	Failure mode
Ground and polished	3.1±0.7	Mainly cohesive
Alkali and heat treated at 600°C	4.0±0.6	Mainly cohesive
Heat treated at 400°C	2.7±1.2	Mainly adhesive

CONCLUSIONS

The present work aimed to define the best surface conditioning treatment of a medical grade Ti_6Al_7Nb alloy substrate obtained by Selective Laser Melting technology with a laser power of 200 W with the aim of coating with hydroxyapatite. The deposition was performed by the dip-coating method. The polished substrates were subjected to two different treatments, as follows: a) alkali surface treatment in NaOHfollowed by a heat treatment at 600°C and b) heat treatment at 400°C, in air. The best coverage, morphology and bonding strength were displayed by the HA coating on the alkali treated Ti_6Al_7Nb substrate.

EXPERIMENTAL SECTION

The substrates were obtained by SLM of the medical grade Ti_6Al_7Nb alloy powder (MCP HEK GmbH), surface conditioned [10]. Specimens with dimensions of42 mm x 13 mm x 3 mm were produced with the same scanning strategy. Two different laser powers, 120 W and 200 W, were employed with a Realizer (MCP) Nd: YAG (Fiber Laser) machine.

The substrates were ground with 180, 400, 600 and 1000 grit SiCabrasive paper. Polishing was performed on a special cloth with 3 μm alumina powder. Ground and polished substrates were ultrasonically washed in distilled water for 10 min, and then dried at 80°C for 30 min. Different surface conditioning treatments were applied to the substrates, as follows:

- Alkali heat treatment consisting in the immersion of the substrates in a NaOH 5M solution at 60°C for 24 h, followed by a final heat treatment at 600°C for 60 min, in air, with furnace cooling;
- Heat treatment at 400°C in air for 60 min., with furnace cooling.

All heat treatments were performed in a Programix (UGIN-Dentaire) furnace.

For dip-coating, a HA solution with pH 4.5 was used. The substrates were immersed in the HA solution for 10 sec., then withdrawnat a rate of 0.6 mm/sec, and dried at 120°C for 15 min. This sequence was repeated for five times. At the end, the coated substrates were heat-treated at 600°C for 30 min, in air, with furnace cooling. The heating rate up to the treatment temperature was 2°C/min.

Coating morphology analyses were carried out witha scanning electron microscope Philips XL30 ESEM equipped with a sapphire Si(Li) EDS detector.

The surface roughness of the SLM specimens was determined with a Mitutoyo tester.

The micro hardness HV0.1 of the Ti alloy substrates was measured witha Paar MHT-4 tester.

Pull-off tests were carried out on a Zwick Z005 Roell universal testing machine, according to ASTM C 633-01. A steel rod with 12 mm diameter was carefully glued on the HA coating surface with an ABRO epoxy resin and hardener.The rod was fixed in the upper grip of the testing machine, while the substrate was fixed in the lower grip by means of a dispositive especially designed to minimize the eventual shear stresses in the coating, during the test. The test speed was 0.5 mm/min.

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