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Coating of ZrO_2 supports with a biological glass

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The possibility of obtaining a good bioactive coating on biomedical devices made with zirconia ceramic was considered. Yttria partially stabilized zirconia was used to produce suitable substrates. The obtained adhesion was good (66 ± 13 MPa) and encouraging for biomedical applications. Small microcrystals formed inside and on the surface of the glass layer. These microcrystals transformed the glass into a glass-ceramic. An accurate investigation of the nature of this microcrystal formation was carried out to verify its compatibility with the planned biomedical applications.

1. Introduction

The experience gained in prosthetic substitution has prompted surgeons to demand increasingly efficient and sophisticated prostheses, ensuring increasingly higher mechanical resistance and, at the same time, the best adhesion to tissues for a stable biological anchoring to bone. These urgent requirements have exerted strong pressure on bioengineers to formulate adequate solutions. In this connection, bioactive surfaces have been proposed in relation to anchoring. The possibility to render bioactive the surface of a biomedical device becomes more and more sought. That can be achieved by using, for example, a layer of a suitable biological glass. The material utilized to make the coating must have a thermal expansion coefficient as similar as possible to that of the substrate. This kind of coating could be useful also in engineering technical applications outside the biomedical field.

Recently, interest in the utilization of partially stabilized tetragonal zirconia (Y-PSTZ) has been spreading in the biomedical field for surgical application of ceramic devices that require very high mechanical performances. This possible solution spurred the present authors to intensify their search for the most suitable type of biological glass coating on a zirconia support. Similar studies have already been successfully carried out on Al_2O_3-based ceramics for use in the auricular field [1, 2]. In vitreous systems, the surface coating of pieces made of ZrO_2 (a support to be sintered at high temperature) requires the use of glassy systems in order to give rise to a liquidus only at high temperature, to avoid both excessive sliding of the bioactive glass and ionic exchange during the process of coating at high temperature. The experiments ascertained a large absorption of glass and the formation of a composite layer constituted of ZrO_2 grains covered by a thin film of glass, with characteristics different from those of the ZrO_2 support, when the coating was done at temperatures greater than 1350 °C on supports fired below 1530 °C. Good coatings, with slight penetration of glass inside the ceramic body, were obtained by firing the support at 1530 °C and applying biological glass at 1300 °C to obtain the coating.

2. Materials and methods

Partially stabilized tetragonal (5.15 ± 0.05 wt%, or 2.88 ± 0.03 mol%, Y_2O_3) ZrO_2 powders Morgan Matroc Ltd, Birmingham, UK) (Y-PSTZ) were utilized to produce samples by die pressing or by injection moulding. The formed green (unfired) samples were fired in a laboratory kiln at different temperatures ranging from 1100–1530 °C in a normal atmosphere. All the green samples had a density of 3.1 (± 0.1) g cm^{-3}.

The green samples obtained by die pressing were shaped into small prismatic bars by means of a monoaxial pressing device with a suitable die of different dimensions (6 mm × 60 mm × 6 mm; 6 mm × 60 mm × 1 mm). The green samples obtained by injection moulding were all of dimensions 4 mm × 50 mm × 3 mm.

The thermal firing cycle was of 100 °C h^{-1} up to the sintering temperature, where it was maintained for 1 h. The cooling rate was set at ~ 200 °C h^{-1}. Samples were fired at 1200, 1300, 1400 and 1530 °C.

The series of fired as well as green samples were covered with a suitable slip of the vitreous compositions: AP40 [1]. The covering of the samples with a layer of biological glass was carried out either by full immersion in an aqueous suspension of powdered glass, or by brushing with the same suspension. The suspension also contained some amount of binders (methylcellulose, polyvinylalcohol, etc.) able to maintain the glass powders up to their softening temperature, just above which the grains of the glass adhere to each other and to the surface of the substrate. The

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TABLE I Chemical composition (wt %) of the vitrous system AP40 used for this study

Glass code	SiO_2	P_2O_5	CaO	Na_2O	K_2O	MgO	CaF_2
AP40	44.3	11.2	31.9	4.6	0.2	2.8	5.0

chemical composition of the biological glass AP40 is shown in Table I.

The temperature was optimized for a suitably good application of the adopted glass layer, according to the sintering temperature of the zirconia substrate. Therefore, the temperatures for application of the glass layer ranged from 1270–1530 °C.

X-ray diffraction analyses (XRD) were carried out on the Y-PSTZ powder to ascertain its mineralogical nature and to identify possible extraneous phases before sintering. The same procedure was followed on the fired samples, either by die pressing or by injection moulding, before and after the application of the vitreous layer to detect all possible crystalline phases forming in the proximity of the external surface. All samples were analysed at the interface by microprobing (EDS) and scanning electron microscopy (SEM).

A microprobe apparatus was utilized to obtain a complete picture of the chemical composition of the vitreous layer and to verify whether any recrystallization or demixing of the glass layer would take place in the event of development of soluble or insoluble phases. Generally such a phase separation may consist either in a mixture of different phases distributed randomly or in stratifications of different compositions.

Analyses were carried out on cross-sections perpendicular to the axis of elongation of the bars to examine the chemical distribution of the most significant elements. Line profiles of such distributions were collected in the direction perpendicular to the external surface of the samples. The layers were analysed for sodium, calcium, silicon, phosphorus, magnesium, zirconium and yttrium by EDS at different depths (0, 5, 10, 20, … , μm) on square areas 30 μm × 30 μm. The measuring time for each point was 4 s. Tests were made to assess Young's modulus, the thermal expansion coefficient of both the bioactive glass and the zirconia support, and the mechanical strength and microhardness of coated and uncoated samples.

Bending strength tests were carried out on all kinds of substrate by the three-point method to evaluate the flexural strength σ of the joining of the biological glass to the ZrO_2 substrate, following the scheme of Fig. 1. The resulting value of σ is 66 (± 13)MPa. Ultimate tensile adhesive strength (UTAS) following BSEN standard 582 : 1984 has given a good value of 32 (± 3) MPa. The best firing cycle adoptable for the manufacture of zirconia samples in the shape of small prostheses is currently under investigation.

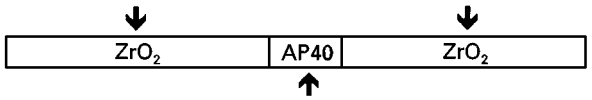

Figure 1 Adhesion ZrO_2-AP40 (Flexural strength 3pts. test).

3. Results

Zirconia samples fired at 1530 °C underwent a shrinkage of ~ 20 (± 0.5)%, reaching a final density of 5.94 (± 0.05) g cm^{-3} which corresponds to a relative density of a theoretical mixture of 80% tetragonal (T) and 20% cubic (C) zirconia. The simultaneous presence of both phases is, however, proved and reported in the literature for Y_2O_3 stabilizer content in the range of that adopted here [3].

A mercury porosimeter was used to test open porosity, whereas SEM investigation on several cross-sections was carried out to determine inner close porosity. Porosity was detected to be practically absent.

Preliminary measurements of ultimate compressive strength gave values of 1800 (± 100) MPa for zirconia samples fired at 1530°C and 800 (± 300) MPa for AP40, whereas the ultimate tensile strength was 600 (± 50) MPa and 110 (± 50) MPa, respectively.

Fig. 2 shows the action of temperature on a sample of a cubic-shaped sample of AP40 glass placed in the mini-kiln of a heating microscope (Leitz type 307–107003) to emphasize the behaviour of the glass at different temperatures. The annealing point is located at about 650 °C. The half-sphere point is approximatively located in the range of 1255 °C, whereas the point of formation of flowing liquidus is above 1270 °C.

3.1. Non-optimized coatings

To represent what occurs when the temperature of the coating process is too high, an example is given by taking into consideration the "monofired" samples. Some samples were prepared by covering green bars with the glass suspension and by firing them only once directly at 1530 °C, to produce simultaneous sintering and formation of the glass layer. A microprobe analysis carried out on a cross-section of every sample of this kind after firing showed no layer of glass alone. The vitreous phase was, in fact, absorbed by the intergranular porosity of the zirconia. A portion of the absorbed glass reacted with zirconia. This is clearly deducible from the chemical profiles of Fig. 3 carried out for a depth of more than 2 mm, in which ΔZr is the decrease of the zirconium intensity signal. Elemental concentration was determined by spot analyses carried out perpendicular to the surface at regular and close intervals. The sites of minima of the zirconium content are filled with the components of the glass. The involved mechanism of absorption is quite complex. In fact, a maximum concentration of the glass components was detected at about 0.7 mm, while an apparent different distribution of the glass components suggested a different speed of ionic migration and a possible formation of compounds with zirconia such as $ZrSiO_4$ (at about 0.5 mm) and $CaZrO_3$. In the same area a martensitic transformation from tetragonal to monoclinic (T → M) was indicated by XRD.

Thin zirconia supports (up to 3 mm thickness) coated with biological glass on one face only and

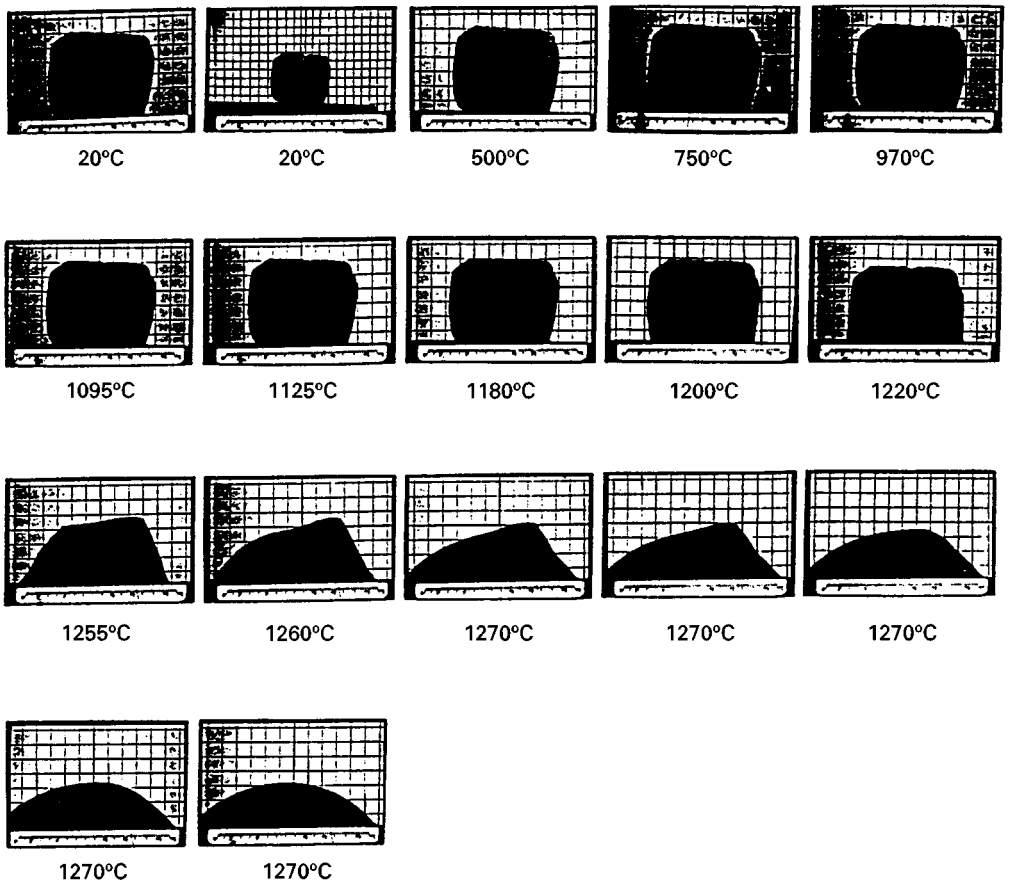

Figure 2 Photographic sequence of the melting of the biological glass AP40 (Leitz heating camera). The reported numbers refer to the temperature value in °C.

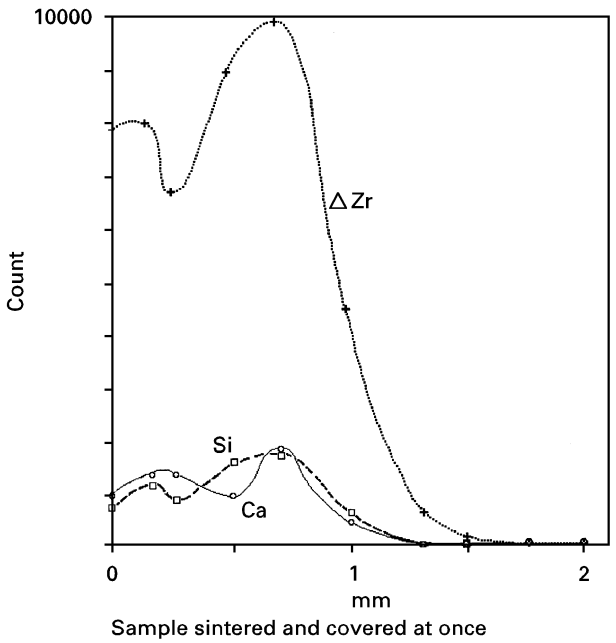

Figure 3 Chemical profiles of the reported elements along the cross section of a monofired sample at 1530 °C vs the depth inside the ceramic (point 0 corresponds to the external border). ΔZr means the decrease of the Zr content compared with the concentration of the innermost part (not interacted with the glass) of the ceramic sample.

sintered at different temperatures revealed conspicuous marking after cooling, with the glassy layer to be seen always on the convex side. From a first evaluation, the marking appeared to be connected with the difference between the glass application temperature and the substrate firing temperature, when the latter temperature was lower than the former. A deformation (though smaller) was, however, observed even when the glass application temperature was too high (> 1350 °C) and the substrate sintering temperature, though higher than the latter, was appreciably lower than the resulting optimal temperature (< 1500 °C).

3.2. Optimized coatings

The best results are achieved from the samples whose zirconia substrate was fired at 1530 °C and reheated at 1300 °C to produce the coating with the biological glass. On these samples, a complete set of tests was performed. This process gives rise to the best coating in terms of thickness, adherence to the substrate and low content of dissolved ZrO_2 with an optimal formation of microcrystalline phases. The thickness of the obtained deposited biological glass layer ranges from 40–100 μm depending on the fluidity of the suspension.

XRD analyses showed similar diffraction patterns both on the samples coated with bioactive glass subjected to a single firing or to refiring at 1530 °C, and on those coated with biological glasses refired at 1300 °C. Fig. 4 shows a diffraction pattern from a sample fired at 1530 °C coated with biological glass and refired for glass application at 1300 °C, compared with the diffraction pattern of the starting powders and of the

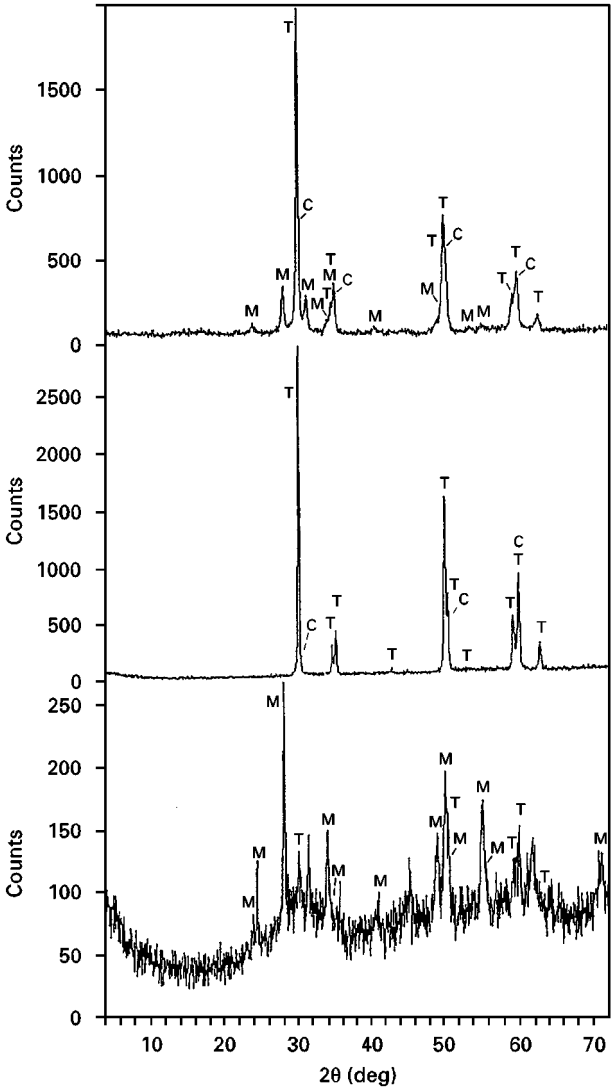

Figure 4 X-ray diffraction spectra of zirconia samples, collected respectively on: unfired zirconia powders (top); the surface of a sample of zirconia fired at 1530°C, not coated with glass (center); the surface of the AP40 glass layer of the coating applied at 1300°C on a sample of zirconia fired at 1530°C (bottom). Reported phase codes: M = monoclinic; T = tetragonal; C = cubic.

substrate fired at 1530 °C. A comparison of the diffraction patterns reveals that the glass contains some recrystallized microcrystals of monoclinic zirconia inside. Further XRD analyses on a wide number of covered samples detected small signals attributable to parawollastonite ($CaSiO_3$), calcium zirconium oxide ($CaZrO_3$), monoclinic zirconia (sometimes also tetragonal). Consequently, the revealed crystalline phases are present only in traces and are detected in a very small number of samples, poorly significative. On the other hand, it was ascertained that the formation of microcrystals inside the coating layer is connected with the cooling rate; for cooling rates greater than 150 °C h^{-1}, glass recrystallization does not occur or is quite negligible.

Mechanical tests on the bars obtained from die-pressing and injection moulding gave the results shown in Table II.

On the basis of scanning electron microscopy (SEM) associated with EDS microprobing, average profiles were made of these samples, whose substrate was produced by die pressing and injection moulding forming techniques. Elemental concentration profiles were collected for calcium, silicon and zirconium perpendicular to the surface interface of all the samples. Figs 5 and 6 show the average profiles of these elements across the substrate/glass interface.

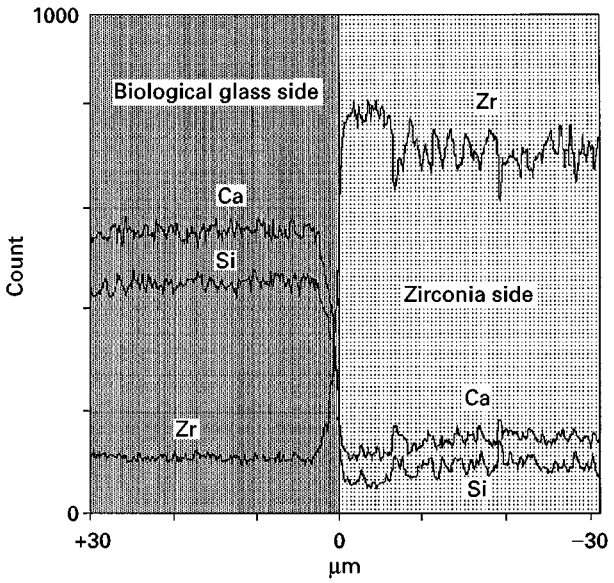

Figure 5 Average profiles of the reported elements on a cross section of covered zirconia ceramic produced by die pressing. The analysis was carried out astride the interface substrate/glass.

TABLE II Mechano-physical parameters of: AP40 biological glass, PSTZ (Morgan Matroc Ltd) and samples ZAP constituted with PSTZ fired at 1530 °C, covered with AP40 and refired at 1300 °C

Sample	Density ($g\,cm^{-3}$)	Flexural strength (MPa)	K_{IC} ($MPam^{1/2}$)	Thermal expansion coefficient (10^{-6} °C^{-1})	Young's modulus (GPa)	Poisson's ratio ν	Microhardness (Vickers; 1 kg) (MPa)
AP40	2.76 (± 0.05)	173 (±12)	2.5 (± 0.5)	9.9 (± 0.5)	85[a] (± 5)	n.d.	7.70 (± 0.80)
ZrO_2	5.94 (± 0.05)	750 (±50)	8.7 (± 2.0)	9.8 (± 0.2)	215 (± 10)	0.298	27.84 (± 1.07)
ZAP	6.00 (± 0.05)	750 (±50)	8.0 (± 2.0)	9.8 (± 0.2)	170 (± 10)	0.290	19.71[b] (± 3.21)

[a] When applied on the substrate to obtain the covering, the value increases to 120.
[b] Measured close to the biological glass layer; the value far from the biological glass layer is 26.45 (±1.80), the same as far uncoated zirconia.

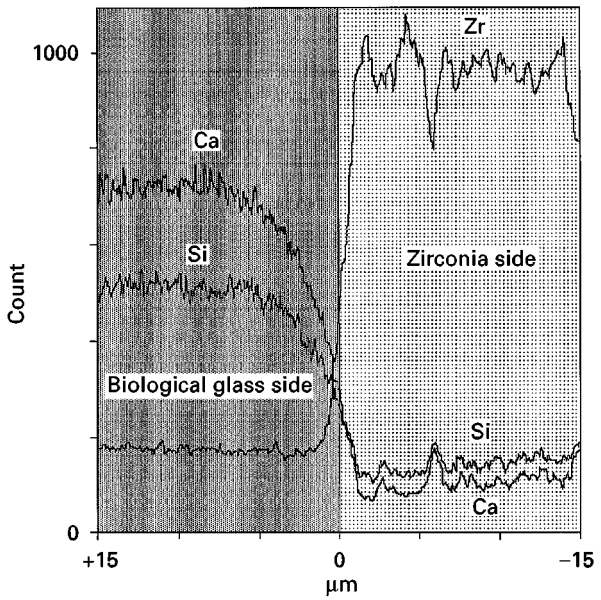

Figure 6 Average profiles of the reported elements on a cross section of covered zirconia ceramic produced by injection moulding. The analysis was carried out astride the interface substrate/glass.

We note that the induced tensile stress of the glass is certainly not due to the different thermal expansion coefficient (Table II). Its decrease is probably due to the precipitation of the microcrystals inside the vitreous system [4].

The formation of such microcrystals inside the glass layer seems to play a positive role in the arrangement of the molecular network of the glass, lowering the residual stresses at the interface [5–7]. With the consequent lowering of free energy, the authors also suppose that a more regular (or a slower) controlled biointeraction with bone tissue should be exerted in *in vivo* implants.

Occasionally, the formation of some microcrystals ($\leqslant 5$ μm) of zircon ($ZrSiO_4$) was observed on cross-sections of a sample just at the substrate/glass interface (Fig. 7). An accurate investigation on many sections of the same sample has shown that these microcrystals grow as small groups which occur only sporadically in an amount of 0.2% (expressed as linear length of photographic profile occupied by these microcrystals on the overall examined profile).

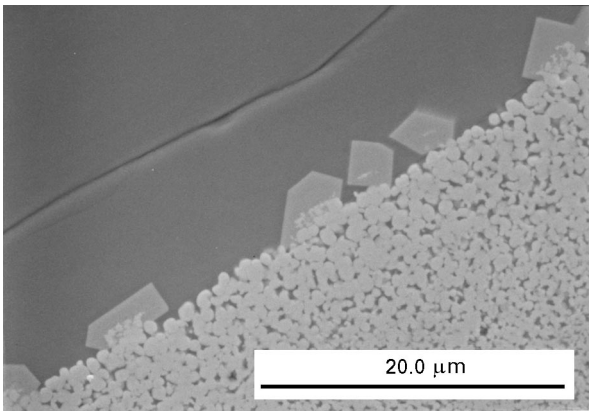

Figure 7 Microstructure of covered zirconia ceramic produced by die pressing at the interface substrate/glass.

A semiquantitative analysis of the content of zirconium dissolved inside the glass layer supplied values of $\sim 4.5\%$ at the substrate/glass interface. Trace concentrations of Y^{3+} were detected, with values about one-tenth of those observed for Zr^{4+}.

The fact that a monoclinic phase of zirconium oxide was formed suggests an impoverishment of stabilizer in the ZrO_2 grains of the surface area. Such impoverishment is arguably due to the dissolution–reprecipitation process occurring at the grains boundaries, with a marked decrease in size of the smaller grains and a consequent increase of the larger grains. This process provides a plausible explanation for the formation of some percentages of monoclinic ZrO_2.

On the other hand, the presence at the same time of a small concentration of Zr^{4+} (as well as traces of Y^{3+}) in the glassy layer overlying the interface strengthens the hypothesis that a dissolution–reprecipitation process took place.

The above value agrees with the literature [8] as regards the low solubility of zirconium oxide in silicate melts and the difficulty of incorporating more than 3% or 4% of this oxide in solution. Values of elemental concentration obtained by spot analysis (square area 10 μm × 10 μm) with a microprobe on a cross-sectioned glass layer in three different peculiar spot location coded *Interface* (5 μm from the interface), *Centre* (50 μm from the interface or centre of the layer) and *Border* (10 μm from the external border) are shown in Table III in relation to samples

TABLE III Concentration of elements expressed as oxides (wt%) in three representative points of the coating glass cross-section, for both cases of preparation of the zirconia substrate (estimated standard deviation 5% on the reported value)

	Die-pressed substrate			Injection-moulded substrate		
Component	Interface	Centre	Border	Interface	Centre	Border
SiO_2	42.2	42.9	43.0	42.9	44.5	44.8
P_2O_5	10.7	10.9	10.9	10.6	10.8	11.0
CaO	30.4	30.9	31.0	30.0	30.1	30.5
Na_2O	4.4	4.4	4.5	3.9	4.0	3.9
K_2O	0.2	0.2	0.2	0.2	0.2	0.2
MgO	2.7	2.7	2.7	2.8	2.8	2.7
CaF_2	4.8	4.8	4.8	4.7	4.9	5.0
ZrO_2	4.5	3.3	2.9	4.6	2.8	1.8
Y_2O_3	0.3	0.2	0.1	0.3	0.1	0.1

with substrates produced by die pressing and injection moulding.

Microstructural analyses on the same area revealed an increase in the mean grain dimensions of the ceramic side and of the intergranular space for both kinds of substrate prepared by die pressing or injection moulding (Figs 8 ad 9). This increase in the grain dimension is gradual and starts from about 35 μm of depth. XRD analysis has shown the formation of small per cent of monoclinic ZrO_2 after application of the biological glass. The phase transition gives rise to an increase in unit cell volume, but probably this is not the only reason for the increase in grain volume. This detail will be discussed further in the next section. No significant rearrangement was revealed, apart from an imperceptible increase of the microporosity up to a depth of about 300 μm from the interface. In conclusion, the ceramic body at depths greater than 50 μm corresponds completely to the body of uncoated samples.

An investigation was carried out on the outer surface of the glass layer. After firing, the surface of the glass layer is generally clear and only in a few cases is a matt film observed. After refiring, the formation of the matt film is more frequent. Attention was therefore devoted to establishing the nature of the matt film. SEM analysis with the aid of a microprobe displayed a spreading of thin surfacial microcrystals, such as those shown in Figs 10 and 11. The nature of such surfacial microcrystals is a mixed composition of CaO, SiO_2, P_2O_5 and K_2O, for the dendrites of Fig. 10, calcium phosphates rich in silica for the globular microcrystals of Fig. 10, and $CaSiO_3$ (wollastonite) for the microcrystalline aggregation visible in Fig. 11.

Microcrystals were not detected along the thickness of the glass layer in many cross-sections, except sometimes along possible vertical cracks connected with the external surface. This suggests that the crystallization phenomena are connected at first with the interface.

The observed surfacial matt film is easily removable by lapping. The formation of microcrystals inside the thickness of the glass layer is mainly attributed to an unsuitably controlled modulation of the cooling-rate conditions. To limit, as much as possible, the microcrystal formation inside the glass, a cooling rate not less than 80 °C h^{-1} is suggested.

Similar results concerning all the measured properties and crystallization phenomena were also obtained in a range of temperatures of application of the glass layer near to 1300 °C. Below this the results are obtained only beginning from 1280 °C. This is the last lower temperature at which the glass layer is able to adhere to the substrate.

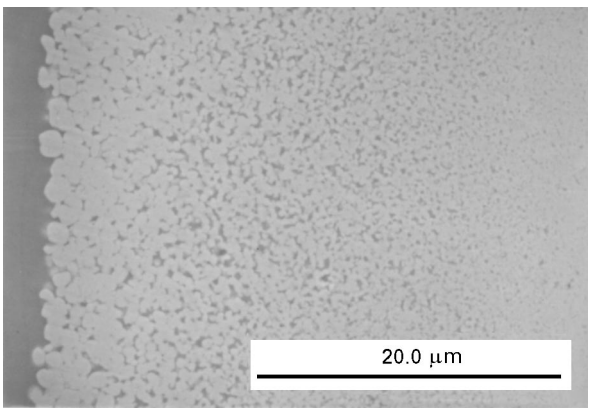

Figure 8 Microstructure of covered zirconia ceramic produced by injection moulding astride the interface substrate/glass.

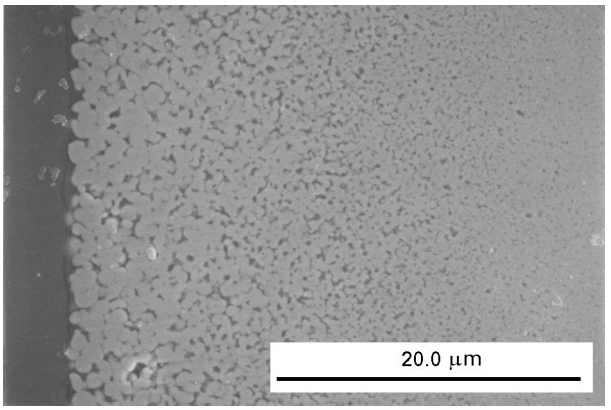

Figure 9 A group of zircon microcrystals sporadically detected on the interface in one examined sample naturally cooled (sample with substrate fired at 1530°C and coated with glass at 1300°C).

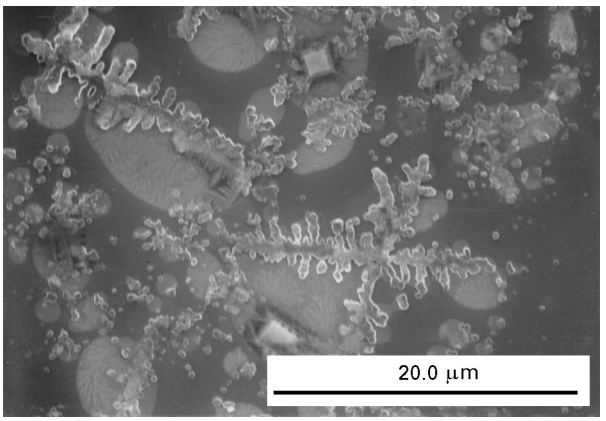

Figure 10 An example of dendritic and globular microcrystals which grow sporadically in restricted areas of the surfaces.

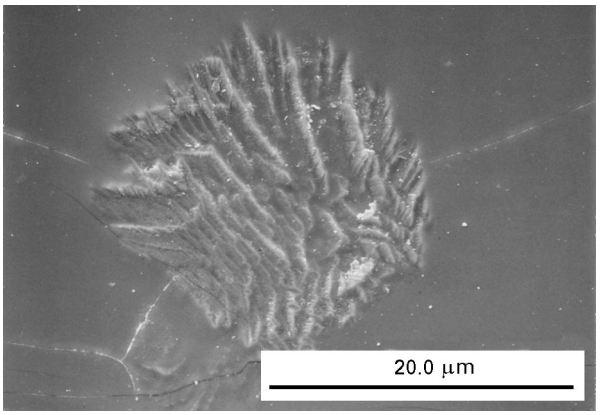

Figure 11 An example of a common crystalline neoformation disseminated homogeneously all over the surfacial thin matt layer.

4. Discussion

Mechanical tests ascertained a good adhesion of the bioactive glass to the zirconia support. We can hence forecast the possibility of coating this ceramic material with a suitable biological glass. Glass deposition on the support does not occur as an adjoined, but as an independent (or separate), phase. The trend of the glass is, in fact, to permeate the ceramic support by a logical mechanism of penetration through the surface porosity defects and intergranular paths of the samples which have been coated as green or fired bodies up to 1450 °C. This penetration is obviously very great when the glass is applied at 1530 °C and slight when applied at 1350°C on substrates fired at 1530 °C. On insufficiently sintered substrates the molten glass utilizes the grain-boundary paths and possible microporosity to penetrate the ceramic bulk and modify densification in the sintering process.

The penetration of the glass into the substrate, however, determines internal stresses and some physico-chemical modifications in the involved volume (a layer about 35 μm) of zirconia ceramic. On this (up to 3 mm thickness) zirconia supports coated on only one face, a marked bending of the supports themselves was observed after their cooling, and the glassy layer appeared always on the convex side. Such deformation, also considering its extent, was attributed to the penetration of the glass in its liquid phase between the zirconia grains on the surface layer of the samples to an average depth of about 35 μm. During the cooling process, in fact, glass increases its viscosity to such an extent that it has difficulties in leaving the intergranular areas towards the outside, because it is restrained by the force that leads to contraction of the zirconia substrate. In this way, part of the glass is trapped between grains of the surface area, and the observed arching occurs as a consequence. These deformations do not appear either on thin zirconia supports coated on their whole surface or on massive supports (> 3 mm) even if only partially coated. On the strength of our observations, however, it can be assumed that thin and partially coated supports are liable to the formation of residual tensile stresses even in their innermost parts as a result of the penetration of glass between grains of surface areas. Residual internal tensile forces should, consequently, arise inside the microstructure of the whole ceramic body. In practice, however (see mechano-physical values of Table II), these forces do not appear to have deleterious effects on the overall qualities of this coated ceramic.

Elemental microprobe profiles have shown that the distribution of elements does not correspond to a distribution by simple bulk diffusion of the glass. In this case, instead, a process favouring a different ionic diffusibility seems to come into play. A portion of the solubilized ZrO_2 reacts with part of the Ca^{2+} ions of the glass, giving rise to the observed formation of calcium zirconates. XRD analysis of the coated surface exhibits small percentages of calcium zirconate and a large amount of monoclinic ZrO_2. This suggests that the glass permeates the ceramic microstructure of the superficial zone through grain boundaries and partially dissolves the grains. It is evident that part of the ZrO_2 is dissolved by the glass and that further penetration of the same glass in depth is favoured as a result. It is obvious that the dissolved ZrO_2 fraction will lose stabilization because Y_2O_3 will be dispersed in the vitreous bulk. The resultant concentration of yttria in the glass is, however, so small that it is difficult to detect by instrumental analyses.

In the cooling stage, surplus ZrO_2 inside the vitreous bulk tends to crystallize; but because it does not have a sufficient amount of Y^{3+} ions to stabilize the network, it will crystallize directly in its monoclinic form. This process will be further favoured by the presence of residual tensile forces supplying an energy sufficient for the transformation from the tetragonal to the monoclinic phase. The formation of $CaZrO_3$ at the highest temperatures of application of the glass is due to the higher mobility of the Ca^{2+} ion with respect to any other that is able to give rise to precipitated compounds. It is assumed that the main process involved in the peripheral transformations of ZrO_2 is that of dissolution–reprecipitation, which could explain both the partial dissolution in the glass, the observed presence of the monoclinic phase and the increase in the original grain volume. $ZrSiO_4$ was sporadically detected only at the interface of one sample with optimized covering and only by the microprobe associated with the SEM. This could be at the basis of the different distribution of the ions specific to the glass composition along the profile.

It is probable that within the portion not involved in the permeation by the glass, no transformation will occur to monoclinic phase, even though it may appear so because of the stresses. To a limited extent this situation may not always be necessarily negative, because the same process that safeguards microcrack propagation through insemination of tetragonal ZrO_2 grains partially stabilized in Al_2O_3 ceramics should take place. Also in this case, when stress-activated microcracking occurs, the transformation of some ZrO_2 grains from tetragonal to monoclinic where there is interaction with biological glass, may preserve the integrity of the ceramic structure. The increased volume of the grains seals the microstructure, closes up possible microcracks and imposes an internal compressive stress that improves response to mechanical stresses. However, transformations at the interface can be controlled by accurately arranging the times of each part of the cycle of application of the glass coating, that is, heating rate, time of permanence at the steady temperature of application, cooling rate. With a cooling rate greater than 200 °C h^{-1} the formation of microcrystals in the glass is largely avoided. Also the temperature of application of the glass also influences the process: the lower the temperature, the lower the leaching rate of zirconium ions into the glass layer (although the times of application at steady temperature have to be greater).

No significant differences between the samples prepared by die pressing or injection moulding were detected, at least for this study.

5. Conclusion

It was ascertained that a very good coating on zirconia supports is obtained with the biological glass AP40. The best tests are obtained from the supports fired at 1530 °C and refired, after coating with AP40, in the range 1280–1300 °C. The results are positive in terms of suitable thickness of the coating on its support and the best coating–support adhesion.

The formation of crystals in the glassy system seems to play a positive role in the arrangement of the whole glassy layer on the substrate and controlled bioresorption in contact with the bone when applied *in vivo*. We note that the material tensions of the glass decrease probably as a result of the precipitation of the microcrystals inside the vitreous system [8].

References

1. A. RAVAGLIOLI, A. KRAJEWSKI, A PIANCASTELLI, G. BERGER, K. ADAM and R. GILDENHAAR, *InterCeram* **49**(2) (1992) 64.
2. P. LAUDADIO, E. CUNSOLO, L. PRESUTTI, A. KRAJEWSKI, A RAVAGLIOLI and L. L. HENCH, "The Importance of the Adhesion through Biological Glass to the Acoustic Membrane of TOR Prosthesis", Proceedings of the 8th International Symposium on Ceramics in Medicine, (Jacksonville, FL), Bioceramics Vol. 8, edited by J. Wilson, L. L. Hench and D. Greenspan, (Pergamon/Elsevier Science, Oxford, 1995).
3. L. RUIZ and M. J. READEY, *J. Am. Ceram. Soc.* **79** (1996) 2331.
4. A. RAVAGLIOLI, A. KRAJEWSKI, P. PONTI, R. VALMORI, S. VALMORI and S. CONTOLI, *J. Phys. Supp.* 2 (*Sci. Ceram. 13*) **47** (1986) C1, 769
5. A. RAVAGLIOLI, A. KRAJEWSKI, *InterCeram.* **32** (1983) 26.
6. *Idem*, *ibid.* **33** (1984) 22.
7. A. KRAJEWSKI and A. RAVAGLIOLI, *Vetzo Informazione* (1985) 19.
8. P. W. McMILLAN, in "Non-metallic solids", Vol. 1, "Glass ceramics", edited by J. P. Roberts and P. Popper, (Academic Press, London, New York, 1964), Ch. 3, p. 64.

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