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Na_2O-CaO-SiO_2 glass-ceramic matrix biocomposites

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Na_2O-CaO-SiO_2 glass- and glass-ceramic matrix/Ti particle biocomposites have been prepared by means of two processes: pressureless sintering and hot pressing. Time and temperature sintering conditions were optimised on the basis of the thermal properties of mixed glass and Ti powders, determined by Differential Thermal Analysis, Differential Scanning Calorimetry, Hot Stage Microscopy, Dilatometry. Each sintered sample was characterised by means of X-ray diffraction, Scanning Electron Microscopy, EDS, density measurements, Young's modulus, induced crack propagation by Vickers indentations, three point bending test, K_{IC} measurements. The *in vitro* bioactivity was investigated on the sintered composites by soaking them in a simulated body fluid (SBF) with the same ion concentration of the human plasma. © *2001 Kluwer Academic Publishers*

1. Introduction

Bioactive glasses and glass-ceramics are more and more studied because of their surface chemical reactivity when in contact with body fluids [1–3]; by a complex mechanism of ions leaching and partial dissolution of the glass surface, the precipitation of bone-like apatite from the solution provides a strong chemical bonding with hard and soft tissues. Since bioactive glasses and glass-ceramic are brittle materials, they are especially used in the field of small bone defects reconstruction, or as coatings on inert substrates for load-bearing prostheses [3]. However, they could be toughened by the addition of biocompatible metallic inclusions [4, 5], obtaining bioactive composite materials, with tailorable and predictable mechanical properties. These new materials could represent a valid alternative to the conventional metallic or ceramic high strength, but inert, implants. In this work, bioactive glass- and glass-ceramic matrix composites, reinforced with Ti particles (SCNT), were prepared by means of pressureles sintering and hot pressing, with the aim of obtaining high strength bioactive materials suitable for load bearing bone substitutions.

2. Experimental procedure

The base glass, named in this work SCN, has the following chemical composition (mol %): 50 SiO_2, 25 CaO, 25 Na_2O; when soaked in a simulated body fluid with ion concentration similar to those of human plasma, it develops a bonelike apatite layer on its surface [6].

This glass has been prepared by melting the starting products (SiO_2, $CaCO_3$, Na_2CO_3) in a platinum crucible, at 1600°C for 1 h (Linn Elektronic 1880). The melted glass was then quenched into cold water, dried at 100°C for 1 h, powdered in a ball mill and sieved up to a grain size of 70 μm. The characteristic temperatures of the glass were determined by means of Differential Thermal Analysis (DTA Netzsch 404 S) and Differential Scanning Calorimetry (Perkin Elmer DSC 7). In order to obtain bars, part of the glass was poured on a stainless steel sheet heated at 300°C (to avoid crack formation due to thermal shock); the bars were successively annealed at 450°C for 2 h, or submitted to a nucleation and growth thermal treatment (600°C for 30 minutes +750°C for 3 hours), in order to obtain glass and glass-ceramic specimens, respectively. The bars were then cut and polished up to a 1 μm finishing, to a final size of $50 \times 7 \times 3$ mm^3. Young's Modulus (Grindosonic Lemmens-Electronic) and density (Archimedean method) measurements were performed on the glass and glass-ceramic bars; the linear expansion coefficient was determined in the temperature range between 25 and 840°C (Netzsch dilatometer 402). The crystalline phase formed during the thermal treatment was determined by XRD analysis (Philips PW 1830).

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TABLE I Characteristics of the glass and glass-ceramic SCN ($*$ = dilatometric)

Sample	T_g (°C)	$T_{soft}*$ (°C)	T_x (°C)	ΔT_l (°C)	α (K^{-1})	E (GPa)	d (g cm^{-3})
SCN	543 ± 2	560 ± 2	665 ± 2	1200-1240	$16{,}6 \times 10^{-6}$	Glass: 77 Glass-ceramic: 88	Glass: 2,72 Glass-ceramic: 2,78

The fracture toughness (K_{IC}) of the bulk glass-ceramic was measured by means of indentation technique, using the formula [7, 8]: $K_{IC} = A(E/H_v)^{1/2}(P/c_0^{3/2})$, where: $A = 0{,}016$, E = Young's Modulus of the material (Pa), H_v = Vickers hardness of the material (N/m^2), P = indentation load (N), c_0 = average value of the cracks length (m), measured from the centre of each tip.

The powdered quenched glass was mixed with 15 % vol of Ti particles (Plasma Technik, 99,99% purity, grain size <50 μm). The behaviour under heating of the glass plus Ti powders was observed by means of differential scanning calorimetry. The linear shrinkages of the glass and glass plus Ti powders were measured between room temperature and 950–1000°C by means of both Hot Stage Microscopy (HSM, Leitz Mod. II A) and dilatometry (heating rate 10 K/min., under Ar flow), on green cubes of $3 \times 3 \times 3$ $(mm)^3$ size and green bars of $50 \times 5 \times 3$ $(mm)^3$ size, respectively.

In order to obtain SCN matrix/Ti particle composites (SCNT), two processes were compared: pressureless sintering and hot pressing. In the former case, a calorimetric study of the sintering process by DSC was performed, as described elsewhere [4, 5, 9], with the aim of preparing sintered samples with the best compromise between high density and low crystallinity. On the basis of this study, a temperature close to the softening point, which induced a not complete crystallisation of the glass-matrix, was determined. Greens of the composite obtained by uniaxial cold pressing (150 MPa load, for 60 sec., using ethanol as liquid binder) were then pressureless sintered at that temperature, for different times (15 to 120 minutes).

The time and temperature conditions for the sintering process by hot pressing were determined on the basis of the thermal properties of the mixed glass and Ti powders previously recorded by DTA, DSC, HSM and Dilatometry.

Each sintered sample was characterised by means of XRD, SEM (Philips 525 M), EDS (Philips EDAX 9100), and density measurements (Archimedean method). A mechanical characterisation was performed on the samples which reached the higher density: Young's modulus, induced crack propagation by Vickers indentations, three point bending test, K_{IC} measurements. At least ten specimens were used for each mechanical test. By means of the uncertainty propagation law, the measure uncertainty for Young's modulus values (u^2E) was estimated to be: $u^2E = 2{,}78 \times 10^{-1}\%$.

An *in vitro* bioactivity test was performed on the sintered composites, by soaking them in a simulated body fluid (SBF) with the same ion concentration of the human plasma [2, 4, 10]: the samples were soaked in 50 ml SBF, into polyethylene bottles, at 37°C, without stirring. After 30 days the samples were removed from the solution, washed in distilled water, dried at room temperature and characterised by XRD, SEM and EDS. For comparative purposes, the same test was performed on bulk SCN glass- and glass-ceramic samples.

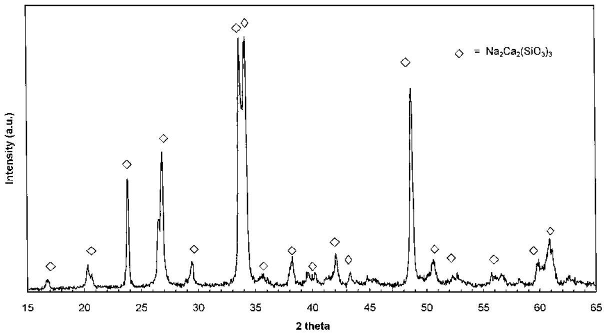


Figure 1 XRD pattern of SCN glass-ceramic.

3. Results and discussion

Table I reports some characteristics of SCN glass and glass-ceramic: glass-transition temperature (T_g), crystallisation temperature (T_x), liquid temperature range (ΔT_l), linear expansion coefficient (α), Young's Modulus (E). The XRD pattern of SCN glass-ceramic is reported in Fig. 1. All the signals have been attributed to the phase $Na_2Ca_2(SiO_3)_3$. The morphology of this crystalline phase is evidenced in Fig. 2 (sample etched by a 10 vol % HF solution).

The linear shrinkages of SCN base glass and SCNT (glass-matrix composite) powder compacts, determined by hot-stage microscopy during the scan between room temperature and 950–1000°C, are reported in Fig. 3. A fast shrinkage above 550°C is observable for the base glass. The highest linear shrinkage (9%) is between 580 and 640°C, and the crystallisation of the glass occurs with few volume expansion. In the case of the SCNT green sample, the highest shrinkage (8%) is between 530 and 710°C. Above this temperature, a gradual expansion occurs, which becomes faster above 800°C. The choice of the pressureless sintering temperature should take in account the high reactivity of titanium at this temperature. However, the percentage of maximum linear shrinkage is comparable for both the glass and the composite greens. These ranges of temperature and the percentages of linear shrinkage have been confirmed by the dilatometric measurements.

The calorimetric study performed on the glass plus titanium powders suggested that isothermal treatments for 60 to 120 minutes at temperature below 600°C induced a not complete crystallisation of the glass-matrix. In fact, a temperature scan performed on different samples previously isothermally treated at different temperatures up to 600 °C still showed the crystallisation peak,

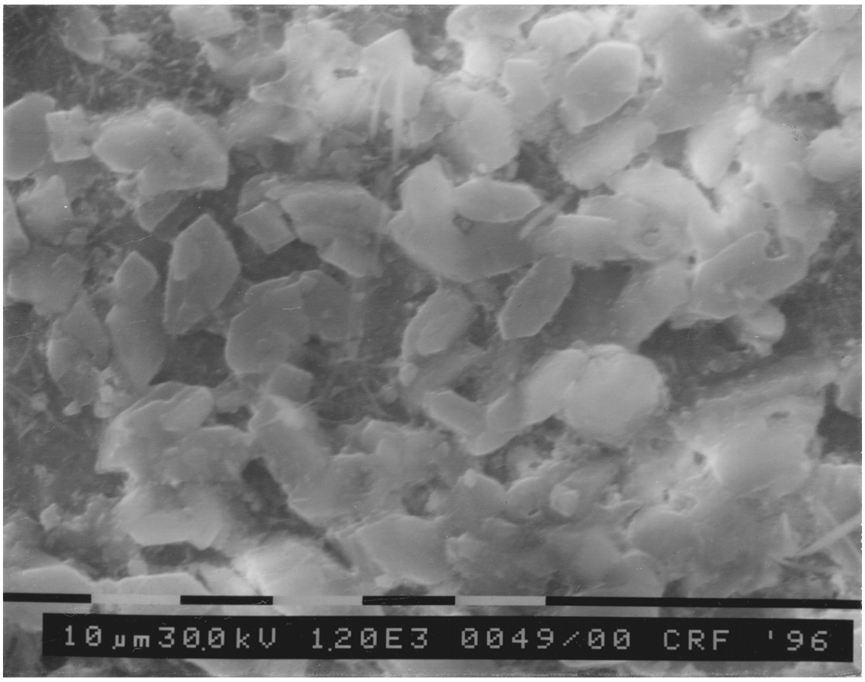


Figure 2 Morphology of the $Na_2Ca_2(SiO_3)_3$ crystalline phase.

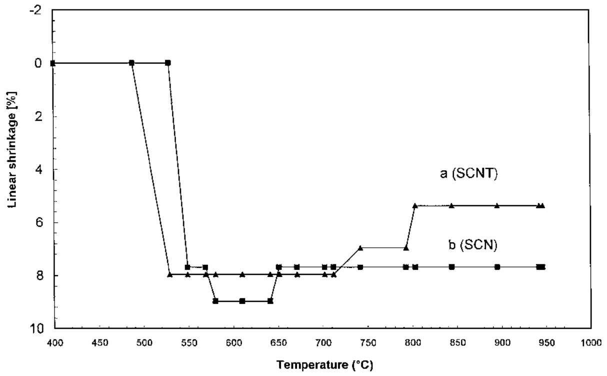


Figure 3 Linear shrinkages of SCN base glass (a) and SCNT glass-matrix composite (b) powder compacts.

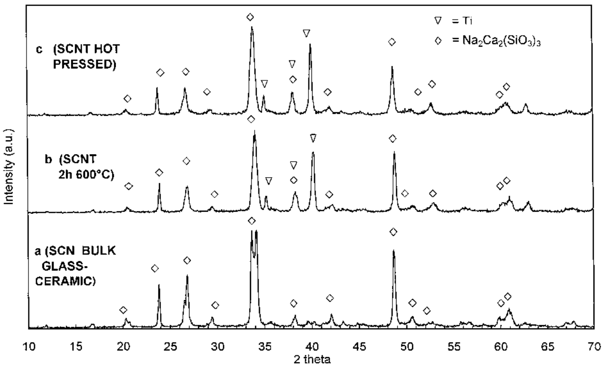


Figure 4 XRD patterns of the pure SCN glass-ceramic (a), of the SCNT composite sintered at 600°C for 120 minutes (b) and of the hot pressed SCNT (c).

even if more and more low. On the other hand, isothermal treatments at temperatures above 600°C produced a total crystallisation: the successive temperature scan on samples isothermally treated at temperatures above 600 °C did not show any crystallisation peak. On the basis of this information and taking into account the shrinkage properties of the green compacts, the temperature of 600°C was chosen for the pressureless sintering. At this temperature, also in presence of a certain crystallisation of the glass matrix, the few amorphous phase still present could enhance the viscous flow and the densification of the green compacts.

XRD analyses were performed on the powdered sintered composites, in order to observe the phase formation at the sintering temperature. In each sample only the crystalline phase $Na_2Ca_2(SiO_3)_3$ and pure titanium were detected. The presence of the Ti particles did not induce any crystallisation of additional phases, as can be observed by comparing the XRD patterns of the pure SCN glass-ceramic and that of the SCNT composite sintered at 600°C for 120 minutes (Fig. 4a and b, respectively). Samples sintered at 600°C for less than 120 minutes did not show relevant differences in the XRD patterns, apart from a slightly more evident amorphous background. The EDS analysis performed on 10–100 μm^2 areas (mean value of several analyses) on the bulk SCN glass-ceramic and on the SCNT composite glass-ceramic matrix, did not revealed any detectable compositional variation following the sintering process.

The maximum density of the as obtained glass-ceramic matrix composites were all close to 80% of the theoretical one (calculate with the law of mixtures). In order to use the SCNT composites as bulk materials a further improvement of the density is necessary. For this purpose hot pressing of the mixed glass and titanium powders was carried out as an alternative to the pressureless sintering process.

On the basis of the thermal properties of the glass plus titanium powders and on their shrinkage properties as green compacts, already determined by thermal analysis, hot stage microscopy and dilatometry, a time and temperature schedule was developed. The

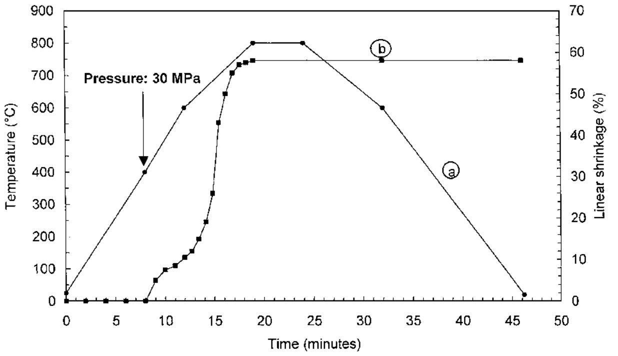


Figure 5 Time and temperature schedule (a) and linear shrinkage (b) of the SCNT composite during the hot pressing treatment.

maximum temperature of 800°C was reached after a two step temperature scan (from 25 to 600°C, heating rate: ≈50°C/min; from 600 to 800°C, heating rate: 10°C/min) and maintained for 5 minutes. Then the temperature was lowered to room conditions (cooling rate ≈40°C/min). A constant pressure of 30 MPa was applied starting form the temperature of 400°C, and maintained up to the end of the thermal treatment. In this case it was possible to exceed the crystallisation temperature because the applied pressure contrasted the expansion observed in the pressureless heating; anyway, the thermal treatment was carried out at temperature not above 800°C and for few minutes in order to avoid as much as possible any reaction between the SCN matrix and the Ti particles.

Fig. 5 shows the as described time and temperature schedule (a) and the linear shrinkage contemporaneously observed (b). Also in this case no crystallisation of additional phases was induced (Fig. 4c), and the EDS analyses did not revealed any detectable compositional variation. Moreover, the SCNT composite obtained in this way reached a density close to 98, 9% of the theoretical one. Fig. 6 shows a polished surface of a hot pressed SCNT composite. The titanium particles are well embedded into the glass-ceramic matrix, and very few porosity is still observable, but it is never localised at the interface between the matrix and the dispersed titanium phase. A very good adherence and no discontinuity were obtained between the two materials, as it is shown in Fig. 7, where a particular of the interface Ti particle/glass-ceramic matrix is reported at higher magnifications.

Since by hot pressing very good results in terms of density and reinforcing phase distribution were obtained, only on these samples a complete mechanical characterisation was carried out. Several Vickers indentations were performed on polished sections of both pure SCN glass-ceramic and SCNT glass-ceramic matrix composite, using different loads, up to 98 N. The indentations at 29, 4 N load on the pure glass-ceramic produced some brittle fracture of the glass-ceramic surface around the indent (see arrows in Fig. 8a) and deep crack propagation. Higher loads caused a catastrophic fracture of the glass-ceramic surface. On the contrary, the composite shows a tougher behaviour (Fig. 8b): no brittle behaviour was observed by indenting the composite up to 98 N load. Few cracks propagated from the indent corners, but they are shorter than those produced in the pure glass-ceramic at lower loads. In Fig. 9 a detail of the crack propagation induced by Vickers indentation (98 N) on a SCNT hot pressed composite is reported: the crack path is deviated by a Ti particle. The toughening mechanism (crack deflection) of the Ti particles embedded into the glass-ceramic matrix is likely to be related to the tensional state originated at the interface between the two materials, which have different rigidity and different linear expansion coefficient. According to the theories exposed by Selsing [11] and Miyata [12], since titanium is more rigid than SCN ($E_{\mathrm{Ti}} = 110$ GPa; $E_{\mathrm{SCN}} = 77$–88 GPa, glass and glass-ceramic respectively) and since its linear expansion

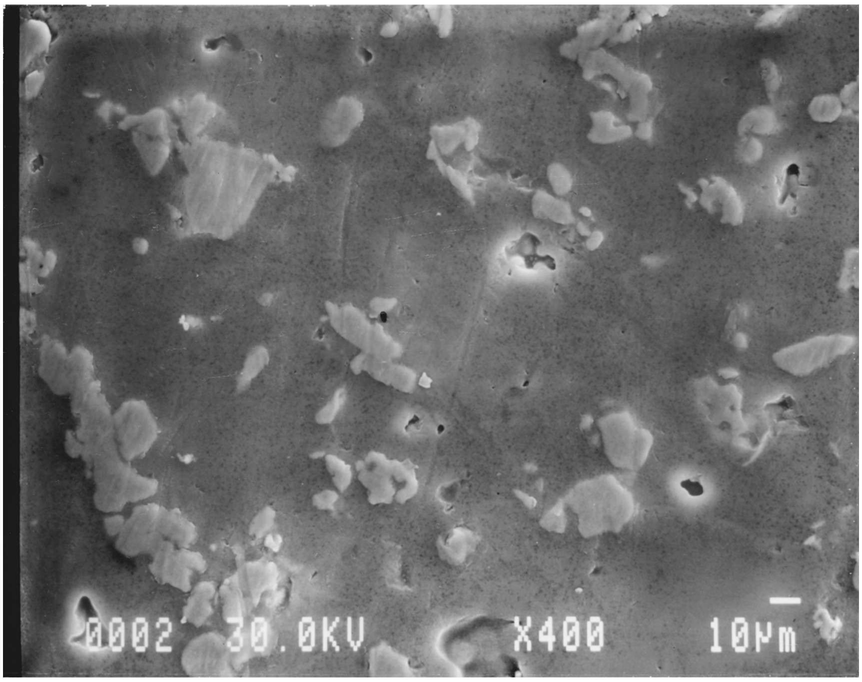


Figure 6 SEM micrograph of the polished surface of a hot pressed SCNT composite.

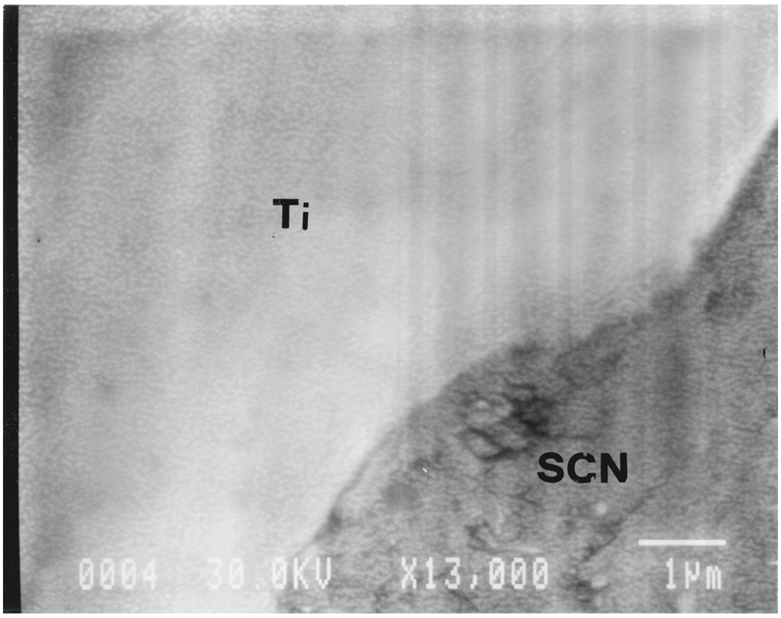
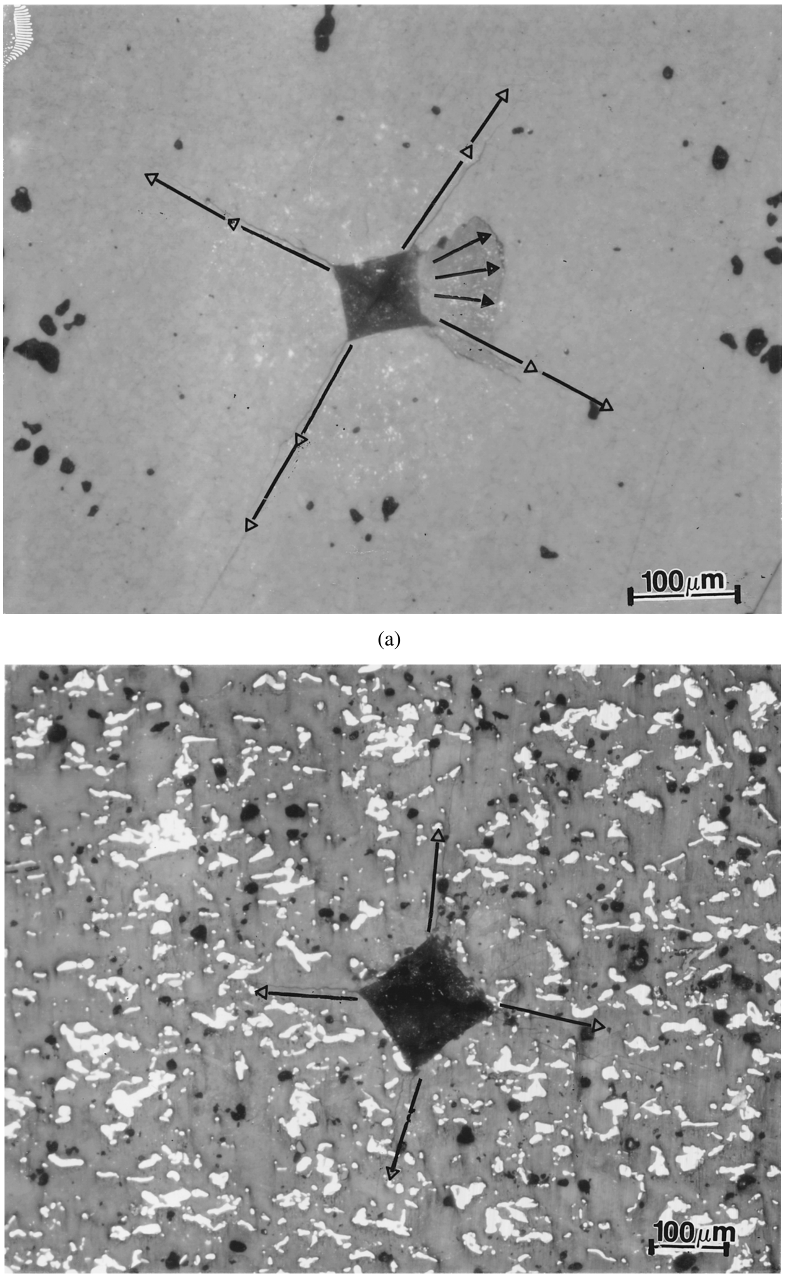


Figure 7 Interface between a Ti particle and the glass-ceramic matrix in a hot pressed SCNT composite.



(a)

(b)

Figure 8 Indentation at 29, 4 N load on the pure SCN glass-ceramic (a) and the hot pressed SCNT composite (b).

TABLE II Mechanical properties of the SCNT composite obtained by hot pressing in comparison to those of the pure bulk glass-ceramic

Sample	K_{IC} (MPa · $m^{1/2}$)	H_v (GN m^{-2})	E (GPa)	3 p.b. strength (MPa)	d (g cm^{-3})
SCN glass-ceramic bulk	$0,58 \pm 0,11$	$4,18 \pm 0,81$	88	-	2,78
SCNT hot pressed	$1,80 \pm 0,40$	$4,15 \pm 0,20$	93	$76,12 \pm 2,2$	3,00

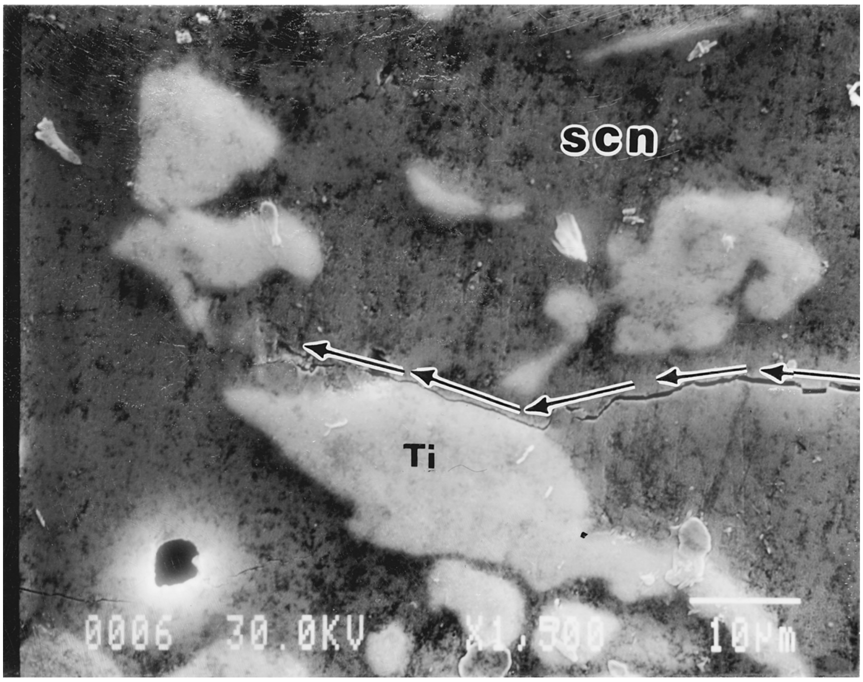


Figure 9 Detail of the crack propagation induced by Vickers indentation (98 N) on a SCNT hot pressed composite.

coefficient is lower than that of SCN ($\alpha_{Ti} = 9 \times 10^{-6}$/K, $\alpha_{SCN} = 16,\ 6 \times 10^{-6}$/K), it is expectable that a crack which propagate near a titanium particle is attracted toward its median plane, and then deflected by running around it.

Table II reports some mechanical properties of the hot pressed SCNT composite in comparison to those of the pure bulk glass-ceramic. The SCNT Young's Modulus is higher than that of the pure glass-ceramic matrix, and in agreement with the theoretical one, calculable by the rule of mixtures. The rule of mixture is valid only if the interface between the matrix and the particles is homogeneous and without defect (pore, cracks). In this way a corrected stress transmission from the matrix to the reinforcing particles is provided, making the composite tougher than the pure matrix. The Young's Modulus value of the composite is related to its very good adherence between the matrix and the titanium particles.

Table II also shows a relevant improvement of the fracture toughness (K_{IC}) of the composite in respect of the pure glass-ceramic matrix; the uncertainties of these two values (0, 58 and 1, 80) are reported as ±3s (three times the standard deviation) and they are comparable one each other (19–22% of average uncertainty). The three point bending test performed on the composite gave good and reliable results (2% of average uncertainty). No significant differences were observed in the Vickers hardness values, apart from a very low uncertainty of the hot pressed composite in comparison to the bulk glass-ceramic (4, 8% and 19% respectively).

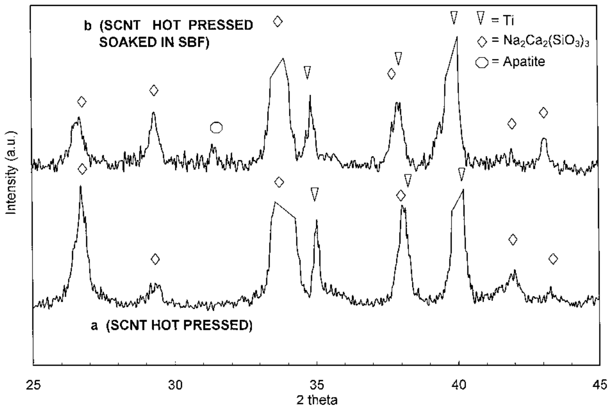


Figure 10 XRD patterns of the hot pressed SCNT composite (a) and of the same composite after 30 days of soaking in SBF (b).

By soaking the hot pressed composite into a simulated body fluid, at 37°C for 30 days, the growth of an apatite thin layer was observed. EDS analysis on this layers showed a Ca/P weight ratio close to the theoretical one for apatite (i.e. = 2.15). This layer was also detected by X-ray diffraction, as reported in Fig. 10: by comparing pattern **a** and **b** it is evident that after 30 days in SBF the strongest signal of apatite was detectable. The bioactivity of the pure base glass is well known and documented by the growth of apatite layer after soaking in SBF [6]. The growth of the same kind of layer on the glass-ceramic matrix/Ti particle composite is an evidence that, not only the crystallisation of the glass-matrix, but also the presence of a metallic disperse phase and the sintering process did not affect the bioactivity of this new material. So it can be concluded that a "biocomposite" has been prepared.

4. Conclusions

By means of two different methods (pressureless sintering and hot pressing) bioactive glass-ceramic matrix/Ti particle biocomposites (SCNT) have been prepared. Only the hot pressing process provided high density composites, on which a complete characterisation has been carried out. The mechanical properties of the hot pressed composite are better then those of the pure bulk glass-ceramic (SCN). The composite, after 30 days of soaking in a simulated body fluid, showed the growth of an apatite layer, which confirms that its bioactivity was not lost during the sintering process.

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References

1. L. L. HENCH, *J. Amer. Ceram. Soc.* **74**(7) (1991) 1487.
2. T. KOKUBO, H. KUSHITAI, C. OHTSUKI, S. SAKKA and T. YAMAMURO, *J. Mater. Sci. Mat. Med.* **3** (1992) 79.
3. L. L. HENCH, *Amer. Ceram. Soc. Bull.* **77** VII (1998) 67.
4. E. VERNÉ, M. FERRARIS, A. VENTRELLA, L. PARACCHINI, A. KRAJEWSKI and A. RAVAGLIOLI, *J. Eur. Ceram. Soc.* **18** (1998) 363.
5. E. VERNÉ, M. FERRARIS and C. JANA, *ibid.* **19** (1999) 2039.
6. H. M. KIM, F. MIYAJI, T. KOKUBO, C. OHTSUKI and T. NAKAMURA, *J. Amer. Ceram. Soc.* **78**(9) (1995) 2405.
7. A. S. RIZKALLA, D. W. JONES and R. P. MILLER, *British Ceramic Transaction* **95**(4) (1996) 151.
8. M. V. SWAIN and N. CLAUSSEN, *Amer. Ceram. Soc. Comm.* Feb. (1983) C-27.
9. M. FERRARIS and E. VERNÈ, *J. Eur. Ceram. Soc.* **16** (1996) 421.
10. T. KOKUBO, in "An Introduction to Bioceramics" (Advances Series in Ceramics, World Scientific Publishing Co. Pte. Ltd., Singapore, 1993) Vol. 1., p. 75.
11. J. SELSING, *J. Amer. Ceram. Soc.* **44** (1961) 419.
12. N. MIYATA and H. JINNO, *J. Mat. Sci.* **16** (1981) 2205.

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