Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 30 (2010) 2031–2039
www.elsevier.com/locate/jeurceramsoc

Different approaches to produce coatings with bioactive glasses: Enamelling vs plasma spraying

V. Cannillo, A. Sola *

Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università di Modena e Reggio Emilia, Via Vignolese 905, 41125 Modena, Italy

Received 25 February 2010; received in revised form 19 March 2010; accepted 12 April 2010
Available online 8 May 2010

Abstract

Two alternative approaches, enamelling and plasma spraying, were tested to deposit coatings made with two different bioactive glasses: the established Bioglass® 45S5, which is considered as a term of comparison, and the experimental BioK. The strong points and weaknesses of the two methods were highlighted. From the analysed samples, it resulted that the enamelling approach works well on thermally stable substrates and creates a strong bond, characterized by a compositional gradient, with alumina substrates. However, the coating thickness must be carefully controlled to limit the thermal residual stresses and the glass formulation should be designed to reduce the glass tendency to crystallize. Instead plasma spraying is suitable for any kind of substrate and is highly automatizable, but the equipment is relatively expensive and the coatings are likely to retain some defectiveness, which makes a post-deposition thermal treatment necessary. Both enamelling and plasma spraying may induce crystallization phenomena, depending on the glass formulation. The introduction of potassium oxide in the glass composition, such as in the BioK, may be useful to hinder the crystallization.

Keywords: B. Microstructure-final; C. Mechanical properties; D. Glass; E. Biomedical applications; Coatings

1. Introduction

In general, bioactive ceramics and glasses are able to develop a mechanically strong bond to bone. Moreover, if their formulation is properly designed, some bioactive glasses are able to bond to soft tissues as well. This behaviour was first observed for a family of bioactive glasses belonging to the SiO_2–Na_2O–CaO–P_2O_5 system, with specific proportions of the constituent oxides.[1] Among them, the glass called Bioglass® 45S5 (hereafter: 45S5) proved to be extremely bioactive and it became the object of extensive studies. Nowadays it is commercially available and effectively used in clinical applications, including orthopaedic, dental, maxillofacial and otolaryngological surgical implants.[2] Nevertheless the mechanical properties of bioactive glasses are relatively poor and it has been reported that the 45S5 is not able to resist cyclic loading or crack growth. The brittle behaviour of bioactive glasses severely limits their use in load-bearing applications.[3]

A possible solution could be the deposition of a bioactive glass coating on to a metal or ceramic substrate. In fact, the tough substrate would provide a sufficient mechanical reliability, while the superficial glass layer would play a double role: first of all it would confer an adequate bioactivity to the implant, moreover it would prevent a direct contact between the substrate and the body fluid, thus reducing the risk of a chemical corrosion and ion release from the substrate.[4]

Various deposition techniques are currently under evaluation to obtain bioactive glass coatings.[5] Each approach has its special properties, advantages and disadvantages, however, among them, enamelling and plasma spraying are of particular interest. Theoretically, enamelling is an easy and inexpensive technique, similar to the process conventionally used to create a glaze on ceramic tiles. For this reason, enamelling has been successfully applied to coat alumina, zirconia and tough ceramic composite substrates.[6] Moreover, if the glass composition and the processing conditions are properly designed, the enamelling can create a gradual change in composition, turning the surface layer into a functionally graded coating, with improved mechanical properties.[7] However, local reactions may occur between the glass and the substrate and diffusion phenomena of alu-

* Corresponding author. Tel.: +39 059 2056229; fax: +39 059 2056243.
E-mail address: antonella.sola@unimore.it (A. Sola).

0955-2219/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2010.04.021

minium into the glass have been reported.[6,8] These collateral effects could modify the original glass formulation, affecting its bioactivity. Moreover some attempts to apply the enamelling technique to metal substrates, especially titanium and titanium-alloy ones, have given promising results,[4,9] but the typical target is represented by thermally stable ceramic substrates. In fact the high temperatures involved could promote the α to β transformation of titanium, which occurs starting from 885 °C.[4] Another hurdle with metallic substrates is the relatively high mismatch in the coefficients of thermal expansion, which could cause residual stresses at the interface during the cooling down step of the enamelling process.[9]

Plasma spraying is a deposition technique in which the coating material in powder form is injected within a plasma flux. The particles are partially or totally melted and driven to impact onto the substrate, where they usually assume a lamellar or splat-like morphology, the coating being formed by their layering.[10] Plasma spraying is a continuous process, flexible and reliable. The deposits are usually thicker than 10 μm and their microstructure depends on the sprayed material as well as on the processing parameters. This is an advantage, because the final microstructure can be controlled by tuning the spraying conditions, but the involved parameters are very numerous and complex.[11] The main benefit of plasma spraying comes from the fact that the substrate temperature remains low, which limits the risk of degradation. So, provided that the coating material does not decompose, dissociate or sublime at high temperature, plasma spraying, in principle, can be used to deposit almost any material onto almost any substrate.[12] Few pioneering attempts have already been done to obtain bioactive glass coatings on metal substrates by plasma spraying and related techniques[13–20] and recently a new method, namely the high-velocity suspension flame spraying (HVSFS) technique, has been successfully proposed to deposit glass–ceramic apatite/wollastonite (A/W) coatings.[21] Nevertheless plasma spraying is more suitable to produce hydroxyapatite coatings than bioactive glass ones. As a matter of fact, it has been recognized that it is extremely difficult to obtain defect-free glass coatings by plasma spraying, due to the low thermal conductivity, low density and relatively high viscosity (with respect to a melted crystalline phase) of glasses.[22]

The present paper is specifically addressed to compare the enamelling and plasma spraying techniques and to evaluate their applicability to the well established 45S5 and to an experimental bioactive glass, the BioK,[23] derived from the former by substituting the sodium oxide with potassium oxide to reduce its tendency to crystallize at high temperature.[24] In particular, the main purpose of the present contribution is to discuss the technological implications of plasma spraying and enamelling and to analyse the effects of both the deposition process and the glass formulation on the final microstructure of the coatings. In fact, a controlled microstructure, a defined mineralogical composition and a good connection to the substrate are fundamental prerequisites to obtain reliable materials. With this aim, each glass was employed to obtain two different types of functionally graded coatings (FGCs) by enamelling on alumina substrates (Kéramo ceramiche tecniche, Tavernerio (CO), Italy): one type was produced with glass in powder form (samples named p-FGC), the other one with glass in bulk form (samples named b-FGC). Moreover, the same glasses were used to deposit plasma-sprayed coatings onto titanium substrates (samples named PSC).

Table 1
Formulations of the 45S5 and the BioK.

Glass	Composition (oxide mol%)				
	SiO_2	P_2O_5	CaO	Na_2O	K_2O
45S5[25]	46.1	2.6	26.8	24.4	–
BioK[23]	46.1	2.6	26.8	–	24.4

2. Experimental

As already mentioned, the formulation of the new BioK[23] was derived from that of the 45S5[25] by substituting all the sodium oxide with potassium oxide. The composition of the two glasses is detailed in Table 1. In order to produce the glasses, reagent-grade powder raw materials (SiO_2, $Na_3PO_4{\cdot}12H_2O$, Na_2CO_3, $CaCO_3$ for the 45S5; SiO_2, $K_3PO_4{\cdot}H_2O$, K_2CO_3, $CaCO_3$ for the BioK; all products were provided by Carlo Erba Reagenti, Italy) were weighed in proper amounts, mechanically mixed in a polyethylene vessel and melted in a platinum crucible following the thermal cycle: from room temperature to 1100 °C at 10 °C/min; at 1100 °C for 1 h; from 1100 °C to 1450 °C at 10°/min; at 1450 °C for 30 min. When melted, each glass was cast in room-temperature water to obtain a frit; alternatively, the glass was poured in a graphite crucible and annealed at 550 °C for 1 h to obtain a bulk.

As regards the FGCs, for each glass composition, the frit was milled in an agate jar and sieved under 75 μm. The resulting powder was used to produce the p-FGCs; with this aim, the powder was dispersed in bi-distilled water (no dispersant was added) and manually applied onto the alumina substrate to create a uniform film. The solid-to-liquid ratio of the dispersion (1.1 for both the 45S5 and the BioK) was experimentally optimised to obtain a stable and homogeneous layer. The percolation of the glass into the alumina substrate was induced by means of a thermal treatment at 1400 °C for 4 h.

In order to obtain the b-FGCs, thin slices of glass were used instead of the powder. In fact, the bulk samples of glass were cut into slices and then polished to obtain 1 cm × 1 cm × 0.1 cm pieces. For each composition, a glass slice was placed on the top surface of an alumina substrate and thermally treated following the same cycle used to obtain the p-FGCs.

As regards the PSCs, the molten glass was milled and sieved following the same procedure used to produce the glass powder for the p-FGCs. The coatings were applied with a Plasma Technik F4 commercial plasma spray torch (Sulzer Metco, Westbury, NY), installed at the Center for Thermal Spray Research, Department of Materials Science and Engineering, Stony Brook University (Stony Brook, NY, U.S.A.). The equipment was operated in air plasma spraying (APS) mode.

Moreover the PSCs underwent a post-deposition heat treatment to modify their microstructure in a controlled way; the samples were treated at 700 °C for 1 h.

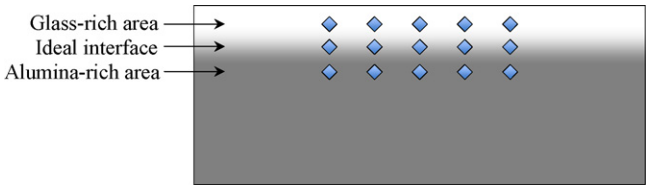

Fig. 1. Distribution of the indentations on the cross-section of a FGC.

An X-ray diffraction (XRD–PANalytical X'pert PRO) was performed on the surface of the as-produced FGCs to verify the development of new crystalline phases as a consequence of the heat treatment. An analogous test was carried out on the as-deposited and heat-treated PSCs, with the aim of identifying possible crystallization phenomena induced by the plasma spraying deposition and/or by the subsequent heat treatment. All patterns were collected in the angular range 2θ: 20°–70°, using a Cu Kα radiation with a scanning rate of $0.02^\circ\ s^{-1}$.

For both the FGCs and the PSCs, the cross-section of the samples was accurately investigated. With this purpose, the samples were cut, mounted in cold-curing resin and polished with diamond papers and diamond finishing sprays (final fineness: 0.5 μm). The cross-sections were investigated with an Environmental Scanning Electron Microscope (ESEM – Quanta-200 FEI Company) operated in high-vacuum mode, coupled with an X-ray Energy Dispersion Spectrometer (X-EDS, Oxford INCA-350). In particular, as regards the FGCs, the local chemical analyses were repeated in several points of each cross-section to track the gradual change in composition resulting from the glass penetration into the polycrystalline structure of the alumina substrate.

To conclude, the local mechanical behaviour was investigated by means of a Vickers microindentation test.[26] As regards the FGCs, the test was designed in order to account for the functional gradient caused by the compositional change. As sketched in Fig. 1, the indents were placed on three different areas of each cross-section, i.e. on the glass-rich area; close to the ideal interface between the glass and the alumina; on the alumina-rich area. A maximum load of 25 gf was applied for 15 s. For each area, at least five valid impressions (clear, not cracked or defective) were considered. As regards the PSCs, the indents were performed midway in the coating thickness; the test was repeated before and after the heat treatment, in order to appreciate its effect on the mechanical behaviour of the coatings.

3. Results

3.1. XRD: crystallization phenomena

The diffraction patterns of the p-FGCs (data not reported) showed the characteristic peaks of alumina (Ref. code: 01-071-1125), probably due to some alumina grains merging from the substrate. However, it was not possible to detect new phases caused by the crystallization of the glass during the thermal treatment.

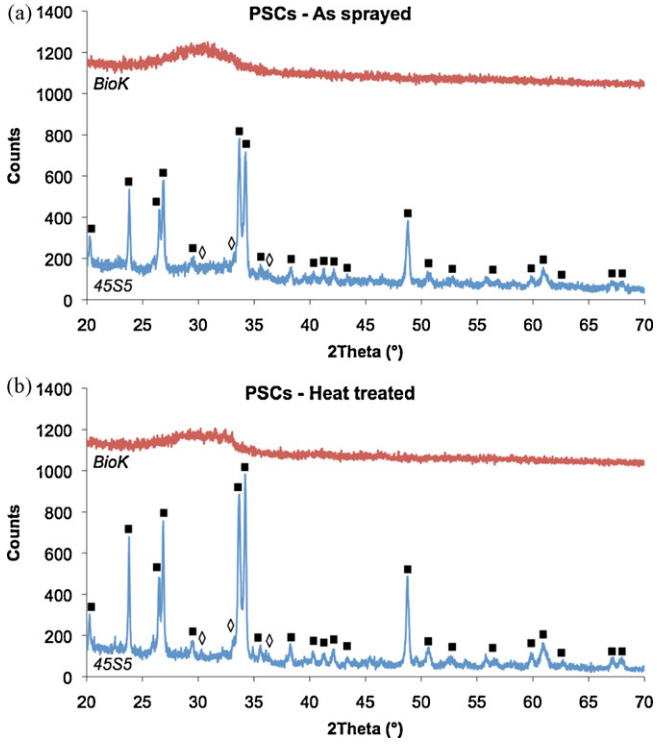

Fig. 2. X-ray spectra collected on the working surface of the PSCs, as-sprayed (a) and heat-treated (b). The black squares indicate the peaks from the sodium-calcium silicate (Ref. code: 01-079-1089), the white lozenges indicate the peaks from the calcium silicate (Ref. code: 00-051-0092).

The alumina peaks could be detected also in the diffractograms of the b-FGCs (data not reported), especially for the BioK sample. However, it is extremely interesting to observe that, while all the peaks in the BioK pattern were caused by the alumina, the spectrum of the 45S5 coating evidenced the development of a new phase, which was identified as a calcium silicate ($CaSiO_3$, Ref. code: 00-046-0044).

The XRD patterns of the as-sprayed PSCs presented in Fig. 2a confirm the reduced tendency to crystallize of the BioK with respect to the 45S5. In fact, while the BioK coating resulted completely amorphous, the 45S5 was rich in crystalline phases, in particular sodium-calcium silicates ($Na_4Ca_4(Si_6O_{18})$, Ref. code: 01-079-1089, black squares in Fig. 2a) and secondarily (traces) calcium silicates ($CaSi_2O_5$, Ref. code: 00-051-0092, white lozenges in Fig. 2a). As shown in Fig. 2b, the BioK coating maintained its amorphous nature even after the heat treatment, while the diffractogram of the heat-treated 45S5 coating revealed the presence of the same crystalline phases identified in the as-sprayed sample. However, a general increase in the peak intensities is indicative of an increased crystallinity of the coating.

Literature analyses of the behaviour of bioactive glasses during heat treatment have proved that the 45S5 (in bulk form) shows an increasing degree of opalescence at 700 °C, associated with the development of $Na_2Ca_2Si_3O_9$; then, at increasing temperatures, the samples reach a completely crystalline appearance.[24] In the present investigation, the b-FGC

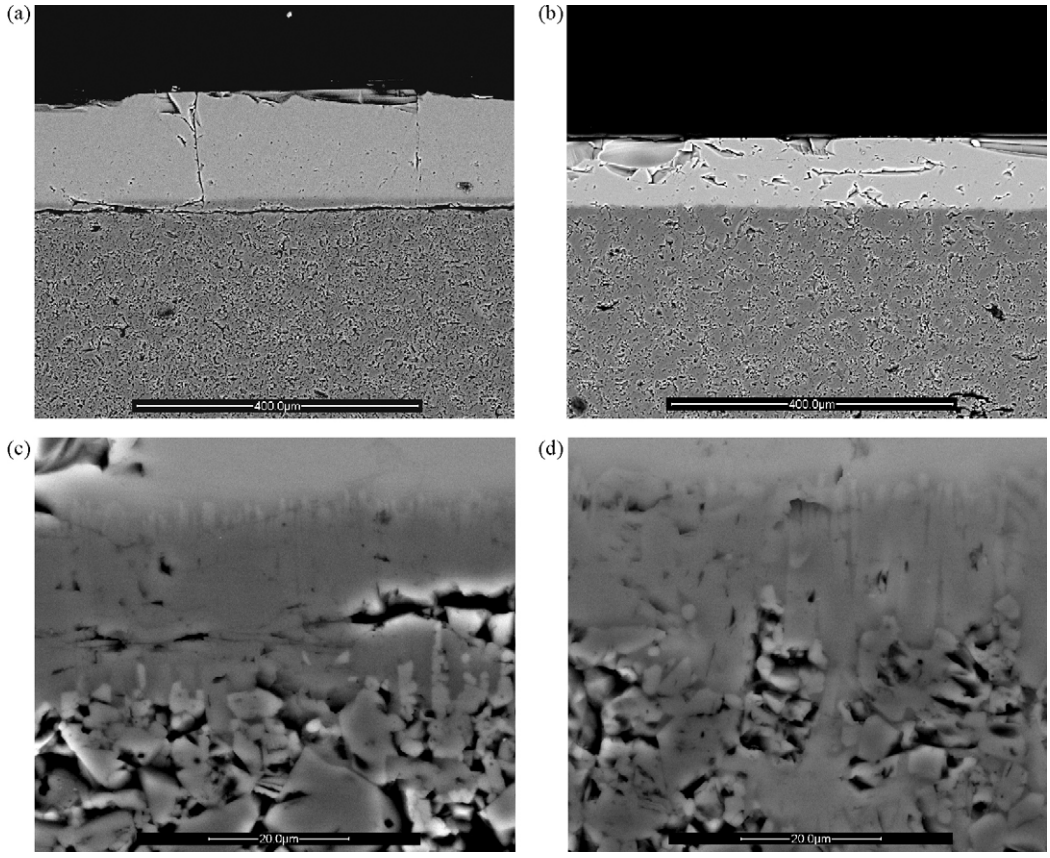

Fig. 3. Cross-sections of p-FGCs: general overview of the samples produced with 45S5 (a) and BioK (b) and corresponding interfaces between alumina substrate and glass coating (c and d).

produced with the 45S5 developed a different crystalline phase, probably because the treatment conditions were sensibly different, since the maximum temperature was much higher (1400 °C) and the glass was in contact with the alumina substrate, which may have altered the crystallization process. As regards the PSCs, it is interesting to note that the main crystalline phase identified in the 45S5 coatings, as-sprayed and heat-treated, is a sodium-calcium silicate analogous to the phase reported in the literature. It may be suggested that the residence at high temperature in the plasma flux may have promoted the crystallization of the 45S5 like a heat treatment. When post-processed at 700 °C, the scarce residual glassy phase in the as-sprayed sample further crystallized into the same sodium-calcium silicate, causing the aforementioned increment in the peak intensity of the diffractogram.

Calcium silicates and sodium-calcium silicates are frequently used as biomaterials[27,28] and hence the development of these new phases is not expected to hinder the bioactivity of the 45S5 coatings. However, the partial crystallization could modify the behaviour of the glass, not only because a new phase appears, but also because the original glass composition is modified. Instead the BioK preserved its amorphous nature, confirming that the addition of potassium oxide can effectively reduce the tendency of the glass to crystallize. This could represent an interesting result for plasma spraying, since the presence of potassium could facilitate the deposition of glass coatings, whose difficulties are still under debate.[22]

3.2. Microstructure

Fig. 3 collects some representative images of the FGCs cross-sections. Since the p-FGCs and the b-FGCs samples having the same composition had similar features, Fig. 3 concentrates on p-FGCs. As shown in Fig. 3a and b, both the 45S5 and the BioK created compact coatings, but the 45S5 p-FGC was thicker. The larger thickness of the 45S5 deposit could be the reason for the development of the cracks that are visible close to the nominal interface between the glass layer and the substrate and within the glass coating itself (Fig. 3a). In fact, when the samples are cooled down at the end of the fabrication heat treatment, thermal residual stresses are likely to arise due to the mismatch in the coefficients of thermal expansion (from 20 °C to 500 °C, for the alumina substrate: $7.5 \times 10^{-6}\,K^{-1}$ – data from the manufacturer; for the 45S5: $12.7 \times 10^{-6}\,K^{-1}$; for the BioK: $13.8 \times 10^{-6}\,K^{-1}$).[23] Such thermal residual stresses depend on both the thickness of the coating and the thermo-elastic properties of the coating and the substrate.[29] In the present research, the substrate is the same (alumina), the elastic properties of the glasses are comparable, and the coefficient of thermal expansion of the BioK is just slightly higher than that of the 45S5.[23] So the higher thickness is likely to induce more intense residual stresses in the 45S5 coating, which therefore undergoes cracking phenomena. This result suggests that the glass layer thickness is a key parameter to limit the entity of thermal residual stresses in enamelled coatings.

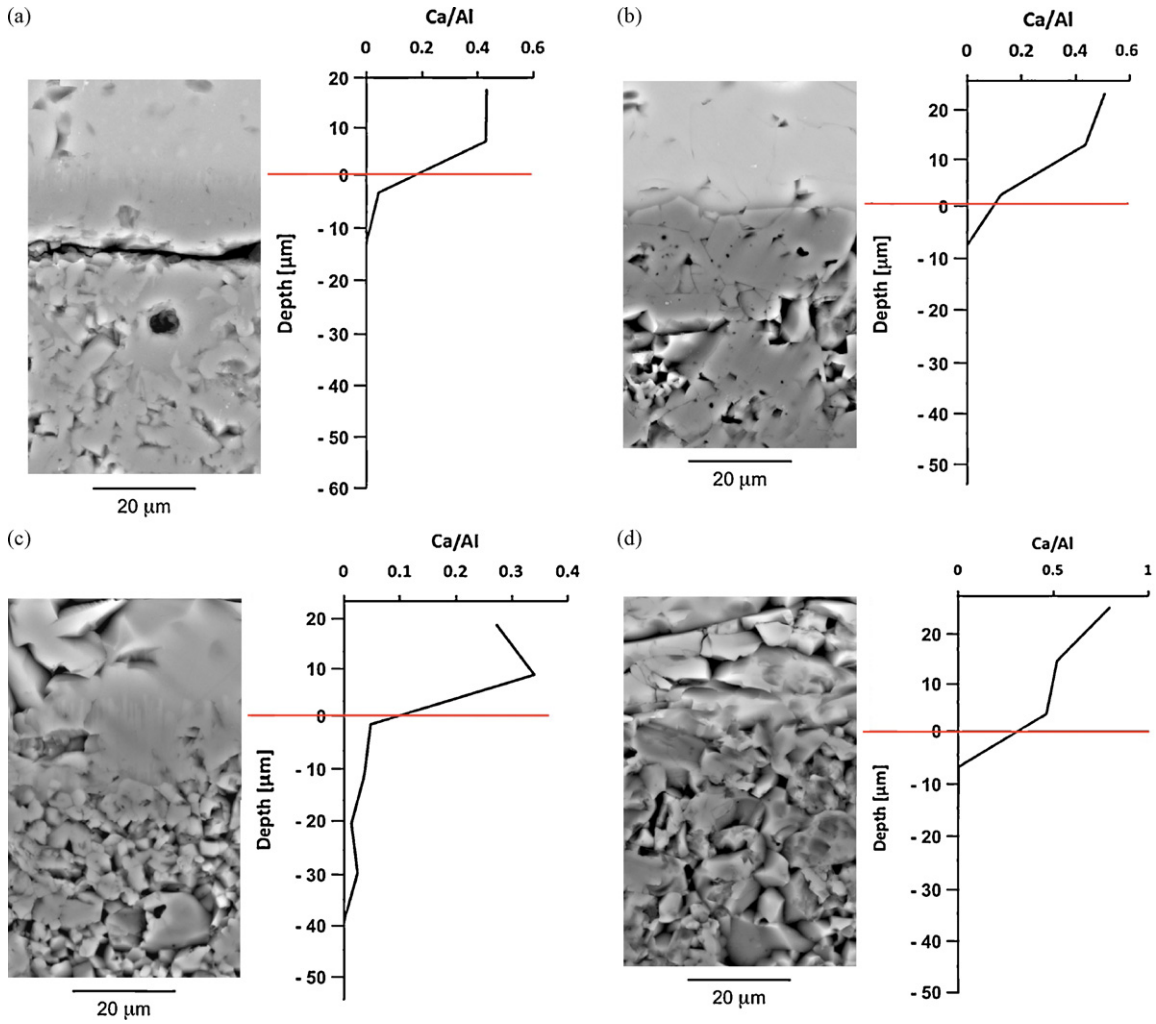

Fig. 4. Compositional gradient between the glass coating and the alumina substrate in the p-FGCs, with 45S5 (a) and BioK (b), and in the b-FGCs, with 45S5 (c) and BioK (d). Red horizontal line: theoretical interface between the glass and the substrate. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

Another very important feature of the coatings obtained by means of enamelling is the interface between the glass and the alumina. As a matter of fact, as shown in Fig. 3c and d, at the end of the thermal treatment there is not an abrupt interface, since the glass penetrated into the alumina substrate, creating a graded interface. For this reason, the enamelled coatings may be considered as functionally graded coatings.[7,30] Even in the cracked samples, such as the 45S5 p-FGC presented in Fig. 3a, the crack paths do not run on this graded zone, but just close to it. In order to appreciate the compositional gradient, local chemical analyses were carried out on the graded zone, focusing on the presence of calcium (representative of the glass) and aluminium (representative of the alumina). Then the calcium-to-aluminium ratio was plotted as a function of the distance from the ideal boundary between the coating and the substrate. The results are shown in Fig. 4, with the corresponding SEM images of the analysed areas. They confirm that the composition smoothly changes over a depth of some tens of microns, creating an interlocking between the coating and the substrate.

The surface and cross-section of the as-sprayed PSCs are presented in Fig. 5. As shown in Fig. 5a, the 45S5 coating is about 150 µm thick, but its thickness is particularly uneven. In fact, as proved by the surface inspection in Fig. 5b, the coating is the result of spherical particles, instead of flatten splats which are typical of plasma-sprayed glass coatings. Similar defective structures have already been described in the literature concerning the plasma spray deposition of pure glass coatings.[22] It may be suggested that the rounded particles visible on the coating surface are the consequence of semi-molten particles in the plasma flux. In fact, if a glass particle partially melts within the plasma flux, it can assume a rounded shape and then stick to the substrate thanks to its outer molten shell. However, the core of the particle, which is not molten, prevents the flattening of the particle, which preserves its sphere-like appearance.

The PSC with the BioK glass is somewhat thicker, about 220 µm, and much more uniform than the 45S5 coating. In fact, as shown in Fig. 5c, splat stacking faults are still visible, as well as pores and cracks, but the splats are more flattened and compacted. In accordance with the improved flattening of the splats, also the surface of the BioK PSC, presented in Fig. 5d, is more regular and planar. Small spherical features are present, but they presumably are secondary droplets caused by the splashing of

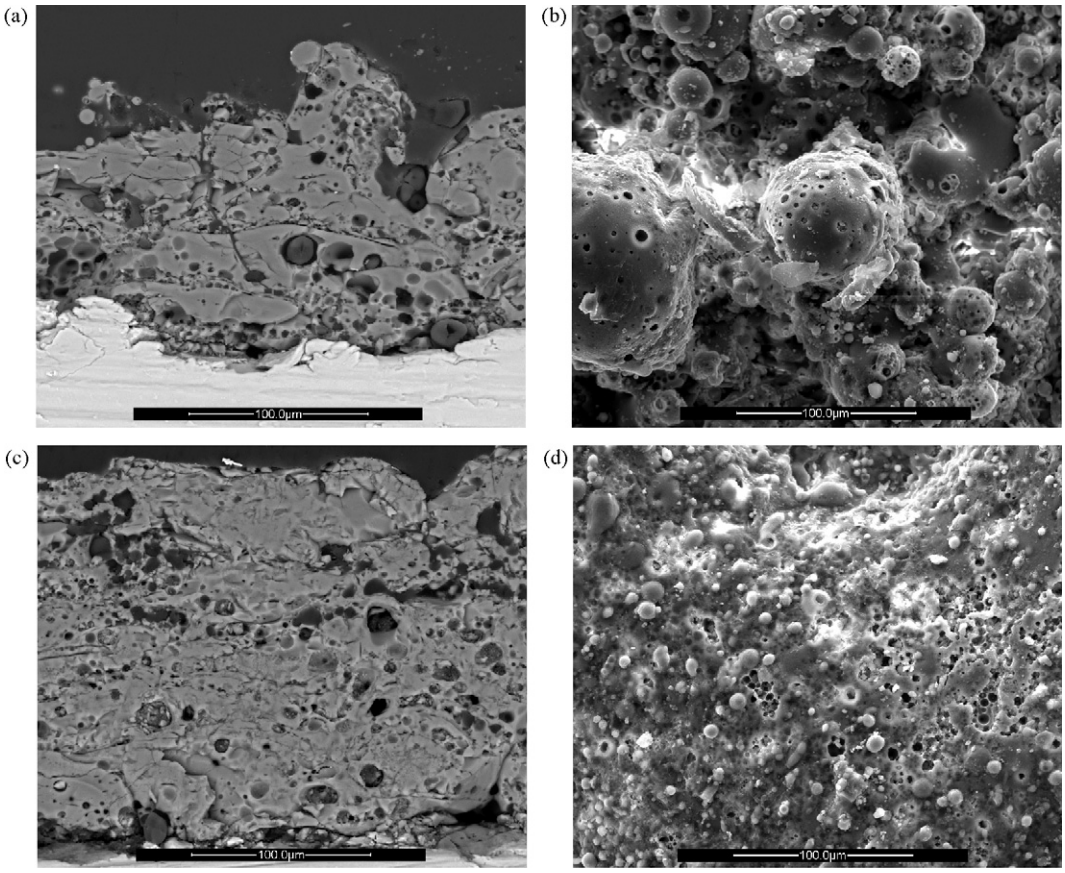

Fig. 5. Cross-section and surface of the as-sprayed PSCs produced with 45S5 (a and b) and with BioK (c and d).

primary drops onto the substrate. It is likely that the different behaviour of the two glasses during the plasma spray deposition depends on their different composition. For example, in silicate binary glasses the surface tension of the melt is higher for Na_2O-modified glasses than for K_2O-modified ones.[31] The formulations considered in the present investigation are not binary, however, it is reasonable that the presence of K_2O instead of Na_2O may have decreased the surface tension of the molten glass, ameliorating the spreading of the splats when impinging onto the substrate. The glass transition temperature was similar for the two glasses, as proved by the differential thermal analysis (data not shown), but the different behaviour of the two glasses during a thermal treatment was confirmed via heating microscopy tests: even if the softening point was higher for the BioK (about 780 °C) than for the 45S5 (about 590 °C), the BioK reached the melting point at about 1000°, the 45S5 at about 1210 °C. Moreover the XRD revealed a wide crystallization of the 45S5 coating; if, due to the low thermal conductivity of the glass, the crystal phase formed but was not able to melt, its presence may have contributed to the poor flattening of the splats observed in the 45S5 PSC.

It is known from the literature that a thermal treatment may be helpful to reduce the defectiveness of plasma-sprayed glass coatings and hence to better their mechanical properties.[32] The results of the heat treatment on the PSCs are presented in Fig. 6. The main effect of the treatment on both the PSCs is a wide sintering, which favoured the consolidation of the *lamellae* and conferred a rounded shape to the residual pores. As regards the 45S5 sample, the on-going sintering process may be clearly appreciated observing the interaction between the spherical particles on the coating surface. An example is given in Fig. 7. The BioK sample sinters as well, but the process is less eye-catching because, as already mentioned, the microstructure of the as-sprayed coating was already more compact than that of the 45S5 sample. Also the coating–substrate interface of the two coatings befitted from the thermal treatment, since the temperature exceeded the glass transition temperature of both the 45S5 and the BioK[23] and therefore the glass could soften and adapt to the substrate.[32]

3.3. Microindentation tests

As shown in Fig. 8, the value of the local Vickers hardness sensibly changed in the cross-section of both the p-FGCs and the b-FGCs, as a result of the compositional gradient observed during the SEM-EDS analysis. In fact, independently of the nature of the glass (45S5/BioK), the hardness progressively increased moving from the glass-rich area to the interface zone to the alumina substrate. The gradual infiltration of the glass created a functional gradient, which ensured a smooth change in local mechanical properties, as frequently observed in functionally graded materials.[33]

As regards the PSCs, it was not possible to obtain reliable data on the as-sprayed samples, probably due to the aforementioned

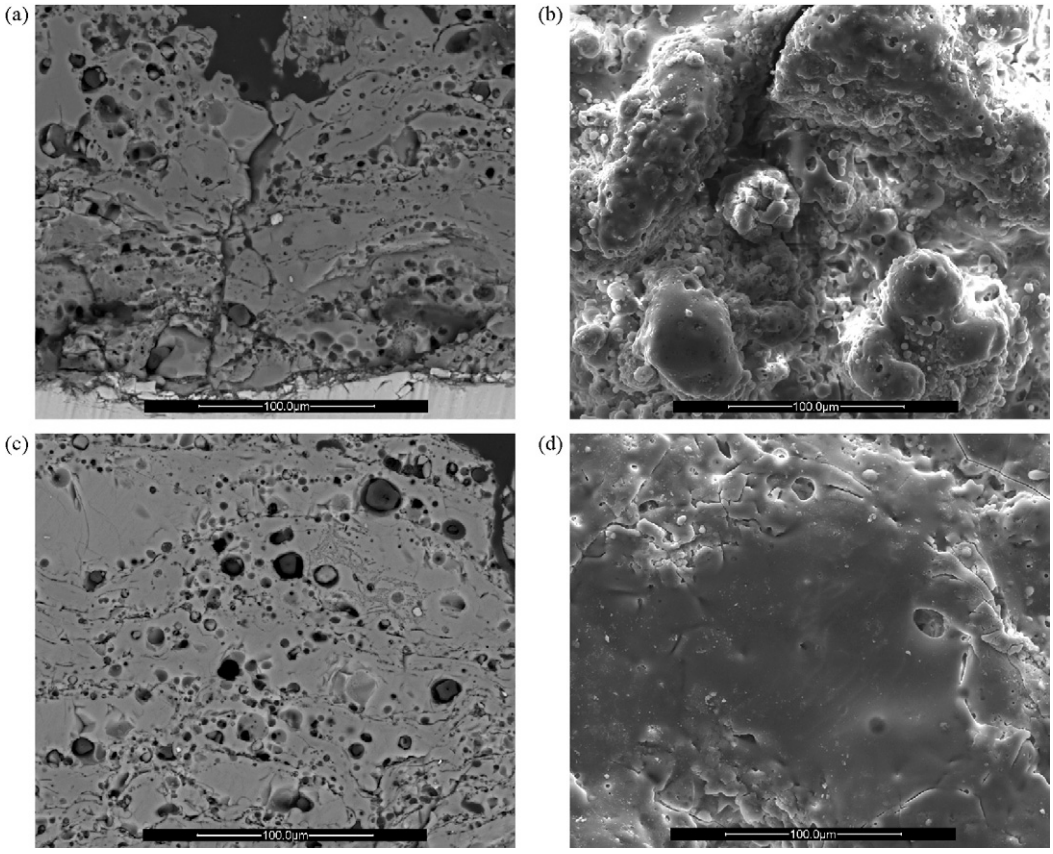

Fig. 6. Cross-section and surface of the heat-treated PSCs produced with 45S5 (a and b) and with BioK (c and d).

pores and defects. Also the 45S5, though partially crystallized, did not give significant results, because the coating was particularly inhomogeneous and very thin. Instead the tests carried out on the heat-treated samples were meaningful, confirming the relevance of a post-deposition heat treatment on the properties of plasma-sprayed glass coatings.[32] The Vickers hardness resulted to be 146 ± 28 HV for the 45S5 and 157 ± 39 HV for

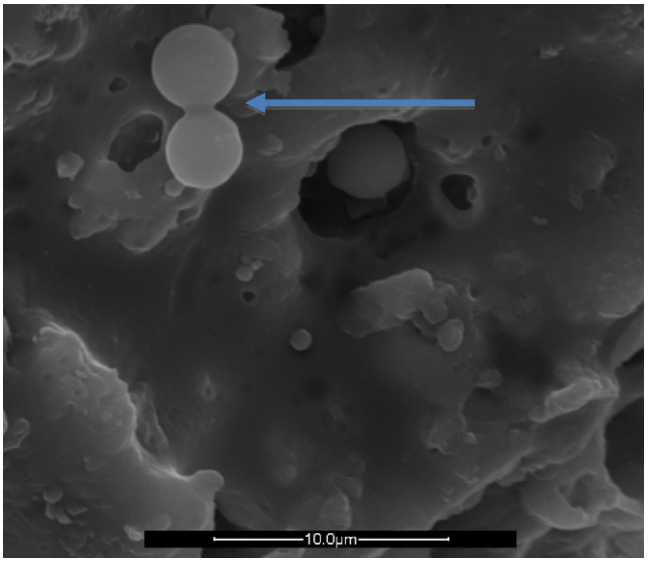

Fig. 7. Sintering process in heat-treated PSCs (45S5 sample).

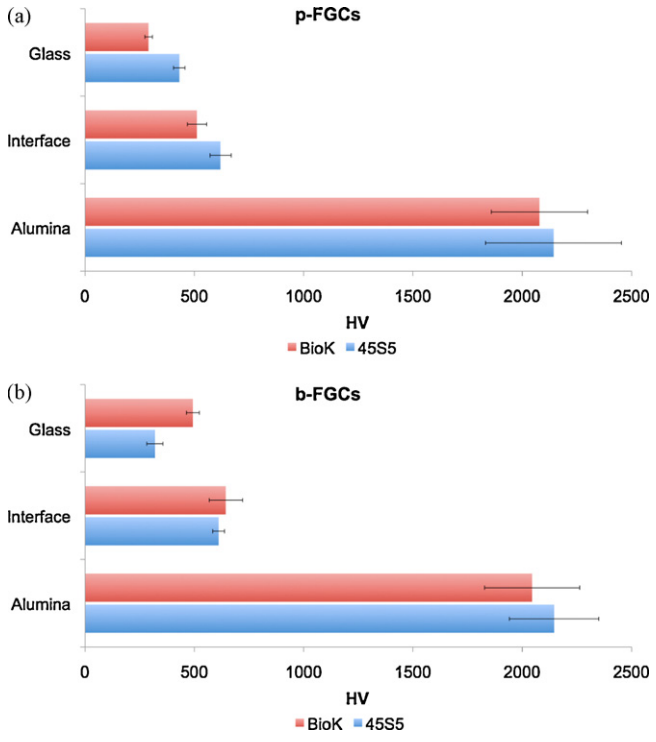

Fig. 8. Values of the local Vickers hardness in different areas (glass-rich; close to the interface; alumina-rich) of the cross-section of the p-FGCs (a) and the b-FGCs (b).

the BioK. Even if the heat-treated 45S5 coating was greatly crystalline while the BioK one was still amorphous, the measured hardness values were substantially the same, suggesting that the local mechanical behaviour was influenced more by the sintering process caused by the heat treatment than by the presence of crystal phases. In spite of the improvement resulting from the heat treatment, the Vickers hardness measured on the sintered PSCs was still lower than that of the respective parent glasses,[23] as frequently observed in plasma-sprayed deposits.[22]

4. Conclusions

Two different techniques, enamelling and plasma spraying, were considered to deposit bioactive glass coatings, addressing their strengths and limits. Moreover, two alternative glasses were used in order to evaluate the effect of the composition on the final deposits obtainable.

Enamelling is an inexpensive and relatively easy technique to coat bioactive glasses on thermally stable substrates, such as alumina ones. It is feasible with various glass compositions and it works well with both glass powders and glass bulks. It generally results in well-adhered deposits, thanks to the gradual infiltration of the glass into the ceramic substrate. However, the high temperatures involved impede its application to metal substrates, such as titanium ones, which could suffer disadvantageous microstructural transformations. Moreover for certain glass compositions, in particular for the 45S5 in bulk form, crystallization phenomena have been observed. In addition, the enamelling technique may engender thermal residual stresses, which may cause the coating to crack. From this point of view, a close control on the coating thickness is mandatory. One more concern with enamelling is the possible interaction between the glass and the ceramic substrate. On the one hand, as a result of the glass infiltration, some alumina may merge to the working surface, but alumina is bioinert and, hence, it is not dangerous. On the other hand, some aluminium may diffuse into the glass, changing its composition. In the present study, this diffusion process was limited, but, if necessary, it could be definitively eliminated by introducing a bond coat.

Plasma spraying is extremely flexible and it is suitable also for metallic substrates, because the substrate remains cold during the deposition. The process is strictly controllable and completely automatizable. However, as-sprayed glass coatings are weakly bonded to the substrate and they are often very defective. As a consequence, a post-deposition heat treatment is strictly required. During this treatment, the exposure to high temperature must be properly designed, in order to induce the glass to sinter without damaging the substrate. Moreover the permanence within the hot plasma flux may cause an uncontrolled crystallization of the glass, which can be limited by formulating the glass in a specific way (in the present context, substituting the sodium oxide with potassium oxide, as proposed in the BioK glass). A further contribution to limit the crystallization may be given by a very accurate calibration of the numerous parameters involved in the deposition process, including substrate temperature and cooling conditions. The equipment itself represents another limit of the plasma spraying technique, since plasma torches are diffusing in the industrial practice, but are currently available at specific research centers (while the enamelling process can be carried out in a simple furnace).

Future developments will be addressed to the bioactivity of the coatings. In fact this contribution mainly focused on the microstructural and compositional features of the glass coatings, but in vitro tests are running to validate the bioactivity of the glasses after deposition. Several ideas can be proposed to develop further the proposed topics, such as the introduction of a bond coat, which could also smooth the mismatch in the coefficients of thermal expansion, or the refinement of the processing parameters via a Design of Experiments. In particular, as regards the plasma spraying approach, the definition of a process map would be extremely useful to direct the future research.

Acknowledgements

Prof. S. Sampath and the Center for Thermal Spray Research, Department of Materials Science and Engineering at Stony Brook University (Stony Brook, NY, U.S.A) are kindly acknowledged for the plasma spraying runs and the precious advices.

References

1. Hench LL. Bioceramics. *Journal of the American Ceramic Society* 1998;**81**:1705–28.
2. Shirtliff VJ, Hench LL. Bioactive materials for tissue engineering, regeneration and repair. *Journal of Materials Science* 2003;**38**:4697–707.
3. Thompson ID, Hench LL. Mechanical properties of bioactive glasses, glass–ceramics and composites. *Proceedings of the Institution of Mechanical Engineers* 1998;**212 Part H**:127–37.
4. Lopez-Esteban S, Saiz E, Fujino S, Oku T, Suganuma K, Tomsia AP. Bioactive glass coatings for orthopedic metallic implants. *Journal of the European Ceramic Society* 2003;**23**:2921–30.
5. Zhao Y, Chen C, Wang D. The current techniques for preparing bioglass coatings. *Surface Review and Letters* 2005;**12**:505–13.
6. Martorana S, Fedele A, Mazzocchi M, Bellosi A. Surface coatings of bioactive glasses on high strength ceramic composites. *Applied Surface Science* 2009;**255**:6679–85.
7. Jitcharoen J, Padture NP, Giannakopoulos AE, Suresh S. Hertzian-crack suppression in ceramics with elastic-modulus-graded surfaces. *Journal of the American Ceramic Society* 1998;**81**:2301–8.
8. Hamadouche M, Meunier A, Greenspan DC, Blanchat C, Zhong JP, La Torre GP, et al. Bioactivity of sol–gel bioactive glass coated alumina implants. *Journal of Biomedical Materials Research* 2000;**52**:422–9.
9. Bloyer DR, Gomez-Vega JM, Saiz E, McNaney JM, Cannon RM, Tomsia AP. Fabrication and characterization of a bioactive glass coating on titanium implant alloys. *Acta Materialia* 1999;**47**:4221–4.
10. Fauchais P. Understanding plasma spraying. *Journal of Physics D: Applied Physics* 2004;**37**:R86–108.
11. Herman H, Sampath S, McCune R, Thermal Spray:. Current status and future trends. *MRS Bulletin* 2000;(July):17–25.
12. Davis JR, editor. *Handbook of thermal spray technology*. ASM International; 2004.
13. Gabbi C, Cacchioli A, Locardi B, Guadagnino E. Bioactive glass coating: physicochemical aspects and biological findings. *Biomaterials* 1995;**16**:515–20.
14. Lee TM, Chang E, Wang BC, Yang CY. Characteristics of plasma-sprayed bioactive glass coatings on Ti–6A1–4V alloy: an in vitro study. *Surface and Coatings Technology* 1996;**79**:170–7.
15. Helsen JA, Proost J, Schrooten J, Timmermans G, Braun E, Vanderstraeten J. Glasses and bioglasses: synthesis and coatings. *Journal of the European Ceramic Society* 1997;**17**:147–52.

16. Verné E, Ferraris M, Ventrella A, Paracchini L, Krajewski A, Ravaglioli A. Sintering and plasma spray deposition of bioactive glass–matrix composites for medical applications. *Journal of the European Ceramic Society* 1998;**18**:363–72.
17. Lopez-Sastre A, Gonzalo-Orden JM, Altónaga JAR, Altónaga JR, Orden MA. Coating titanium implants with bioglass and with hydroxyapatite, a comparative study in sheep. *International Orthopaedics (SICOT)* 1998;**22**:380–3.
18. Schrooten J, Van Oosterwyck H, Vander Sloten J, Helsen JA. Adhesion of new bioactive glass coating. *Journal of Biomedical Materials Research* 1999;**44**:243–52.
19. Schrooten J, Helsen JA. Adhesion of bioactive glass coating to Ti6Al4V oral implant. *Biomaterials* 2000;**21**:1461–9.
20. Goller G. The effect of bond coat on mechanical properties of plasma sprayed bioglass–titanium coatings. *Ceramics International* 2004;**30**:351–5.
21. Bolelli G, Cannillo V, Gadow R, Killinger A, Lusvarghi L, Rauch J. Microstructural and in vitro characterisation of high-velocity suspension flame sprayed (HVSFS) bioactive glass coatings. *Journal of the European Ceramic Society* 2009;**29**:2249–57.
22. Bolelli G, Cannillo V, Lusvarghi L, Manfredini T. Glass-alumina composite coatings by plasma spraying. Part I. Microstructural and mechanical characterization. *Surface and Coatings Technology* 2006;**201**:458–73.
23. Cannillo V, Sola A. Potassium-based composition for a bioactive glass. *Ceramics International* 2009;**35**:3389–93.
24. Arstila H, Hupa L, Karlsson KH, Hupa M. Influence of heat treatment on crystallization of bioactive glasses. *Journal of Non-Crystalline Solids* 2008;**354**:722–8.
25. Jedlicka AB, Clare AG. Chemical durability of commercial silicate glasses. I. Material characterization. *Journal of Non-Crystalline Solids* 2001;**281**:6–24.
26. Ponton CB, Rawlings RD. Vickers indentation fracture test. Part 2. Application and critical evaluation of standardised indentation toughness equation. *Materials and Science and Technology* 1989;**5**:961–80.
27. Zhao W, Wang J, Zhai W, Wang Z, Chang J. The self-setting properties and in vitro bioactivity of tricalcium silicate. *Biomaterials* 2005;**26**:6113–21.
28. Zhao Y, Ning C, Chang J. Sol–gel synthesis of Na_2CaSiO_4 and its in vitro biological behaviors. *Journal of Sol–Gel Science and Technology* 2009;**52**:69–74.
29. Shiue S-T, Lien P-T, He J-L. Effect of coating thickness on thermal stresses in tungsten-coated optical fibers. *Journal of Applied Physics* 2000;**87**:3759–62.
30. Miyamoto Y, Kaysser WA, Rabin BH, Kawasaki A, Ford RG. *Functionally graded materials. Design, processing and applications*. Kluwer Academic Publishers; 1999.
31. Navarro JMF. *El Vidrio*. Madrid: C.S.I.C.; 1991.
32. Bolelli G, Cannillo V, Lusvarghi L, Manfredini T, Siligardi C, Bartuli C, et al. Plasma-sprayed glass–ceramic coatings on ceramic tiles: microstructure chemical resistance and mechanical properties. *Journal of the European Ceramic Society* 2005;**25**:1835–2185.
33. Kawasaki A, Watanabe R. Concept and P/M fabrication of functionally graded materials. *Ceramics International* 1997;**23**:73–83.