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Glazing of alumina by a fluoroapatite-containing glass-ceramic

E. VERNÈ, C. VITALE BROVARONE
Materials Science and Chemical Engineering Department, Polytechnic of Torino, Torino, Italy
E-mail: enrica.verne@polito.it

C. MOISESCU
Johnson & Matthey B. V. Fregatweg 38-6222 NZ, Maastricht, Nederland

Glazing of alumina substrates was performed in order to prepare bioactive glass-ceramic coatings for biomedical applications. The coating material was a fluoroapatite-containing glass-ceramic (SAF) with a good degree of bioactivity. A careful optimisation of the coating conditions was carried out. The obtained coatings were characterized by means of scanning electron microscopy (SEM), compositional analysis (EDS), X-Ray diffraction (XRD), and *in vitro* tests (soaking into a simulated body fluid). Direct firing of SAF powders on the ceramic substrates gave unsatisfactory results in terms of crack propagation and bioactivity, due to the nucleation of a non-bioactive Al-rich phase (leucite) with high linear expansion coefficient. The use of an intermediate layer based on a SiO_2-CaO glass (SC) was necessary in order to avoid Al ions diffusion through the coating and thus the formation of undesired additional phases. The coatings obtained with the optimised processing parameters resulted to be adherent, defect-free, and characterized by unchanged composition and structure as well as unmodified bioactivity if compared with the bulk SAF glass-ceramic.

1. Introduction

Bioactive glasses and glass-ceramics have been widely studied in the last decades and proposed as bone substitutes because of their peculiar property of promoting new tissue formation [1–4]. Different bioactivity mechanisms can be identified in consequence of the glass composition and the presence of specific crystalline phases [5, 6].

Bioactive glasses show a specific chemical reactivity when in contact with body fluids, due to alkali or alkaline earth ions leaching (usually by cation exchange with H_3O^+ ions), network dissolution, by breaking of Si—O—Si bonds and formation of silanols (or silica-rich gel layer), and precipitation of a calcium-phosphate rich layer on the glass surface. The bioactivity of glass-ceramics can be enhanced if hydroxyapatite or fluoroapatite are present as crystalline phases [7, 8]. In fact, in this case, the bioactivity of the residual glassy phase will be combined with the osteoconductivity of the crystalline phase. In any case, a common requirement to bond to living bone is recognized to be the formation of a layer of hydroxyapatite on their surfaces, when put in contact with biological fluids.

This feature is often observable during *in vitro* tests, by soaking these materials in an acellular simulated body fluid (SBF) [9]. Bioactive glasses and glass-ceramics are generally proposed as not load bearing implants or as coatings on high strength ceramic or metallic substrates [10]. Several works are reported in literature about glass and glass-ceramic coatings on alumina for medical applications [11–14]. Alumina is widely used in several biomedical applications due to its high wear resistance and fracture toughness. This ceramic is considered an almost inert material because it does not exhibit any chemical bonding with bone *in vivo*, but it shows only a morphological fixation, and the formation of a non-adherent fibrous capsule at the tissue interface that can cause the implant loosening and clinical failure [15]. The use of a bioactive coating can improve the alumina osteointegration.

A simple way to coat alumina substrates by bioactive glasses or glass-ceramics is conventional glazing, i.e. firing of glass powders directly on the substrates at optimised time/temperature conditions. However, some difficulties are involved in the coating of alumina, due to its low thermal expansion coefficient and its high reactivity with glasses and glass-ceramics at high temperatures. In order to reduce Al^{3+} diffusion from the substrate toward the coating surface and thus to avoid its contamination, it is possible to interpose an intermediate layer [14] between alumina and the bioactive glass. Besides, this intermediate layer can positively affect the adhesion of the coating to the substrate by increasing the wetting ability and by allowing a proper match of the thermal expansion coefficients. In this work, the preliminary studies connected with the optimisation of the preparation process of bioactive double-layer glass-ceramic coatings on alumina are described. The proposed double-layer structure is composed by an inner SiO_2-CaO amorphous layer and a fluoroapatite based glass-ceramic outer one. Coatings prepared with the optimised conditions found with this work, showed a promising index of bone material integration by *in vitro* biocompatibility tests [16, 17]. The objective of the present work is to examine and describe the influence of the inner layer on the crystallisation of the outer coating, depending on the reactions with the substrate.

2. Experimental

2.1. The coating materials

The wt% compositions and some properties of the two coating materials are reported in Table I [16]. A glass based on the system SiO_2-CaO (SC) was used as inner intermediate layer, and a glass-ceramic based on the system SiO_2-Al_2O_3-P_2O_5-K_2O-CaO- F^- (SAF) was used to produce the outer layer. The SC glass was prepared by a conventional melting and pouring route: the raw products (SiO_2, $CaCO_3$) were intimately mixed and then molten in a platinum crucible at 1600°C for 1 h; the melt was then poured on a preheated stainless steel plate, in order to obtain a bulk material without residual stresses.

The SAF glass-ceramic was prepared by a three-step route as follows:

– melting of the starting products (SiO_2, K_2CO_3, $CaCO_3$, $Al(PO_3)_3$, K_3AlF_6 and AlOOH H_2O) in an alumina crucible at 1500°C, pouring the melt in cold water and grounding to obtain powders,

– re-melt of the powders in a platinum crucible at 1550°C and then pouring on a carbon mould, obtaining a bulk material,

– thermal treatment of the poured SAF bulk to induce the crystallisation of a needle-shape fluoroapatite [8].

The nucleation and growth of fluoroapatite was induced in order to improve the osteoconductivity of SAF glass-ceramic, and its *needle-shape* morphology was engineered in order to mimic the shape of human bone hydroxyapatite. The SAF glass-ceramic was cut obtaining bars of a final size of 5 × 5 × 25 mm^3. The thermal expansion coefficient of SAF glass-ceramic was determined on the as obtained bars by dilatometry (Netzsch, Model 402 E, Exton, PA) whereas the thermal expansion coefficient of SC was known from literature [6].

TABLE I wt% compositions and some properties of SC and SAF

Constituents (wt%)	SC	SAF
SiO_2	53.7	26.2
Al_2O_3	–	17.9
P_2O_5	–	17.5
CaO	46.3	19.6
K_2O	–	10.5
F^-	–	8.3
Thermomechanical properties		
Density (g cm^{-3})	2.8	2.3
Thermal expansion coefficient (α)	10.3×10^{-6} K^{-1}	$8 \div 9 \times 10^{-6}$ K^{-1}
T_{soft} (°C)	-	900–1000

The as obtained SC (glass) and SAF (glass-ceramic) were then ball milled to obtain powders and sieved to a grain size <63 μm.

2.2. Optimization of the coating process

Specimens of full density medical-grade α alumina (1 cm^2 surface) were used as substrates. They were ultrasonically cleaned in acetone for 10 min in order to avoid the presence of contaminants. Weighed amount of SC or SAF powders were mixed with a proper quantity of ethanol in order to obtain a suspension that was poured in a beaker where the alumina substrates were displaced. By gravity-controlled deposition, the powders uniformly covered the beaker underside and thus the alumina substrates. The amount of the suspended powders was chosen in order to produce a deposited layer of desired thickness. The reactivity of the SAF glass-ceramic with the substrate was carefully investigated by means of several preliminary coating experiments.

2.2.1. SAF coatings

A first series of coatings was realised depositing a SAF layer in direct contact with the alumina substrate; gravity decantation of a SAF suspension in ethanol was used at this purpose. The SAF powders deposition took a few hours and when it was complete the liquid medium was again transparent. Afterwards, the ethanol was driven away by drying the system at 70°C for a few hours until only a green coating on alumina was left. The green coating was then thermally treated at temperatures between 1325 and 1350°C for 10 min, and then annealed at 600°C for 2 h. Aiming to realise coating of uniform thickness, sometimes a second SAF layer was applied on top of the first one and the sample was fired again. Table II resumes the different time and temperature conditions used to realize the coatings.

2.2.2. SC + SAF coatings

The bi-material coatings were prepared in two steps by pouring two different powders suspensions in ethanol (SC and SAF respectively) on the alumina substrates. In this case, a first deposition of an SC layer on the substrate was carried out, followed by a drying stage to drive off the ethanol and a last firing treatment at 1450°C for 20 min. The coating was then cooled down

TABLE II Time and temperature conditions used to realize the SAF coatings

Condition ident. number	First layer	Second layer	Annealing
1	SAF 1350°C-5 min	SAF 1325°C-5 min	600°C-2 h
2	SAF 1325°C-5 min	–	600°C-2 h
3	SAF 1350°C-5 min	–	600°C-2 h

TABLE III Time and temperature conditions used to realize the SC/SAF coatings

Condition ident. number	First layer	Second layer	Annealing
4	SC 1450°C-20 min	SAF 1350°C-5 min	600°C-2 h
5	SC 1450°C-20 min	SAF 1350°C-10 min	600°C-2 h
6	SC 1450°C-20 min	SAF 1375°C-5 min	600°C-2 h
7	SC 1450°C-20 min	SAF 1375°C-10 min	600°C-2 h
8	SC 1450°C-20 min	SAF 1400°C-5 min	600°C-2 h
9	SC 1450°C-20 min	SAF 1400°C-10 min	600°C-2 h

and a SAF layer was deposited on top of it by gravity decantation of the powders suspension on the SC coated substrates. This second layer was fired at temperatures between 1350 and 1400°C for 10 min and annealed at 600°C for 2 h. Table III resumes the different time, temperature and type of layers used to realize the coatings.

3. Characterisation of the coatings

On the as obtained coatings several phase analyses by X-ray diffraction (X'Pert Philips diffractometer) were carried out using the Bragg Brentano camera geometry and the CuKα incident radiation. The morphology and composition of the coatings were investigated by scanning electron microscopy (SEM Philips 525 M) and compositional analysis (energy dispersion spectrometry—EDS, Philips-EDAX 9100). For comparative purposes, bulk SAF glass-ceramic specimens, were characterized by X-ray diffraction.

4. Results and discussion

4.1. SAF coatings

The coatings obtained by directly firing one or two layers of SAF glass-ceramic on alumina gave almost the same results, differing only in the coating thickness and the surface quality. Coatings of about 80 to 300 micron thickness have been produced, depending on the deposition parameters. Fig. 1 shows a cross section of a coating obtained firing the SAF powders in the condition n. 5 (see Table I). The coating is characterised by a high degree of homogeneity, a good quality of the interface with the alumina substrate and a glass-ceramic nature. Some cracks are still evident from the surface toward the interface (one of them is evidenced in the picture). EDS analyses, performed both on the coating section and surface, revealed the presence of Al, Si, P K and Ca, as expected by the SAF chemical composition, with few excess of Al in respect to the content expected in the pure SAF glass ceramic, (see at this purpose Fig. 2 where the EDS pattern registered on a cross-section of a sample prepared in the conditions n. 1 is reported in comparison to that recorded on the bulk SAF).

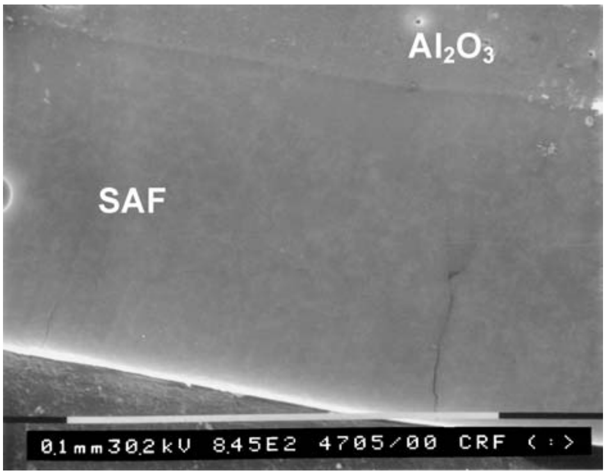


Figure 1 Cross section of a coating obtained firing the SAF powders in the condition no. 5.

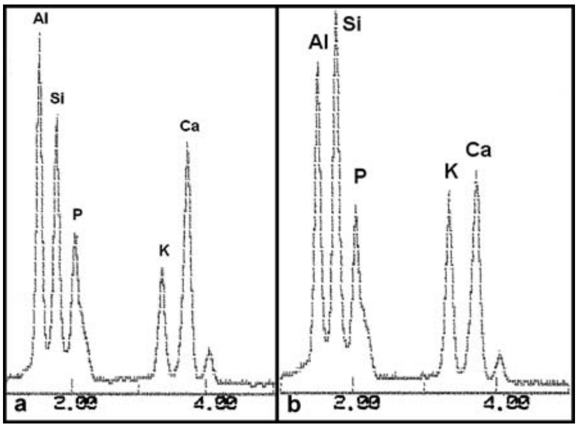


Figure 2 EDS patterns registered near the interface with the substrate of a sample prepared in the conditions n. 1 (a) and on the bulk SAF (b).

The phase analysis performed on the SAF surface revealed its glass-ceramic nature, and two different crystal phases were detected. A progressive lowering of the fluoroapatite signals was noted as the coating time and temperature increased, with the contemporaneous increasing of the signals of leucite ($K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$). Fig. 3 reports the XRD patterns of bulk SAF glass–ceramic (pattern a) compared with one obtained on a SAF coated alumina (pattern b). In the second one it is evident the presence of strong signals of leucite and the lowering of the fluoroaptite ones.

The presence of leucite (an Al containing phase) in all these coatings can be explained by the reactivity between the coating and the substrate, even if the firing process did not exceed five minutes. The little enrichment in Al of the glass-ceramic at the firing conditions was sufficient to modify the chemical composition of the original SAF glass-ceramic inducing the nucleation and growth of an additional crystalline phase (leucite beside fluoroapatite). The influence of the alumina substrate in the formation of leucite was confirmed by firing some SAF powders in the same conditions used for the coatings preparation on a platinum sheet. A phase analysis performed by XRD on the samples fired on platinum gave as result the presence of only fluoroapatite.

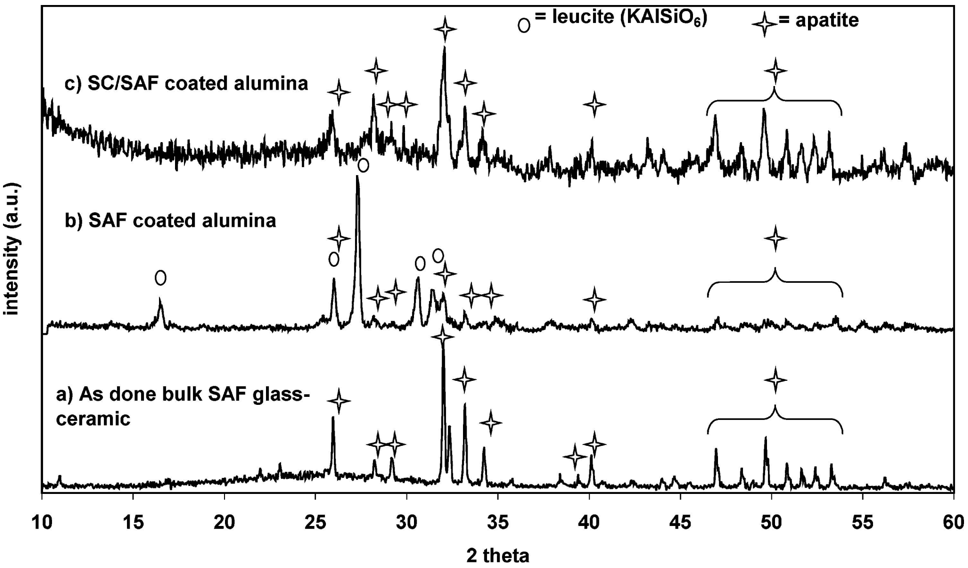


Figure 3 XRD patterns of bulk SAF glass-ceramic (pattern a) of a SAF coated alumina (pattern b) and of a SC/SAF coated alumina (pattern c).

Ceramics containing leucite are commonly used in dental applications where a ceramic-to-metals contact is needed, due to the high thermal expansion coefficient of this crystalline phase (2,5 × 10^{-5} °C^{-1}) [18]. However, leucite is not bioactive, so its presence in the SAF coatings on alumina is considered an undesirable feature, since in our case a bioactive coating with thermomechanical properties close to alumina is needed. This can partially explain the poor mechanical performances in terms of crack nucleation and propagation during cooling (see Fig. 1) revealed in the SAF coatings. We did not assess the volume fraction of leucite in our coatings, but applying the mixtures-law [19] to the α values of leucite and of SAF glass-ceramic, an estimation of the thermal expansion coefficient in the coating for different amounts of leucite in the glass-ceramic was done. As deducible from Table IV, for leucite contents higher than 10%vol, the thermal expansion coefficient of the coating rises to very high values, which do not match with the alumina one and can lead to tensile residual stresses on the coating.

The time and temperature processing conditions have been carefully calibrated to achieve a good control on the reactivity of alumina toward the coatings, so very short treatments were chosen, in order to avoid strong reaction and deep compositional modifications. Otherwise, the temperatures reached to assure the necessary wettability of the softened SAF glass-ceramic on alumina were still too high to completely avoid the aluminium diffusion in the coatings, so the formation of leucite was induced.

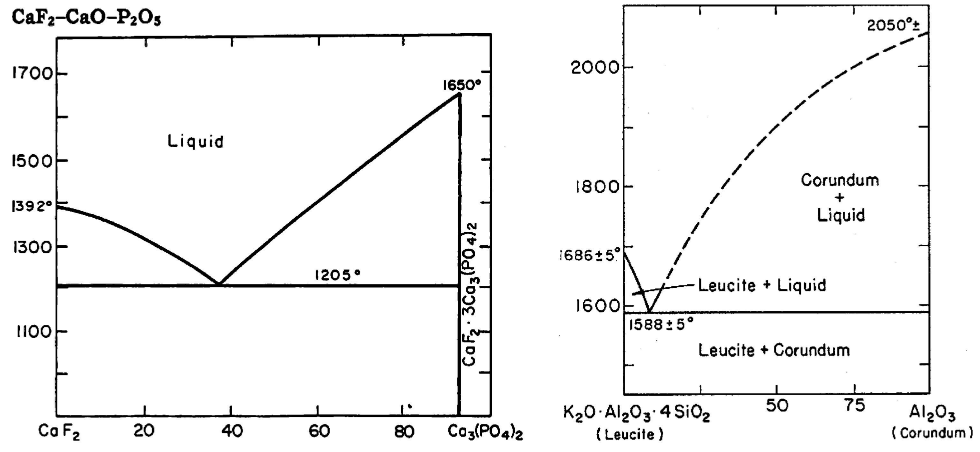
TABLE IV Estimation of the thermal expansion coefficient in the coating for different amounts of leucite in the glass-ceramic

Hypotetical leucite-containing glass-ceramic thermal expansion (10^{-6} °C^{-1})	Leucite volume fraction (%)
8.5	0
10.15	10
11.8	20
13.45	30
15.1	40
16.75	50

The analysis of the phase diagrams [20] (Fig. 4a and b) of the crystal phases involved in this process is useful to give a further explanation for such results. The growth of needle-shaped fluoroapatite crystals is usually stimulated, in the bulk SAF glass-ceramic, at 1200°C. The stability range for fluoroapatite reaches about 1680°C. During the firing process (performed at temperatures below 1350°C) the fluoroapatite crystals should not decompose. However, at these temperatures a certain degree of softening, due to the viscous flow of the residual amorphous phase, can be expected, since a good degree of wettability of SAF toward the ceramic substrate was achieved. The presence of a liquid-like phase could produce a consistent dissolution of fluoroapatite crystals. In these conditions, also a certain Al^{3+} diffusion from alumina substrates towards the softened amorphous phase can occur, producing the Al enrichment and thus a compositional modification compatible with the competitive crystallization of fluoroapatite and leucite, a crystal phase with a stability range over high temperatures (more than 1680°C). A firing process involving lower temperatures would be preferable in order to eliminate the Al enrichment and thus the leucite formation. However, some coatings obtained at lower temperatures (<1300°C) showed a high tendency to delaminate due to low wettability of SAF on alumina, because of its very high viscosity. So this approach did not produce the desired properties.

4.2. SC + SAF coatings

The processing schedule developed to prepare the two-component coatings involved two different thermal treatments. Each of them was optimised as a function of the different properties of SC and SAF (thermal expansion coefficient and viscosity), in order to reduce as much as possible the Al diffusion from the substrate, to reach a high degree of softening of the coating materials (i.e. a good wetting of the substrate),



(a) (b)

Figure 4 Phase diagrams of CaF_2-$Ca_3(PO_4)_2$ system (a) (from R. Nacken, Zentr. Mineral.Geol., 1912, p. 548) and of the $K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$–$Al_2O_3$ system (b) (from J. F. Schairer and N. L. Bowen, *Am. J. Sci.* **253**(12) (1955) 719).

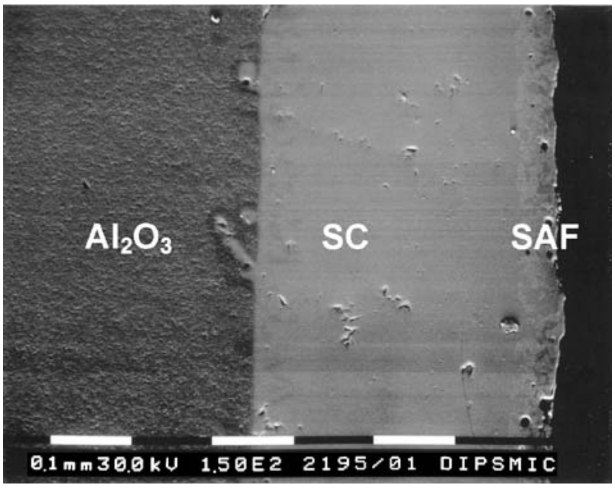
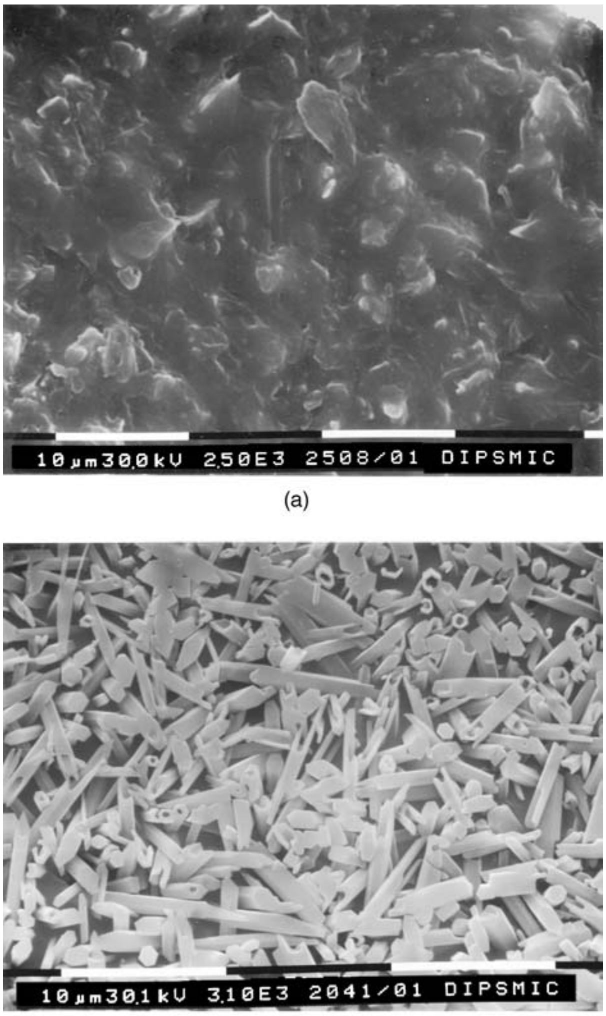


Figure 5 Polished cross section of a specimen coated by a SC/SAF layer.



(a)

(b)

Figure 6 SEM picture of the surface of a SC/SAF coated specimen, before (a) and after and (b) a chemical etching (HF:HNO_3 1:5 vol%).

and to avoid any undesired modifications of the structure of the bioactive layer (SAF) in terms of crystalline phase. During the first step the SC layer was fired on the substrate, reaching a deep softening and producing a good wetting of alumina. During the second step, the SAF glass-ceramic was sintered on the SC coating at a temperature close to its softening point, providing a uniform layer, without detrimental reactions or compositional mixing. Fig. 5 shows the polished cross section of a specimen coated by a SC/SAF layer. The whole coating, about 350 to 400 μm thick, is adherent to the ceramic substrate and shows a high degree of homogeneity. The SC intermediate layer (about 300 to 350 μm thick) shows a very good adhesion to the alumina substrate without residual porosity. The first 50 micron in the glass, close to the interface with alumina, shows a very few degree of crystallinity, but this phase did not produced severe thermal expansion mismatches (since no cracks are visible in this area), and was not investigated by XRD. The outer SAF layer (about 50 μm thick) shows a glass-ceramic nature, a very sharp interface with SC, and very little porosity. The best results in terms of homogeneity, adhesion and crystallization of fluoroapatite in the outer SAF layer were obtained by coating the substrates by treatment at 1350°C for 10 min. The EDS analyses made on top of the coatings, compared with those performed on bulk SAF, revealed that the SAF glass-ceramic did not undergo to any compositional modification after the firing process on the SC layer [17]. Fig. 6a and b reports two SEM pictures of the coating surface, before and after a chemical etching (HF:HNO$_3$ 1:5 vol.%) respectively. The crystals morphology evidenced in Figure 6b is a *needle shape* one, with crystals of an average length of 5–10 μm. The hollow morphology of the crystals is an effect of the exposure at temperature higher than 1200°C, as reported elsewhere [21]. The firing process used to coat the alumina substrates by the SC layer, was performed at a temperature close to its liquid/melting range (1450°C). This temperature was effective to induce a marked viscous flow of the glass on the substrate, which was uniformly covered by a liquid SC layer. The SAF layer was realised at a slightly lower temperature (1350–1400°C), which induce a lower softening of the inner SC layer. At these temperatures, the SC layer already present on the substrates probably flowed less than during its deposition, but this viscous flow, joined to the viscous properties of the outer SAF layer, was favorable to produce a good adhesion between the two layers.

The phase analysis performed by XRD on the coating surface confirmed the presence of only fluoroapatite as crystalline phase. Fig. 3 (pattern c) reports the XRD diagram of a coating obtained in these optimized conditions, where only the diffraction peaks of fluoroapatite are present.

The shear strength of the optimized coatings has been investigated by a comparative method using a "single-lap" specimen configuration [16]. The results obtained for this kind of coating (up to 30 MPa ± 0.3) are comparable with those of other bioactive coatings (bioactive glasses, bioactive composites, hydroxyapatite), mechanically tested in the same conditions [22–24]. The failure occurred without debonding of the coating from the substrate, but mainly by decohesion or by detachment of the glue from the metallic grips.

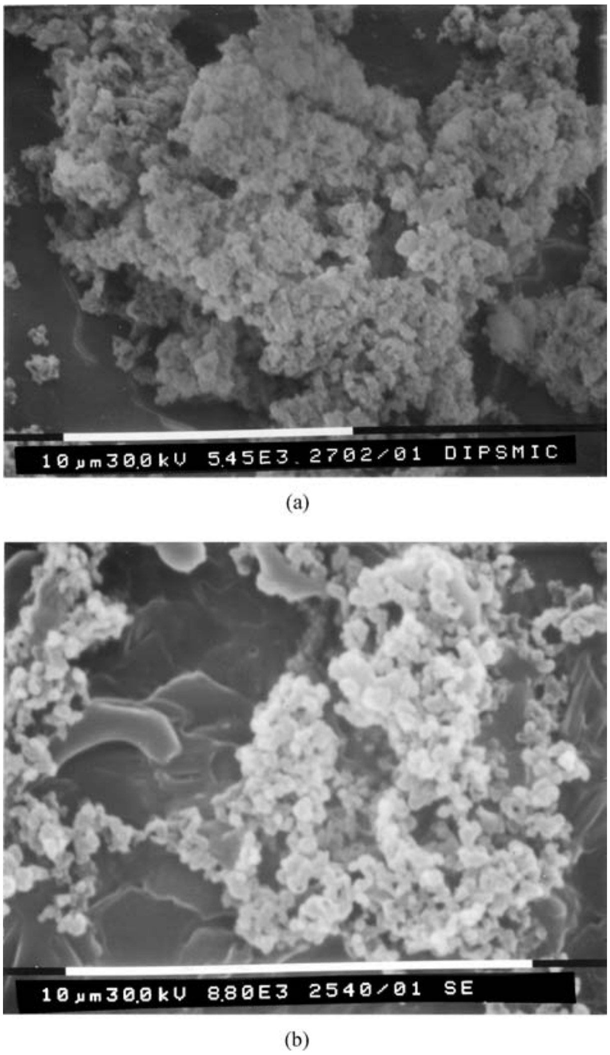


Figure 7 Surfaces of a bulk SAF (a) and a SC/SAF alumina coated specimen, and (b) respectively, after soaking in SBF.

4.3. *In vitro* tests

The bioactivity of the different coatings was tested by soaking them in an inorganic Simulated Body Fluid (SBF), as reported in ref. [17]. The coating realized by covering alumina only by SAF showed very little precipitation of hydroxyapatite, after soaking in SBF. It was impossible to detect any evident modification of the XRD patterns after soaking, and the morphological observation of the coated surfaces did not revealed the presence of any precipitated phase. The presence of leucite (bio-inert ceramic) into the coating was sufficient in order to inhibit the bioactive behaviour of the starting glass-ceramic. On the contrary, by using the intermediate SC layer, an outer SAF coating with unmodified composition and reactivity was obtained. In fact, on the SC/SAF coated substrates agglomerates of precipitated hydroxyapatite have been observed after 1 month of soaking in SBF. Fig. 7a and b report two micrographs of the surfaces of a bulk SAF and a SC/SAF alumina coated specimen respectively, after soaking in SBF. In both case white agglomerates with the typical morphology of the precipitated hydroxyapatite can be observed. The result of EDS analyses performed on these agglomerates showed the presence of Ca and P in proportion analogous to those of hydroxyapatite [17]. The XRD analysis performed on bulk SAF glass-ceramic and the SC/SAF coated sample after soaking in SBF only slightly showed the presence of precipitated apatite, due to the correspondence of its signals to those of the substrate. For the same reason it was difficult to observe the precipitation of this phase earlier than one month.

5. Conclusions

Glazing of alumina substrates was successfully performed in order to prepare bioactive glass-ceramic coatings for biomedical applications. The coating material, a fluoroapatite-containing glass-ceramic (SAF), was applied on the substrates by two different methodologies: (a) direct firing of SAF powders on alumina and (b) deposition of a double-layer coating composed by an intermediate SiO$_2$-CaO based glass layer (SC) covered by an outer SAF layer.

The first one gave unsatisfactory results, due to the nucleation of leucite, which affected the bioactivity and the mechanical performances of the coating.

The double-layer coatings were useful in order to avoid the formation of undesired additional phases due to Al ions diffusion through the coating. In fact the

SC+SAF coatings revealed their adherence to the substrates, the lack of defects, and their unchanged composition and structure. They also showed similar *in vitro* bioactivity compared to the bulk SAF glass-ceramic.

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References

1. L. L. HENCH, *J. Am. Ceram. Soc.* **74**(7) (1991) 1487.
2. W. HOLAND, *J. Non-Crystalline solids* **219** (1997) 192.
3. L. L. HENCH, *J. Am. Ceram. Soc.* **81**(7) (1998) 1705.
4. *Idem.*, in "Materials Science Forum" (Trans. Tech. Pub. Switzerland, 1999) Vol. 293, p. 37.
5. T. KOKUBO, *J. Non-Crystalline Solids* **120** (1990) 138.
6. R. D. RAWLINGS, *Clinical Materials* **14** (1993)155.
7. C. MOISESCU, C. JANA, S. HABELITZ, G. CARL and C. RUSSEL, *J. Non-Cryst. Solids* **248** (1999) 176.
8. C. MOISESCU, C. JANA and C. RUSSEL, *ibid.* **248** (1999) 169.
9. T. KOKUBO, H. KUSHITANI, S. SAKKA, T. KITSUGI and T. YAMAMURO, *J. Biomed. Mater. Res.* **24** (1990) 721.
10. J. M. GOMEZ VEGA, E. SAIZ, A. P. TOMSIA, G. W. MARSHALL and S. J. MARSHALL, *Biomaterials* **21** (2000) 105.
11. A. RAVAGLIOLI, A. KRAJEWSKI, A. PIANCASTELLI, G. BERGER, K. ADAM and R. GILDENHAAR, *Interceram* **41**(2) (1992) 69.
12. E. VERNÉ, C. VITALE BROVARONE, A. RAVAGLIOLI and A. KRAJEWSKI, in "Bioceramics" (World Scientific Publishing Co. Pte. Ltd., Singapore, 1999) Vol. 12, p. 491.
13. C. VITALE BROVARONE, E. VERNÉ, A. KRAJEWSKI and A. RAVAGLIOLI, *J. Eur. Ceram. Soc.* **21** (2001) 2855.
14. C. Y. KIM and S. S. JEE, *ibid.* **23** (2003) 1803.
15. S. F. HULBERT, in "An introduction to Bioceramics" (World Scientific Publishing Co. Pte. Ltd., Singapore, 1993) Vol. 1, p. 25.
16. E. VERNÉ, M. BOSETTI, C. VITALE BROVARONE, C. MOISESCU, F. LUPO, S. SPRIANO and M. CANNAS, *Biomaterials* **23** (2002) 3395.
17. M. BOSETTI, E. VERNÉ, C. VITALE BROVARONE, C. MOISESCU, L. ZANARDI and M. CANNAS, *J. Biomed. Mat. Res.* **66A** (2003) 615.
18. O. TOSHITAKA, T. MINORU, Y. IWAO and S. HISAO, *J. Am. Ceram. Soc.* **76**(9) (1993) 2379.
19. M. FERRARIS and E. VERNÉ, *J. Eu. Ceram. Soc.* **16** (1996) 421–427.
20. E. M. LEVIN, C. R. ROBBINS and H. F. MCMURDIE, in "Phase Diagrams for Ceramists" (The American Ceramic Society Ed., USA, 1964) p. 1969.
21. C. MOISESCU, PhD thesis, F.S.U. Jena, Germany, 2000.
22. M. FERRARIS, E. VERNÉ, P. APPENDINO, C. MOISESCU, A. KRAJEWSKI, A. RAVAGLIOLI and A. PIANCASTELLI, *Biomaterials* **21** (2000) 765.
23. E. VERNÉ, M. FERRARIS, C. JANA and L. PARACCHINI, *J. Eur. Ceram. Soc.* **20** (2000) 473.
24. E. VERNÉ, M. FERRARIS, C. MOISESCU, A. RAVAGLIOLI and A. KRAJEWSKI, in "Bioceramics" (Pergamon, Paris, 1997) Vol. 12, p. 491.

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