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Double-layer glass-ceramic coatings on Ti6Al4V for dental implants

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Abstract

Double-layer bioactive glass-ceramic coatings were prepared on Ti–6Al–4V substrates by dipping and firing. A SiO_2–CaO–Na_2O–MgO–P_2O_5–K_2O (SCP) based glass was used as first layer in direct contact with the metallic substrate and a SiO_2–Al_2O_3–P_2O_5–K_2O–CaO–F^- (SAF) based glass-ceramic was used as outer bioactive layer. The deposition of the intermediate SCP layer was necessary in order to obtain a good adhesion of the coating to the substrate, to minimize the reactivity between the substrate and the outer glass-ceramic coating and thus to preserve the nature of its crystalline phases. The coated samples were characterised by means of X-ray diffraction (XRD), scanning microscopy (SEM), and compositional analyses (EDS). The bioactivity of the coated samples was studied by soaking them in simulated body fluid (SBF) in order to observe the growth of an apatite layer on their surface. The optimised coating method was then used to coat Ti6Al4V screws for dental applications.

Keywords: Apatite; Biochemical applications; Glass; Glass ceramics; Implants

1. Introduction

Ti and Ti-based alloys are widely used in several fields of bone substitution due to their biocompatibility, high corrosion resistance and good mechanical properties. Many kinds of prosthetic implants have been developed for both orthopaedic and dental applications.

It is well known that, when implanted, titanium alloys do not bond with the bone by a chemical or biological interaction, but simply by morphological connection to the bone. This insufficient adhesion to the bone, due to the lack of a specific biological response from the living tissues, can progressively form a non-adherent fibrous capsule around the implant, leading, in some cases, to interfacial displacements, and clinical failure.[1] Moreover, a certain degree of chemical degradation of these metals may occur.[2]

Several bioactive materials are able to induce a biological bonding with both soft and hard tissues. Among them, bioactive glasses and glass-ceramics have been widely studied, because of their controlled surface reactivity and good bone bonding ability.[2,3] These materials, when put in contact with biological fluids, are able to provide a strong bonding with the surrounding tissues, by a complex mechanism based on ion leaching, controlled dissolution of the glass surface and precipitation of an apatite layer from the solution.

Titanium alloys can be coated by bioactive glasses, using different methods such as conventional enamelling, sputtering techniques and Vacuum Plasma Spray.[3–8] The as-obtained implants can offer several advantages, in terms of the high mechanical properties of the metallic substrate combined with the bioactivity of the coating. Moreover, a good protection of the substrate from corrosion is provided. The sputtering and Plasma Spray techniques could present some problems related to the difficulty of coating complex shapes, to the eventual compositional modifications of the coating, and to their high cost. On the contrary, the enamelling technique is a very inexpensive way to coat a lot of substrates, even of complex shape, and it is easily applicable to glasses and glass-ceramics because of the peculiar softening properties of these materials. For this

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reason, bioactive glasses and glass-ceramics do represent a good alternative to hydroxyapatite, commonly used as bioactive coating on metallic prostheses in order to improve their adhesion to the bone.

In this work we used a low cost and simple method to produce bioactive glass-ceramic coatings on a Ti6Al4V alloy. For this purpose, the enamelling technique was used and a multilayered coating was produced. The optimised method has been then extended to coat metallic screws for dental applications with layers of controlled thickness.

2. Experimental

The double-layer coating was prepared by using two different materials: a glass belonging to the system SiO_2–CaO–Na_2O–MgO–P_2O_5–K_2O (named SCP in this work) having a linear expansion coefficient of 9×10^{-6} $°C^{-1}$, and a bioactive SiO_2–Al_2O_3–P_2O_5–K_2O–CaO–F^- based glass-ceramic (named SAF in this work) with a linear expansion coefficient of 9×10^{-6} $°C^{-1}$. The compositions of the coating materials[8–11] are reported in Table 1.

The SCP glass was prepared by melting the constituents (SiO_2, $CaCO_3$, K_2CO_3, $MgCO_3$, Na_2CO_3, $Ca_3(PO_4)_2$) in a platinum crucible at 1600 °C for 1 h and by pouring the melt on a preheated stainless steel plate. This glass belongs to a system developed at the Lawrence Berkeley National Laboratory (Berkley, CA, USA), by modifying the Bioglass® base composition, with the aim of preparing a biocompatible and low-softening glass for coatings on Ti alloys substrates.[8,9]

The SAF glass-ceramic preparation involved a two step preparation. In the first one, the costituents (SiO_2, Na_2CO_3, K_2CO_3, $CaCO_3$, $Al(PO_3)_3$, Na_3AlF_6, K_3AlF_6 and $AlOOH{\cdot}H_2O$) were melted in an alumina crucible at 1500 °C, and then poured in H_2O. After this first step, the obtained material was ground and re-melted in a platinum crucible at 1550 °C and then poured on a carbon mould. The as obtained base glass was then thermally treated at 1200 °C for 1 h in order to stimulate the crystallisation of a fluoroapatite phase with a needle-shape morphology.[10,11] Both SCP and SAF were separately ball milled and sieved to a grain size $<30\mu m$. A part of bulk SAF glass-ceramic was cut and polished down to a 1 μm diamond paste, in order to produce small bars of a final size of $50\times5\times5$ mm^3. Dilatometric measurements (Netzsch dilatometer) were performed on bars in order to determine the softening point of the glass-ceramic.

Table 1
Compositions (wt.%) of the SCP glass and SAF glass-ceramic

wt.%	SCP	SAF
SiO_2	61.1	26.2
Al_2O_3	–	17.9
Na_2O	10.3	–
P_2O_5	6.0	17.5
CaO	12.6	19.6
K_2O	2.8	10.5
MgO	7.2	–
F^-	–	8.3

In order to remove the surface TiO_2 layer, each Ti6Al4V substrate (10×10 mm^2 surface, 1 mm depth) was chemically cleaned by the following route: washing in acetone, soaking in a 0,06 M $Na_3PO_4{\cdot}12H_2O$ solution at 80 °C, washing in hot water, soaking in acid solution (5 ml HF 40%vol + 35 ml HNO_3 70%vol in 60 ml H_2O) for 5 min, washing in water and drying.

The as cleaned Ti6Al4V substrates were then coated by a two-step firing process. Suspensions of SCP and SAF were separately prepared mixing weighed amounts of powders in a beaker containing a proper amount of ethanol as liquid medium. The suspension was then agitated with a magnetic stirrer until a partial liquid uptake occurred, in order to reach a satisfactory degree of viscosity. The titanium alloy sheets were coated first with SCP slurry by dipping into the above described suspension. The dipped sheets were placed on a refractory substrate as schematized in Fig. 1. A similar set up was successfully used by other authors[12] to coat carbon-carbon composites with a protective glass-coating. After the solvent evaporation the samples were thermally treated for 15 s at 840 °C, i.e. above the softening temperature of the SCP glass (620 °C, given in the literature)[8,9] and below the $\alpha\rightarrow\beta$ transition temperature of the Ti6Al4V alloy (955 °C). In this way, a continuous glass coating was obtained on five sides of the metallic

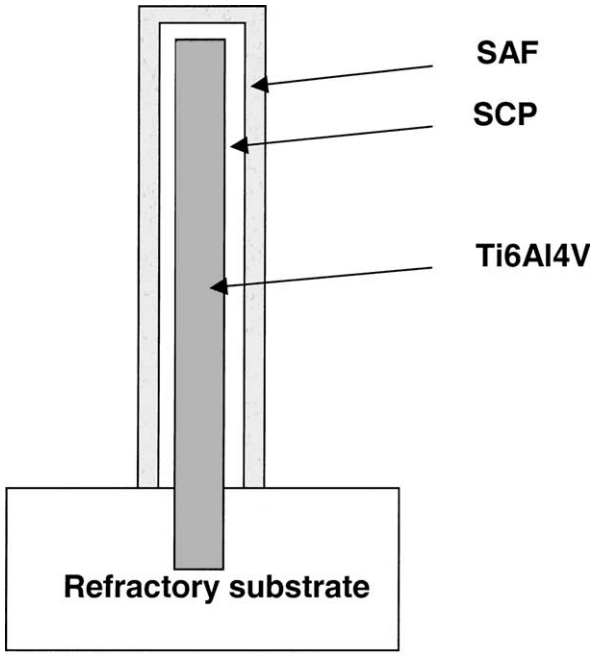

Fig. 1. Set up of the titanium alloy sheet for the coating process.

sheets. After this first treatment, a layer of SAF glass ceramic was deposed on the SCP one, by dipping the samples in a SAF suspension and firing at 950 °C for 30 s, using the same set up as for the first layer. All the thermal treatments were carried out in conventional atmosphere.

On the as coated samples a complete characterisation was carried out. The coating structure was investigated by X-ray diffraction (X'Pert Philips diffractometer) using the Bragg Brentano camera geometry and CuK_α incident radiation. The morphology and composition of the coatings were assessed by scanning electron microscopy (SEM Philips 525 M) and by energy dispersion spectrometry (EDS, Philips-EDAX 9100). An in vitro evaluation of the bioactivity of the coatings was performed, by soaking them in a simulated body fluid (SBF) with the same ion concentration of the human plasma:[13] the samples were soaked in 50 ml SBF, in polyethylene bottles, at 37 °C, without stirring. After 60 days, the samples were removed from the solution, washed in distilled water, dried at room temperature and characterised by XRD, and SEM observations.

Some preliminary mechanical tests (comparative shear tests by means of a Schenck-Trabel equipment) were performed on the coated specimens. 10×10 mm^2 coated sheets were glued together with Araldite AV 119 (Ciba-Geigy) and cured for 40 min at 120 °C, as described in the literature.[14] At least ten specimens for each sample were used for this test.

After the coating process optimisation on titanium alloy sheets, the same set up and time/temperature schedule were used to coat Ti6Al4V threaded screws for dental implants, in order to study the possibility of extending the process to complex shape medical devices.

3. Results and discussion

The time and temperature processing conditions were carefully optimised by a series of preliminary firing experiments. Some coatings, prepared by depositing a SAF layer in direct contact with Ti6Al4V at 950 °C for different times, showed a high tendency to delaminate. The high viscosity of SAF and its low wettability on Ti6Al4V, induced a poor protection towards the furnace atmosphere and thus a strong oxidation of the substrates occurred, leading consequently to a poor adhesion of the SAF coating. It was impossible to coat the titanium alloy sheets with a SAF layer at higher temperatures because of the oxidation and phase transformation problems already mentioned. For this reason, the intermediate low softening SCP layer was used. Works in the literature showed a good adhesion of this glass to Ti6Al4V.[8,9]

The as-obtained coatings showed a bilayered structure: an amorphous SCP layer in direct contact with the metallic substrate and an outer SAF glass-ceramic layer deposited on top of it. In Fig. 2, a dilatometric curve of bulk SAF glass ceramic is reported (heating rate 10 °C/min). This shows a broad and low-intensity expansion effect in the range 450–800 °C followed by a shrinkage due to a beginning softening above 800 °C and very sharp shrinkage above 1000 °C due to more intense viscous flow.

Fig. 3a shows a polished cross section of one of the coated samples, after chemical etching by a 1:1 HF/HNO_3 aqueous solution (5%vol): coatings of about 200 μm thickness were obtained. The outer SAF layer (about 100 μm thick) shows a homogeneous interface with SCP. The chemical etching revealed its glass-ceramic structure

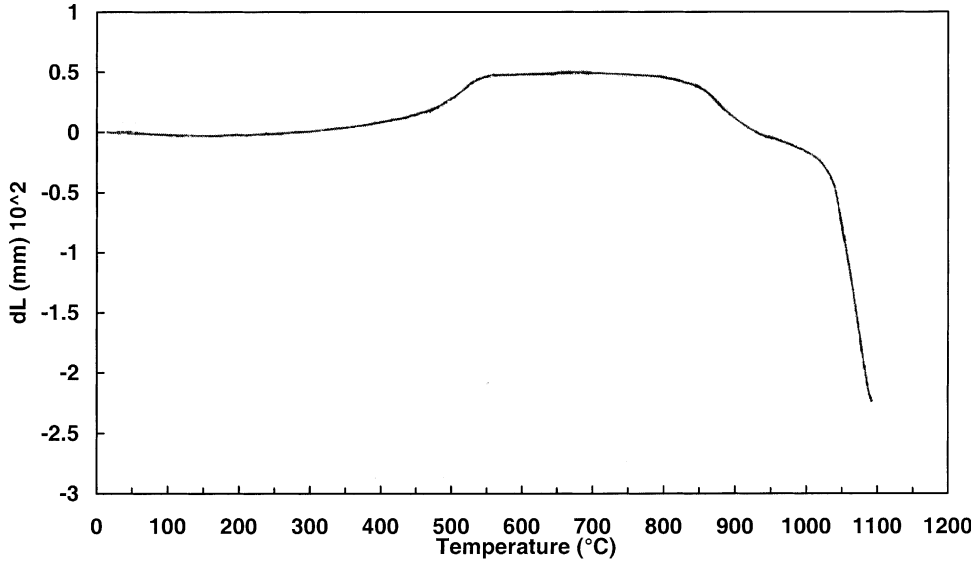

Fig. 2. Dilatometric curve of a bulk SAF glass ceramic.

and the presence of some residual porosity due to the production process. In fact, as highlighted by the dilatometic measurements, even if the SAF glass-ceramic reaches a low viscosity above 1000 °C, it also shows a softening effect above 800 °C. Thus, the firing process carried out in order to produce the outer SAF layer was more a sintering process than an enameling one. The SCP intermediate layer (about 100 μm thick as well) shows a very good adhesion to the titanium substrate with very few indications of residual porosity. This glass belongs to a low-melting system and so the temperature used to prepare this first layer was close to the liquid/melting range. A detail of the interface between the metallic substrate and the SCP layer is reported in Fig. 3b, where the high degree of adhesion and the absence of detrimental reaction layers can be observed

The first firing process, used to coat the Ti alloy sheets by the SCP layer, was performed for few seconds at 840 °C. °Since the process was very fast, this treatment did not induce a strong oxidation of the metallic substrate. Moreover the substrate was immediately covered by a liquid SCP layer. This temperature was close to the liquid/melting point for this low softening glass and was high enough to induce a certain viscous flow of the glass on the substrate. For this reason it was possible to induce a good adhesion of the SCP glass to the metallic sheets and so it was not necessary to fire the samples at a higher temperature. The SAF layer was produced at a slightly higher temperature (950 °C), because of the different softening properties of this glass-ceramic. However, since a glassy SCP layer already covered the substrate on which the SAF was deposited, it was possible to operate at this relatively high temperature without inducing detrimental reactions at the interface between the metal and the first SCP layer. At this temperature, the SCP layer already present on the Ti sheets probably flowed more than during its deposition, and this viscous flow was favourable to produce a good adhesion with the SAF glass-ceramic layer. Thermal treatments at temperatures lower than 950 °C did not produce a sufficient adhesion between SCP and SAF, nor an adequate cohesion of the SAF layer. Thermal treatments at higher temperatures were also not suitable, in order to avoid strong diffusion effects between SCP and SAF, and thus compositional and structural modifications in the coating, due to the low softening properties of the SCP layer.

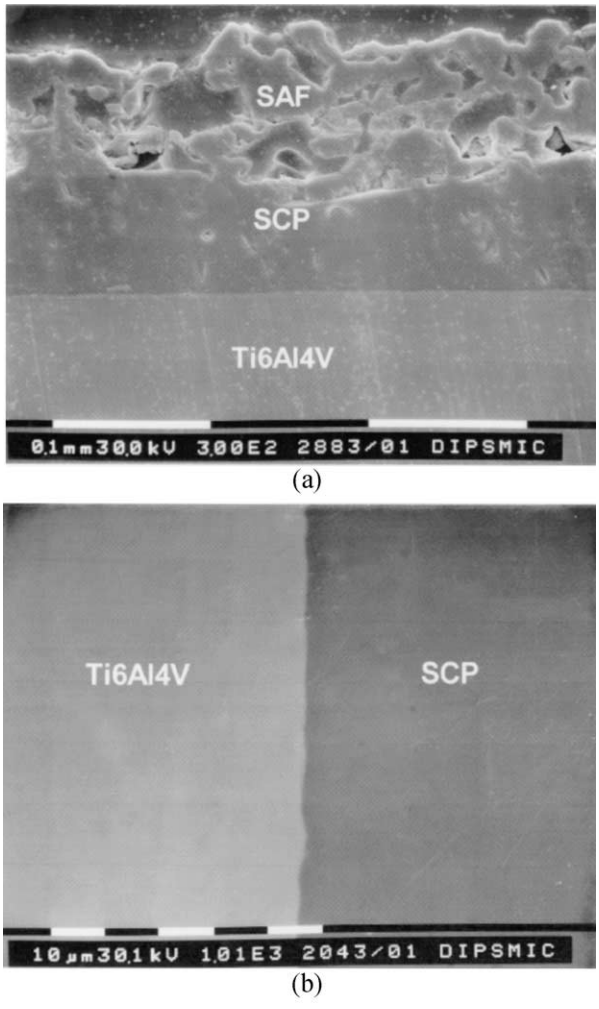

Fig. 3. (a) Polished cross section of a coated sample, after chemical etching by a 1:1 HF/HNO_3 aqueous solution (5%vol). (b) Detail of the interface between the metallic substrate and the SCP layer.

Fig. 4a shows a top view of a coated sample, where the rough morphology of the surface is evidenced. This feature is related to the temperature reached during the firing process, which did not involve the complete melting of the SAF glass-ceramic but only the softening of its residual amorphous phase by a viscous-flow sintering process. A rough surface is not detrimental for coated implants, since a tailored roughness can enhance osteointegration. In Fig. 4b a top view of a coated sample is reported, after chemical etching, which shows the presence of the needle-shaped crystals.

Mean EDS analyses made on the different layers show that the SAF glass-ceramic and the SCP glass do not remarkably diffuse one into each other during the firing process. In Fig. 5a and b the EDS results of mean analyses performed on the SCP and SAF layer respectively are reported: it is evident that the different composition of the two layers is retained, due to the absence of remarkable interdiffusion (the unlabelled signal close to that of phosphorous in Fig. 5b, is due to the thin gold layer applied on the samples for SEM observation).

XRD analysis performed on top of the double coatings confirmed the glass-ceramic structure of the outer layer. In Fig. 6 the XRD pattern of the SAF coating is reported (pattern a): as expected, all the detected peaks correspond to the fluoroapatite one.

By soaking the coated samples at 37 °C for 60 days in simulated body fluid, the growth of an apatite layer was observed. This layer was also detected by X-ray diffrac-

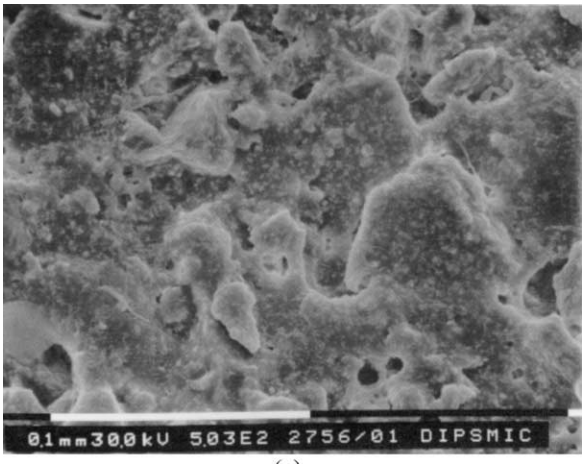

Fig. 4. Top view of a coated sample before (a) and after (b) chemical etching.

tion, as reported in Fig. 6 (pattern b): by comparing pattern a and b it is evident, after 60 days in SBF, that a broadening of some of the strongest signals of apatite occurs (see 2 theta 38.5, 32.22 and 28.9) due to the growth of this phase from an aqueous solution (it is not possible to discern between different kinds of apatite in terms of peak position, since all apatites have, more or less, the same pattern). Fig. 7 reports a micrograph of a coated sample after 4 weeks of soaking into the simulated body fluid, in which globular agglomerates of hydroxyapatite are evidenced over the surface.

The good biological properties of the SAF glass-ceramic are well-known and documented elsewhere[15,16] both for pure bulk SAF glass-ceramic and for SAF coatings on alumina. The growth of the apatite layer on the glass-ceramic coating on titanium alloy substrates shows that the firing process used for the coating preparation did not affect the bioactivity of this material. Moreover, on the basis of the X-ray results and the morphological observations we conclude that the coating process did not strongly affect either the nature of the crystalline phases present or their shape and thus we can reasonably state that the biological response of the realised coatings would resemble that of bulk SAF.

The adherence of the coatings to the substrate was evaluated by means of preliminary shear tests. The results ($\tau = 3 \div 7$ MPa) are still below those obtained for analogous coatings tested in similar conditions, obtained by VPS techniques ($\tau = 26 \div 36$ MPa).[14] A morphological observation performed on the specimens after mechanical tests revealed an adhesive failure. This feature must be improved in order to produce implantable devices, by means of a further surface optimisation

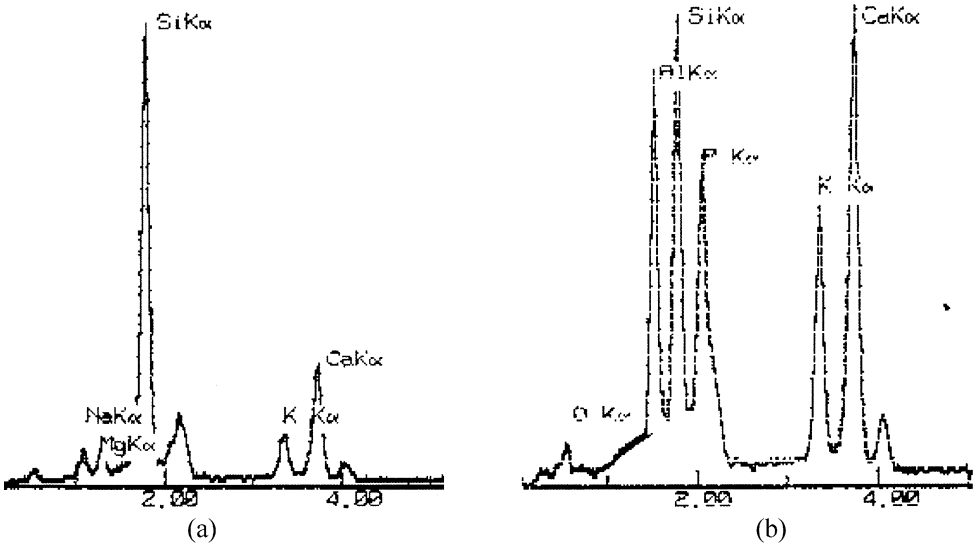

Fig. 5. EDS results of mean analyses performed on the SCP (a) and SAF (b) layers.

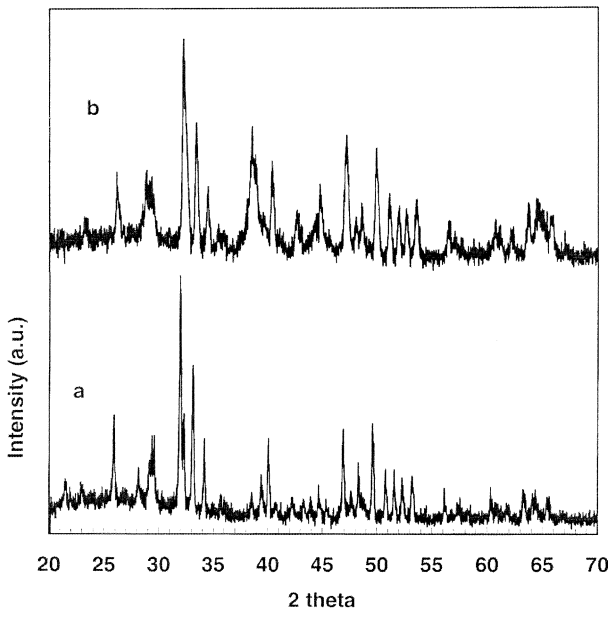

Fig. 6. XRD pattern of the SAF coating before (a) and after (b) soaking in SBF.

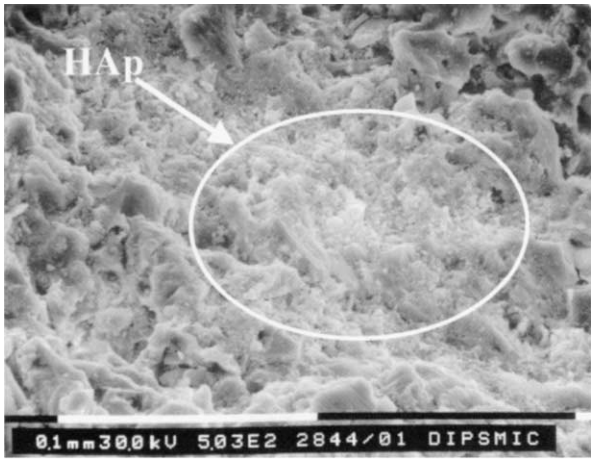

Fig. 7. Top view of a coated sample after 4 weeks of soaking into simulated body fluid.

Fig. 8. General view of the threaded screw coated by the optimised two-step firing process.

of the substrates before coating (e.g. roughening or controlled preoxidation).

The two-step coating process was successfully used in order to coat some threaded Ti6Al4V screws for dental implants. Coatings with the same morphology, composition and structure as those obtained on the sheets were observed. Globally, a good quality of the coating was achieved. Fig. 8 shows a general view of a threaded screw coated with a double-layer coating by the optimised two-step process.

4. Conclusions

In this work, a simple and low cost firing method was optimised in order to coat Ti6Al4V substrates by a double-layer bioactive glass-ceramic coating. Due to the need to work below the $\alpha \rightarrow \beta$ transformation of the Ti alloy, the use of a low-melting intermediate glass layer was necessary to ensure the adhesion of the outer bioactive layer, based on a high-softening glass-ceramic. The intermediate layer was also chosen in order to match the thermal expansion coefficient of both the metal and the outer glass-ceramic. The process used for the coating preparation did not affect the bioactivity of the glass-ceramic surface and did not modify either the nature of the crystalline phases or their shape. The optimised method was successfully used to coat Ti6Al4V screws for dental applications.

References

1. Hench, L. L., Bioceramics: from concept to clinic. *J. Am. Ceram. Soc.*, 1991, **74**(7), 1487–1510.
2. Hench, L. L., Bioactive glasses. In *An Introduction to Bioceramics, vol. 1*, ed. L. L. Hench and J. Wilson. World Scientific Pub, 1993, pp. 41–62.
3. Ferraris, M., Rabajoli, P., Brossa, F. and Paracchini, L., Vacuum plasma spray deposition of titanium particle/glass-ceramic matrix biocomposites. *J. Am. Ceram. Soc.*, 1996, **79**(6), 1515–1520.
4. Verné, E., Ferraris, M., Ventrella, A., Paracchini, L., Krajewski, A. and Ravaglioli, A., Sintering and plasma spray deposition of bioactive glass-matrix composites for biomedical applications. *J. Eur. Ceram. Soc.*, 1998, **18**(4), 363–372.
5. Verné, E., Ferraris, M., Jana, C. and Paracchini, L., Bioverit®I base glass/Ti particulate biocomposite: in situ vacuum plasma spray deposition. *J. Eur. Ceram. Soc.*, 2000, **20**, 473–479.
6. Ferraris, M., Rabajoli, P., Brossa, F. and Paracchini, L., Vacuum plasma spray deposition of titanium particle/glass-ceramic matrix biocomposites. *J. Am. Ceram. Soc.*, 1996, **79**(6), 1515–1520.
7. Jana, C., Nisch, W. and Grimm, G., Production and characterization of thin films of Bioverit—type glasses deposited by RF magnetron sputtering. In *Advances in Science and Technology, vol.12 (Materials in Clinical applications*, ed. P. Vincenzini. Techna, Faenza, 1995, pp. 257–262.
8. Gomez Vega, J. M., Saiz, E., Tomsia, A. P., Marshall, G. W. and Marshall, S. J., Bioactive glass coatings with hydroxyapatite and Bioglass particles on Ti-based implants. *Processing. Biomaterials*, 2000, **21**, 105–111.

9. Pazo, A., Saiz, E. and Tomsia, A. P., Silicate glass coatings on Ti-based implants. *Acta Mater*., 1998, **46**(7), 2551–2558.
10. Moisescu, C., Jana, C. and Rüssel, C., Crystallization of rod-shaped fluoroapatite from glass-melts in the system SiO_2–Al_2O_3–CaO–P_2O_5–Na_2O–K_2O–F^-. *J. Non-Cryst. Solids*, 1999, **248**, 169–175.
11. Moisescu, C., Jana, C., Habelitz, S., Carl, G. and Rüssel, C., Oriented Fluoroaptite glass-ceramics. *J.Non-Cryst. Solids*, 1999, **248**, 176–182.
12. Isola, C., Appendino, P., Bosco, F., Ferraris, M. and Salvo, M., Protective glass-coating for carbon-carbon composites. *Carbon*, 1998, **36**(7–8), 1213–1218.
13. Kokubo, T., Kushitai, H., Ohtsuki, C., Sakka, S. and Yamamuro, T., Chemical reaction of bioactive glass and glass-ceramics with a simulated body fluid. *J. Mater. Sci.: Mat. Med.*, 1992, **3**, 79–83.
14. Verné, E., Bona, E., Angelini, E., Rosalbino, F. and Appendino, P., Correlation between microstructure and properties of bio-composite coatings. *J. Eur. Ceram. Soc*., 2002, **22**, 2315–2323.
15. Moisescu, C., Jana, C., Russel, C., Habelitz, S. and Carl, G., Glass-ceramics with oriented needle-shape apatite crystals produced by extrusion. In *Advances in Science and Technology, (Materials in Clinical applications)*, ed. P. Vincenzini. Techna, Faenza, 1999, pp. 41–48;.
16. Verné, E., Bosetti, M., Vitale Brovarone, C., Moisescu, C., Lupo, F., Spriano, S. and Cannas, M., Fluoroapatite glass-ceramic coatings on alumina: structural, mechanical and biological characterisation. *Biomaterials*, 2002, **23**, 3395–3403.