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Optimisation of the synthesis of glass-ceramic matrix biocomposites by the "response surface methodology"

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Abstract

In this work a Bioverit®III glass-ceramic matrix composite, containing Yttria-stabilised zirconia (Y-PSZ) particles as toughening phase, was prepared, with the aim of improving the glass-ceramic mechanical properties. In order to prepare the composite, a pressureless sintering process has been optimised. The aim of the work is to determine the best processing conditions, i.e. time and temperature of sintering. For this purpose traditional methods (thermal, morphological and mechanical analysis) have been supported by the statistical method called "Response Surface Methodology" (RSM). On the basis of these studies two sintering series have been performed, so that we could determine the region where the best process conditions could be found.

Keywords: Bioceramics; Composites; Glass ceramics; Response surface methodology; Sintering; ZrO_2

1. Introduction

Since the 1970′s, when it was first realized that the properties of glasses and glass-ceramics could be exploited to provide better materials for certain implant applications, the field of bioactive ceramics has expanded enormously.[1] These biomaterials have been developed to be used in applications where a specific interaction with the human body is expected. They have chemical characteristics that insure non-toxic reaction in contact with the tissues and an active behaviour into the physiological environment, which ensures the new tissues growth. In this work the attention is focused on bioactive materials used for bone substitution in different fields of medicine: orthopaedics, odontoiatry, etc. One of the most restrictive problems of these materials is the combination of good mechanical properties as well as biocompatibility and bioactivity. One solution to this problem is the development of composite materials, so that the mechanical properties of the bioactive matrix can be improved by the addition of a second phase.[2–8] Zirconia is one of the best candidates to strengthen ceramic and glass materials and it was already successfully used in order to prepare several kind of bioactive composites based on both hydroxyapatite and bioactive glass-ceramic matrix.[5–8]

In this work the production process of a glass-matrix composite, toughened by the addition of Yttria-stabilised zirconia particles (Y-PSZ), has been optimised. The glass-ceramic matrix Bioverit®III[9–11] is a bioactive phosphate based glass-ceramic, which does not contain silica. It belongs to the P_2O_5–Al_2O_3–CaO–Na_2O system. The base glass shows an "invert glass" structure (characterised by mono- and diphosphate units) and the bioactivity of the resulting glass-ceramic has been proved by in vivo experiments.[9]

As toughening phase Y-PSZ was chosen because of its very good mechanical properties, good biocompatibility[12] and chemical compatibility with the glass-ceramic composition, which contains small amounts of ZrO_2.

This work follows a research line on Bioverit®-type glass-ceramics.[4,8,11] In order to optimise the production process (a viscous flow pressureless sintering process)

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the "Response Surface Methodology" (RSM)[13] has been used for the first time in our research line. This method is used in empirical studies in order to evaluate the influence of some input parameters on a group of dependent variables that are significant for the process that is being studied. Two different sintering series (at two different conditions of time and temperature) have been performed; each sintered sample has been characterised in terms of density and Young's modulus. The RSM was applied using the densities and Young's modulus data as dependent variables. In this way it was possible to determine the best sintering process conditions.

2. Experimental procedure

The chemical composition of Bioverit®III used is (wt.%): 51.4 P_2O_5, 16.0 CaO, 9.0 Al_2O_3, 14.6 Na_2O, 1.8 F^-, 4.5 ZrO_2, 2.7 TiO_2. The base-glass was prepared by melting high purity raw materials.

The composite (B3/Y-PSZ) has been prepared starting from the base-glass of Bioverit®III. The bulk glass was ball-milled and sieved. A bimodal particle size (70% in the range 106–20 μm, 30% < 20 μm) was used in order to optimise the particle distribution during the green compact preparation.[14]

A mixture of glass powders and reinforcing phase was obtained by the addition of 17%wt of Y-PSZ particles (ZrO_2–3%Y_2O_3, Tosoh, grain size < 38 μm). The mixture was prepared in an ethanol suspension, and stirred until complete evaporation of the solvent. The percentage of reinforcing phase was chosen on the basis of previous studies.[3,4,8,11,15]

In the research of the best process conditions, two different time and temperature ranges of sintering have been investigated, as described in next sections.

In order to prepare the composite by a low temperature pressureless sintering process, a thermal analysis has been done, by means of Differential Scanning Calorimetry (Perkin-Elmer DSC7). As described in previous works,[3,11,15] several isothermal treatments have been performed on glass and glass plus Y-PSZ powders in a temperature range close to the glass-transition temperature, in this case between 520 and 560 °C, for 30 min. Each isothermally treated sample was than submitted to a standard temperature scan between 400 and 700 °C (heating rate 10 °C/min), in order to determine if the isothermal treatment had induced any crystallisation of the glass-matrix.

A simulation of the sintering process was also carried out by Hot Stage Microscopy (Model A II, Leitz, Gmbh) and by dilatometry (Netzsch, Model 402 E, Exton, PA). Defect-free green compacts of glass and glass plus Y-PSZ powders were obtained by cold uniaxial pressing. In order to simulate the sintering process in a range of temperatures comprehensive of the glass transition ($T_g = 503 \pm 2$ °C) and the first crystallisation temperature ($T_{x1} = 546$ °C ± 2 °C),[11] the linear shrinkage of each kind of green compact was determined both by Hot Stage Microscopy on 3×3×3 mm^3 cubes and by dilatometry (heating rate 10 °C/min) on 3×5×30 mm^3 bars, in the temperature range between 25 and 900 °C. The first range of sintering temperature was chosen at the beginning of the shrinkage, at the highest isothermal temperature after which the T_x peaks can still be evidenced by a standard DSC scan.

The RSM is used in the empirical study of the relationships between the value of one or more measured property (such as density) and a number of input variables (such as time, temperature or concentration). This methodology establishes a group of mathematical models that represents the response surfaces of the measured property (those of the density and the Young's Modulus, in this case) by a given set of input variables (time and temperature of sintering, in this case) over some specified region of interest. In this work the RSM was used to find the maximum of a specific response (i.e. the maximum Young's modulus) determining the input variables (i.e. the sintering conditions) that produced the maximum response, and so, the best process conditions.

In this way, a first viscous flow sintering temperature range was found. Rectangular shaped (70×10×5 mm^3 size) green compacts of the glass plus Y-PSZ powders were prepared by uniaxial cold-pressing using a pressure of 20 MPa. The first sintering series have been done at temperatures of 510–550 °C. Five different sintering temperatures have been chosen, as shown in Table 1.

Each sintered sample was characterised by means of X-ray diffraction (XRD, Philips PW1830), Scanning Electron Microscopy (SEM, Philips 525 M), compositional analyses (EDX, Philips-EDAX 9100). As above mentioned, two different variables have been considered, as the output parameters for evaluate the sintering degree in those conditions. The first output parameter was the geometrical density (simply measured as the mass/volume ratio), and the relative density variation was calculated as the geometrical/theoretical density ratio. The theoretical density for the composite was calculated by the mixtures law, by using as theoretical density of the pure matrix the measured density of a bulk Bioverit®III base-glass previously thermally treated at the same time

Table 1
Time and temperature schedule of the first set of sintering

Temperature (°C)	Time (min)	Log time
510	15	1.2
510	60	1.8
530	30	1.5
550	15	1.2
550	60	1.8

and temperature conditions of the composites, and containing the same kind and relative content of crystalline phase as the composite glass-ceramic matrix (checked by XRD). The second variable was the Young's Modulus measured by resonance (standard method ASTM C623–71) on at least 10 specimens. The sintering conditions in this first range of temperature did not allow to get high density composites. In fact, by analysing the shape of the surface response, the process conditions research was addressed toward a region of higher temperature, at the end of the shrinkage range, but below the liquidus/melting temperature of the glass-matrix.

Again, five different sintering points have been chosen, in a temperature range between 720 and 760 °C, as shown in Table 2. Each sintered sample, obtained by these new conditions, were characterised by means of XRD, SEM, EDX. Also in this case density and Young's Modulus measurements allowed to represent the response surface, and to determine the region in which will probably be the best sintering conditions.

After this process optimisation a new set of sample was sintered at the best temperature and time conditions, in order to perform a more accurate characterisation. The K_{IC} was determined on these samples by a Vickers indentation technique, using the following formula:[16,17]

$$K_{IC} = A \cdot \frac{P}{c_0^{\frac{3}{2}}} \cdot \left(\frac{E}{H}\right)^{\frac{1}{2}} \quad (1)$$

where:

A = constant (=0.016) not depending on the tested material;
E = Young's modulus of the material (N/m^2);
H = Vickers hardness of the material (HV);
P = indentation load (N);
c_0 = average value of the cracks length, measured from the centre of each indentation (m).

This K_{IC} value was compared to that obtained for the pure Bioverit®III sintered at the best conditions, in order to prove the toughening effect of the Y-PSZ particles.

Table 2
Time and temperature schedule of the second set of sintering

Temperature (°C)	Time (min)	Log time
720	15	1.2
720	60	1.8
740	30	1.5
760	15	1.2
760	60	1.8

3. Results and discussions

3.1. Thermal properties

The sintering conditions of a glass-ceramic matrix composite must be chosen in order to fully utilise the low viscosity of the matrix, due to a relatively high process temperature, without modifying its chemical composition nor inducing any additional crystallisation in respect of the pure matrix. Moreover, the formation of any crystalline phases during heating could affect the particles viscous flow, resulting in a low density product.[11] Therefore, as discussed in previous works,[11,15] we choose to prepare the glass-ceramic matrix composites starting from amorphous powders, i.e. in this case from the base-glass of Bioverit®III (in order to work with a completely amorphous matrix, at the beginning of the process) and to perform the calorimetric study of the sintering process in the temperature range in which the highest shrinkage occurs. Fig. 1 reports the DSC scans, between 300 and 700 °C, carried out on the Bioverit®III base-glass plus Y-PSZ powders previously isothermally heated for 30 min at the temperature labelled on each curve. The first curve is related to the pure Bioverit®III base-glass mixed with zirconia particles. It is evident the T_g signal at about 500 °C and a broad crystallization peak between 550 and 650 °C. This broad signal can be explained in terms of a partial overlapping of the first and the second crystallization peaks (T_{x1} and T_{x2}) of the glass-matrix. As reported in Ref. 11, the pure Bioverit®III base-glass shows a T_{x1} onset at 570 °C and a T_{x2} at about 650 °C. These signals can be ascribed to the crystallization of apatite and Al–Ca phosphates respectively. The presence of a second phase (zirconia particles in this case) is likely to be the cause of a T_{x2} shift towards lower temperatures, due to a nucleation inducing mechanism. The same behaviour was observed in the DSC scan performed on a mixture of Bioverit®III base-glass and Ti particles.[11]

By comparing the thermograms in Fig. 1, it is evident that above 540 °C a 30 min isothermal treatment induced a partial crystallisation of the glass (the first crystallisation peak becomes less intense), while up to 530 °C the glass could be isothermally treated for 30 min without inducing any crystallisation.

The softening range and the maximum linear shrinkage of glass plus Y-PSZ green compacts were determined by the temperature scan performed by hot stage microscopy. The linear shrinkage of the composite powder compacts during the scan between room temperature and 900 °C is reported in Fig. 2a. The glass undergoes a fast shrinkage above 490 °C. The highest linear shrinkage is between 540 and 650 °C and the crystallisation of the glass occurs with a volume expansion not detectable with this technique. This behaviour was confirmed by the dilatometric analysis performed on the green compacts, as shown in Fig. 2b.

3.2. Research of the sintering conditions

Before starting the process to analyse the sintering conditions, it is necessary to understand the real measurement possibilities connected with the output parameters, density and Young's modulus, chosen as indicators of sintered product quality. The first necessary step was to evaluate the measurement uncertainty to be compared with the expected values of output parameters. It is, in fact, evident that the real evaluation possibility depends on an adequate value of the ratio between the expected variation of the considered output

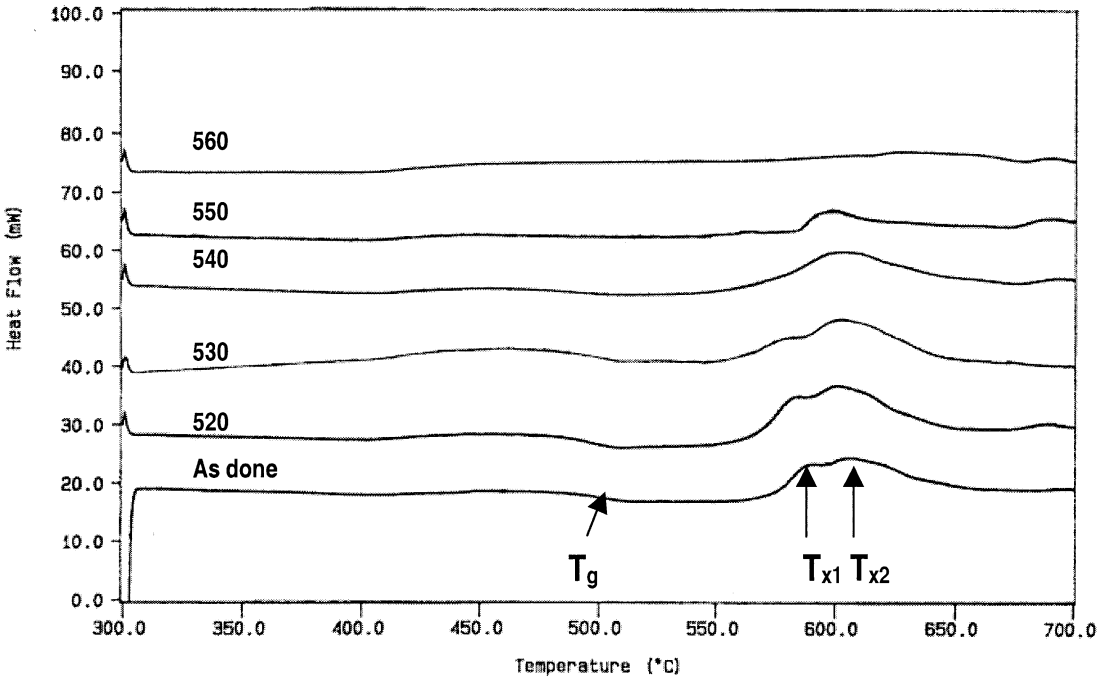

Fig. 1. DSC scans of the Bioverit®III base-glass plus Y-PSZ powders previously isothermally heated for 30 min at the temperature labelled on each curve.

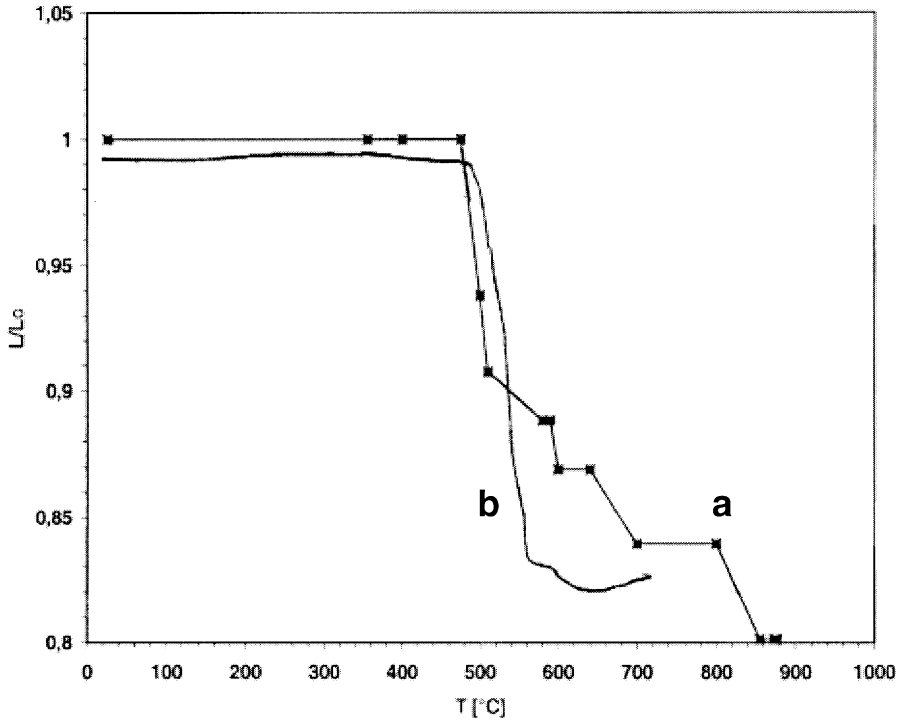

Fig. 2. (a) Linear shrinkage of the composite powder compacts during the scan between room temperature and 900 °C; (b) dilatometric analysis performed on the composite green compacts.

parameters and its measurement uncertainty, as this plays here the role of signal to noise ratio.

For this reason an accurate analysis of the uncertainty of the output parameter measurement techniques has been done.

The expanded uncertainties, at a confidence level of 95%, $U(d)$ and $U(E)$ of the density d and Young's modulus E respectively, have been calculated using the nominal value of each parameter involved in the measure. The results, together with the ratio of the expected values to the said uncertainties are given in Table 3.

The Young's modulus shows a definitely better signal to noise ratio, therefore should be preferred as performance indicator, nevertheless the signal to noise ratio for density, in the range of 40, is sufficient to perform a good analysis.

3.2.1. First sintering series

On the basis of the results obtained by the thermal analysis, the first sintering series was performed at low temperature, choosing the best compromise between low viscosity (which means high temperature) and low crystallisation (which means low temperature). Each sintered sample was then characterised, in order to observe the sintering degree obtained in those conditions. The density values were very similar for each sintered composite, i.e. about 83% of the theoretical value (3.0 g/cm^3). On the contrary, the Young's Modulus values were enough different from each other in order to find

Table 3
Expanded uncertainties, at a confidence level of 95%, of the density, $U(d)$, and Young's modulus, $U(E)$, respectively, and ratio of the expected values

	Expanded uncertainty U	Expected value	Signal to noise ratio
d (g/cm^3)	0.08	3.0	≈40
E (GPa)	0.3	76	≈250

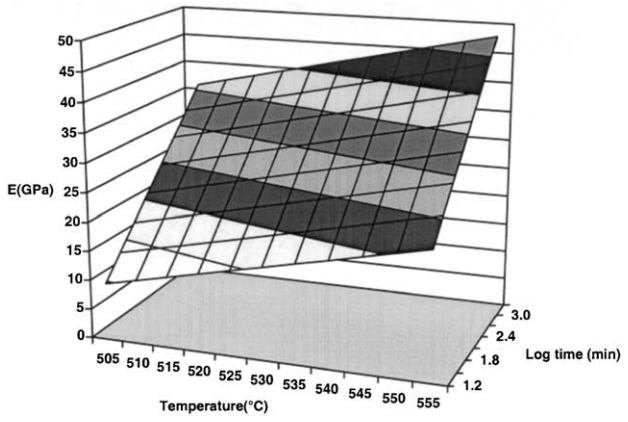

Fig. 3. Least squares secant plane of the Young's Modulus surface calculated by the Response Surface Method for the first set of sintered composites.

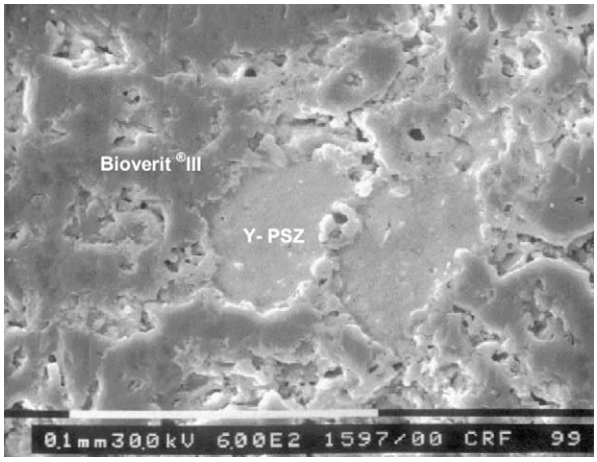

Fig. 4. Polished cross section of a B3/Y-PSZ composite sintered at 530 °C for 30 min (scanning electron micrograph).

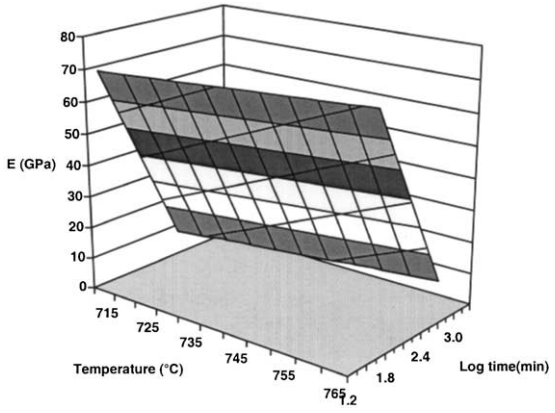

Fig. 5. Least squares secant plane of the Young's Modulus surface calculated by the Response Surface Method for the second set of sintered composites.

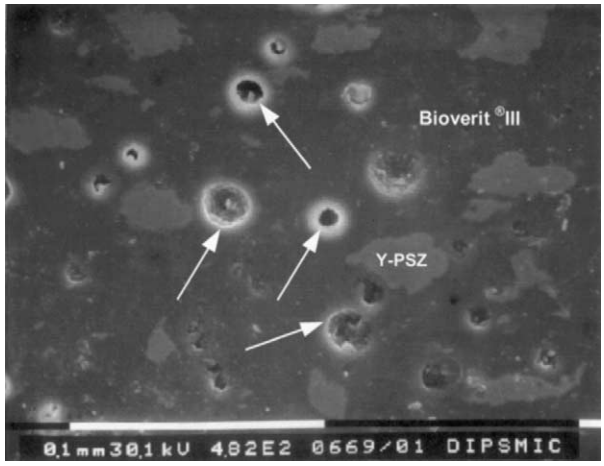

Fig. 6. Polished cross section of a B3/Y-PSZ composite sintered at 740 °C for 30 min (scanning electron micrograph).

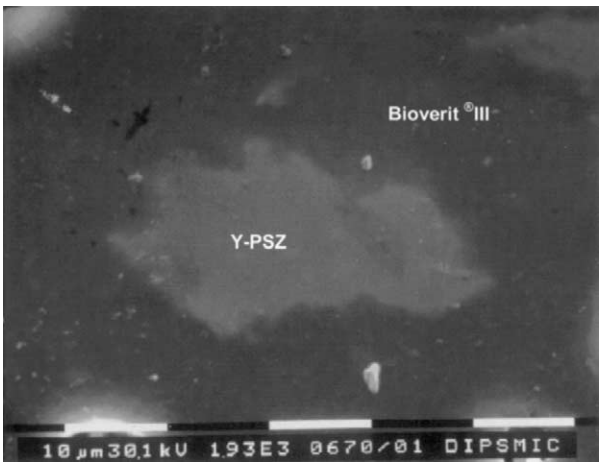

Fig. 7. Detail of the interface between the glass-ceramic matrix and the Y-PSZ particle in the composite sintered at 740 °C for 30 min (scanning electron micrograph).

the best sintering conditions by the Response Surface Method. The Young's Modulus surface for this conditions was calculated, and its least squares secant plane has been also represented, in order to make the trend more clear (Fig. 3).

Looking the shape of the secant plane to the response surface, it is evident that the sintering temperature has to be increased in order to improve both the Young's Modulus of the composite, and its degree of densification. These results were sustained from the morphological characterisation, as it is shown in Fig. 4. This figure report a scanning electron micrograph of the composite obtained by sintering at 530 °C for 30 min. It can be observed a discontinuous interface between the Y-PSZ particles and the matrix, and the presence of open porosity, which indicates that the sintering process is not concluded. Moreover, from the phase analysis made by XRD, it was observed that the original glass matrix still undergo to a partial crystallisation during the sintering process (even if not so evident during the sintering simulation), probably due to the presence of Y-PSZ particles which acted as nucleating agents. This feature could affect the viscous flow at low temperature, and inhibits the densification of the composite. Anyway, no additional crystalline phases, due to uncontrolled reactions between the glass-ceramic matrix and the Y-PSZ particles were observed, apart from Y-PSZ itself and the crystalline phases usually present in the Bioverit®-III glass-ceramic[11] (i.e. apatite and some mixed aluminium and calcium phosphates).

3.2.2. Second sintering series

Moving up the secant plane, a second sintering conditions series has been chosen, at higher temperature, at the end of the shrinkage range, below the base-glass liquidus/melting temperature, around 740 °C. The sintering conditions are shown in Table 2.

Again, all sintered samples have been characterised by means of density and Young's Modulus measurements, in order to represent the Response Surface. In this case, both values have resulted to be higher than in the first sintering series. The best sample (sintered at 740 °C), had a relative density of 93% of the theoretical value, and Young's Modulus of 76 GPa, also much more higher than before. The Response Surface, and the

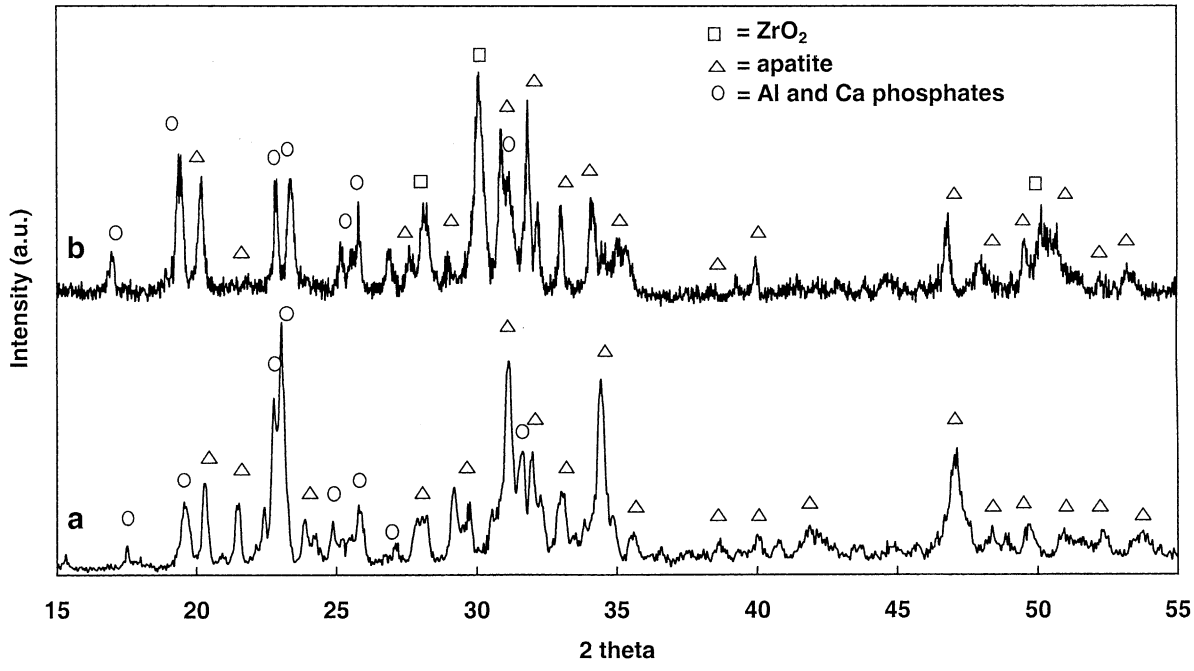

Fig. 8. XRD pattern of the glass-ceramic matrix composite (curve a) compared with that of the pure glass-ceramic sintered at 740 °C for 30 min (curve b).

secant plane for these second series conditions were represented. As shown in Fig. 5, the region of the maximum response (i.e. the maximum Young's Modulus value) have been individuated. This region should be around the sintering point at 740 °C. As shown below, increasing the temperature we move into a lower Young's Modulus region, which does not fit our purposes.

These results have been also supported by SEM, EDX and XRD analyses. The morphology of the as sintered composites is shown in Fig. 6 (sample sintered at 740 °C for 30 min). In this second sintering series each composite shown a very homogenous interface between the matrix and the Y-PSZ particles. Few close porosity, typical of a pressureless viscous flow sintering process, was observable on the polished cross section (see arrows in Fig. 6). Fig. 7 shows a detail of a Y-PSZ particle embedded into the glass-ceramic matrix.

A partial infiltration of the glass-ceramic matrix into the Y-PSZ particle was observed, due to the fact that the sintering process was performed close to the liquidus/melting temperature of the matrix. The EDX analysis confirms the partial infiltration of the matrix into the Y-PSZ particles, but it doesn't indicate any detectable compositional variation in the matrix composition.

By comparing the XRD patterns of the as obtained glass-ceramic matrix composite with that of the pure glass-ceramic sintered at 740 °C for 30 min (Fig. 8) it is evident that also in this case no additional phases were formed, apart from the crystalline phases usually present in the pure glass-ceramic. These phases are likely to be formed during the composite cooling from the process temperature to room conditions.

3.3. Mechanical characterisation

Once the region with a good process conditions has be found, the K_{IC} was evaluated on a third set of samples sintered at these conditions (740 °C for 30 min). In order to evaluate the toughening effect of the Y-PSZ particles, the mechanical test was performed on both the sintered composites and on the pure Bioverit®III glass-ceramic sintered at the same conditions. Several Vickers indentations were performed on polished sections in both cases. The glass-ceramics composites were indented with different loads up to 200 N. The composite showed an evident tougher behaviour in respect to the pure sintered glass-ceramic, as demonstrated in Fig. 9a and b. The 100 N load indentation on the pure glass-ceramic (Fig. 9a), produced deep crack propagation, while the same load on the composite (Fig. 9b) did not induce any crack propagation. The K_{IC} results, calculated from the formula (1) using higher loads, were in agreement with this qualitative characterisation and with the elastic properties of the sintered samples. Table 4 reports the Young's modulus and the K_{IC} of the sintered glass-ceramic and of the glass-ceramic matrix composite. They are both higher than that of the pure bulk glass-ceramic, ($E = 45$–56 GPa, $K_{IC} = 0.6$ MPa $m^{1/2}$ as reported in Ref. 9). The K_{IC} results revealed a higher fracture toughness of the glass-ceramic matrix composite in respect of the pure sintered glass-ceramic. The obtained values represent a very encouraging improvement. They are of the same order of magnitude of the dense AW glass-ceramics one, even if the material prepared in this work still presents some residual porosity, due to the intrinsic limits of the pressureless sintering method. However, a more complete comparison with literature data concerning bioceramics should be done on full density specimens, obtained for example by a hot pressing method, but this is not the objective of this work.

The glass-ceramic composites have a higher Young's Modulus when compared to the corresponding pure sintered matrix. These results pointed out that a continuous interface exists between the matrix and the particles, and no defects are present in a sufficient amount to affect the stress transmission from the matrix to the reinforcing particles.

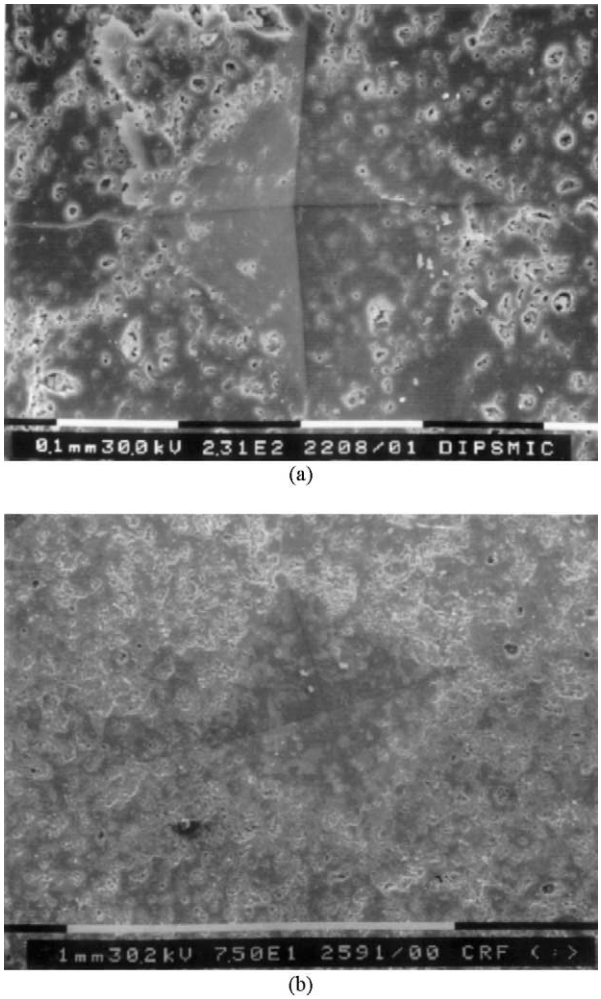

Fig. 9. Induced crack propagation in the pure sintered glass-ceramic (a) and in the composite (b) (scanning electron micrograph).

Table 4
Mechanical properties of bulk Bioverit®III, sintered Bioverit®III and sintered composite

	Bulk Bioverit®III	Sintered Bioverit®III	Sintered composite
E (GPa)	45	47	76
K_{IC} (MPa $m^{1/2}\pm0.1$)	0.6	2.6	3.0

4. Conclusions

Bioverit®III glass-ceramic matrix/Y-PSZ particles composites were successfully prepared by means of a pressureless sintering method. The sintering process was carefully optimised by means of both traditional characterisation methods (thermal, morphological and mechanical analysis) and the statistical "Response Surface Methodology". The sintering conditions were chosen in order to obtain high density composites avoiding unnecessary experimental work. The best results were reached by means of a viscous flow process at temperature close to the liquidus temperature of the matrix, obtaining nearly full density glass-ceramic matrix composites. A tougher behaviour was shown by the composites when compared both to the corresponding pure bulk and sintered matrix, confirming the toughening effect of the Y-PSZ particles.

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