Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 2929–2934

www.elsevier.com/locate/jeurceramsoc

Strength and toughness of tape cast bioactive glass 45S5 following heat treatment

D.C. Clupper[a,*], L.L. Hench[a], J.J. Mecholsky[b]

[a]*Centre for Tissue Engineering, Department of Materials, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BP, UK*

[b]*Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA*

Received 5 January 2003; received in revised form 19 May 2003; accepted 25 May 2003

Abstract

Tape cast and sintered (TCS) bioactive glass 45S5 has been shown to exhibit in vitro bioactivity in SBF and Tris, despite the formation of a crystalline phase ($Na_2Ca_2Si_3O_9$) during heat treatment. In this work, the effective porosity, hardness and flexural strength of TCS bioactive ceramic (composed of bioactive glass 45S5 prior to heat treatment) was determined as a function of the processing conditions (800, 900, and 1000 °C for 3 h and 1000 °C for 6 h). Additionally, the fracture toughness of the highest strength samples (1000 °C for 3 h, 1000(3)C, 83±13 MPa) was estimated by two independent methods: indentation strength and fractographic analysis. Hardness increased (0.2–5.7 GPa) with processing temperature and time, and this increase was inversely proportional to the decrease in effective porosity (1.14–0.02 cm^3/g). The strength was also found to increase with temperature for samples heated for 3 h (30±4 to 83±13 MPa). The fracture toughness values obtained using the indentation strength method and fractographic analysis ranged from 0.9±0.2 to 1.1±0.2 $MPam^{1/2}$. In addition, a higher porosity 1000(3)C type TCS bioactive glass-ceramic could also be fabricated without significantly decreasing the fracture toughness.

Keywords: Bioactivity; Glass; Hardness; Strength; Tape casting; Toughness

1. Introduction

It is well known that bioactive glasses and glass-ceramics are able to bond to bone through the formation of a hydroxyapatite surface layer.[1,2] More recent studies have demonstrated that the dissolution products released from bioactive glass have a strong role in stimulating bone cells as well.[3,4] Methods for producing such materials in complex shapes are desirable for patient-tailored structural applications.

Tape casting is one such method for producing a complex shape, as the final structure is built up layer by layer. Furthermore, this method is easily amenable to composite formation; i.e. through the use of laminae of varying composition or properties.[5–7] Interfacing such a method with rapid prototyping could potentially allow for tailor-made composites to be produced with increasing ease.

Tape cast and laminated bioactive glass 45S5 particulate has been shown to retain bioactivity in both SBF[8] and Tris buffer[9] following heat treatment between 800–1000 °C. The bioactivity reaction stages of this material, which predominately forms the crystalline phase $Na_2Ca_2Si_3O_9$ when heated [8], are similar to that of amorphous 45S5 bioactive glass.[9,10] Although hydroxyapatite forms relatively rapidly on the surface of tape cast and sintered (TCS) bioactive ceramic in vitro, the reaction rate is slightly lower than that of amorphous 45S5 glass.[11,12] Such decreases in the reaction rate have also been observed for bulk monolithic crystalline 45S5.[13,14] Crystallization, and the subsequent decrease in reaction rate, may be desirable in certain applications, however. TCS bioactive glass-ceramic also supports and enhances osteoblast proliferation in vitro.[15]

Previous studies showed that the effective toughness, or work of fracture, of TCS bioactive glass-ceramic can be increased by lamination with ductile stainless steel

* Corresponding author. Tel.: +44-207-589-5111×56753; fax: +44-207-594-6809.
E-mail address: d.clupper@ic.ac.uk (D.C. Clupper).

0955-2219/03/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0955-2219(03)00363-7

316L or titanium layers.[16] In this investigation, the flexural strength, hardness and effective porosity of TCS bioactive ceramic laminated monoliths were investigated as a function of processing temperature. For samples with flexural strength near that of cortical bone, the fracture toughness was characterized by two independent methods: indentation strength and fractography.

2. Materials and methods

Bioactive glass 45S5 particulate (3 μm average diameter) was donated by USBiomaterials Corp., Alachua, Florida. Tape casting slurries were produced by thoroughly mixing 42.3 weight percent jet milled Bioglass® 45S5 particulate (1–10 microns, 3 micron average), 37.9% toluene, 10.7% ethanol, 6.3% polyvinyl butyral, and 2.8% phthalic acid. Tape casting was performed using an Incetek model 104 tape caster (Integrated Ceramic Technologies, Inc., San Marcos, California) using a casting speed of 43 cm per min.

Samples were allowed to dry prior to punching 31.8 mm diameter wafers. Approximately 20–25 wafers were stacked and then laminated under low heat and pressure for 3 min (150 °C and 20 MPa). Green bodies were then fired up to 470 °C for 16 h prior to ramping at 1 °C/min to the maximum temperature (800, 900 or 1000 °C for 3 h or 1000 °C for 6 h; such samples are hereto referred to as 800C, 900C, 1000(3)C and 1000(6)C, respectively). A second type of sample, with significant porosity, were produced by altering the lamination step: 3 g tape was introduced in a random fashion (in contrast to the ordered stacking of wafers) in to the steel mold and heated at 150 °C under 20 MPa for 3 min.

The effective porosity was measured using a mercury porosimeter (Quantachrome Poremaster 33). Hg intrusion volume during the high pressure loading phase was determined in cm^3 per unit sample weight.

Hardness was determined using samples polished down to a 1 μm finish using diamond paste. A Vickers indent load of 100 g was then applied to the polished surface using with a Micromet 3 micorhardness testers (Buehler LTD, Lake Bluff, IL, USA) using a 30 s dwell time. Hardness was given by:

$$H = P/(\alpha a^2) \tag{1}$$

where $\alpha = 2$ and a is the half diagonal of the indent [17].

Flexural test specimens ($n \geqslant 10$) were then cut from sintered discs using a diamond saw. The fracture stress of the specimen beams in four point flexure was determined using:

$$\sigma = \frac{3P(S_o - S_i)}{2wt^2} \tag{2}$$

where P is the fracture load, S_o the outer span length, S_i the inner span length, w the specimen width, and t the thickness. Samples (approximately 1.5 mm thick, 2.0 mm wide, and 25 mm long) were loaded to failure at 0.5 mm/min. The inner and outer alumina spans measured 6.7 mm and 19.9 mm, respectively. Scanning electron microscopy (SEM) of fracture surfaces was performed using a JEOL 6400.

Fracture toughness was determined for 1000(3)C TCS bioactive glass-ceramic using both indentation strength and fractographic methods. The equation for the indentation toughness method was developed by Chantikul et al.[18]:

$$K_c = \zeta_z\ (E/H)^{1/8}\ \left(\sigma_f\ P^{1/3}\right)^{3/4} \tag{3}$$

where K_c is the toughness, E the elastic modulus, P the indentation load, H the hardness, σ_f the applied stress at fracture, and ζ_z an empirical constant (0.59 ± 0.12).

The above equation can be applied to calculate the fracture toughness of TCS bioactive glass-ceramic if the log-log plot of the fracture stress vs. indent load yields a slope of $-1/3$. This condition occurs when the toughness is constant over a range of indent loads. Mathematical manipulation of Eq. (1) yields:

$$\text{Log}\ \sigma = -1/3\ \log\ P + \log\ c \tag{4}$$

where σ is the fracture stress, c a constant, and P the indent load.

The fracture toughness was also be obtained by directly measuring the flaw size ($n \geqslant 6$) and using:

$$K_C = \sigma Y \sqrt{c} \tag{5}$$

where K_C is the fracture toughness, σ the applied stress at fracture Eq. (1), Y a geometrical constant (1.65 for indented specimens), and c is the flaw size. Specifically, the term c is the equivalent semi-elliptical crack size, i.e., $c = \sqrt{(ab)}$, where b is the semi-major axis and a is the semi minor axis of an elliptical crack. Statistical analysis of the fracture toughness data was performed using ANOVA ($\alpha = 0.05$) and the Student's t-test ($\alpha = 0.05$) where appropriate.

3. Results

3.1. Laminated TCS bioactive ceramic

Densification of TCS bioactive ceramic was characterized by mercury porosimetry and hardness measurements. As shown in Fig. 1, the effective porosity, or Hg intrusion volume, decreased with increasing processing temperature (1.14, 0.40 and 0.08 cm^3/g for 800C, 900C, and 1000(3)C, respectively). Further densification of TCS bioactive ceramic occurred between 3 h and 6 h at 1000 °C; i.e. to 0.02 cm^3/g.

Hardness was inversely related to the effective porosity; i.e., hardness increased and porosity decreased with increasing processing temperature and soak time (Fig. 1). Hardness values for 800C, 900C, 1000(3)C and 1000(6)C TCS bioactive glass-ceramic were 0.2, 2.5, 5.5, and 5.7 GPa, respectively.

The flexural strength values for 800C, 900C, 1000(3) and 1000(6)C tape cast and sintered bioactive glass-ceramic were 30±4, 66±9, 83±13 and 61±9 MPa, respectively (Fig. 2). The Weibull plot for the highest [1000(3)C] and lowest (800C) strength TCS bioactive ceramic samples are shown in Fig. 3. The Weibull modulus for 800C TCS bioactive ceramic was 7, and for 1000(3)C was 5.

3.1.1. Indentation strength

In order to assess the mechanical reliability of this material, the size of the fracture-initiating crack should be controlled. The strength indentation technique enables us to compare the strength of materials at approximately the same crack size, and thus, compare toughness values. Samples were indented with a Vicker's diamond and loaded to failure in four point flexure. The 1, 3, and 5 kg indents yielded fracture strengths of 56±11 MPa, 46±9 MPa and 37±7 MPa, respectively. A log–log plot of the fracture stress vs. indent load is shown in Fig. 4. The data points fell along a line of slope −0.3 ($R^2 = 0.95$).

3.1.2. Fracture toughness determination

The fracture toughness (K_C) of 1000(3)C TCS bioactive ceramic was determined using the indentation strength method [Eq. (3)] as well as by using fractographic methods [Eq. (5)]. The fracture origin of a 1000(3)C flexure bar (5 kg indent) is outlined in Fig. 5. As shown in Fig. 6, the two methods agreed well over the range of indent loads used. The average fracture toughness of the six sample types ranged from 0.9 to 1.1 MPa $m^{1/2}$. There were no statistically significant differences between the six conditions (ANOVA, $\alpha = 0.05$, $P = 0.36$). Specifically, the indentation strength method resulted in K_C values of 1.0±0.1, 1.1±0.2, and 1.0±0.2

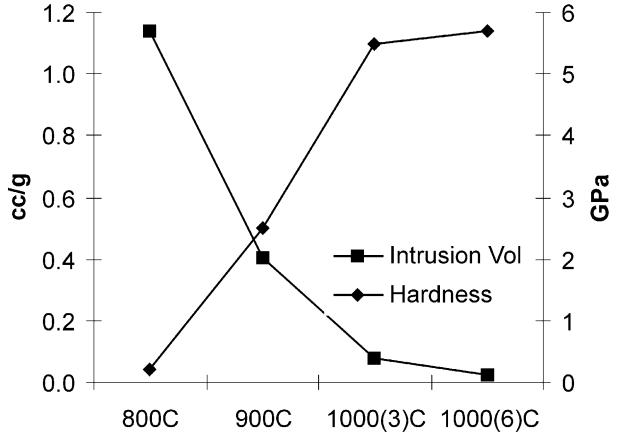

Fig. 1. Effect of processing schedule on hardness and effective porosity of TCS bioactive ceramic. From left to right, samples were processed at 800, 900, 1000 °C for 3 h, and 1000 °C for 6 h, respectively, in air.

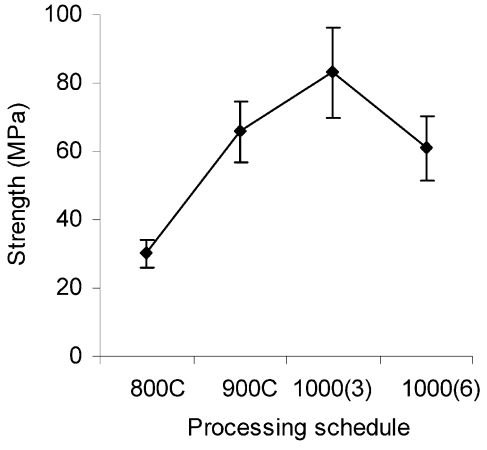

Fig. 2. Effect of processing schedule on the flexural strength (four point bend) of TCS bioactive glass-ceramic.

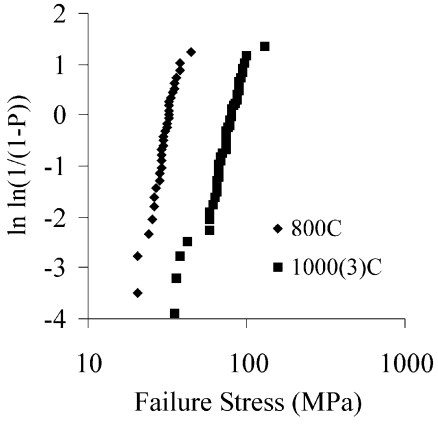

Fig. 3. Weibull plots of 800C and 1000(3)C TCS bioactive glass-ceramic tested by four point flexure. The Weibull modulus 800C was 7, whereas that of 1000(3)C was 5.

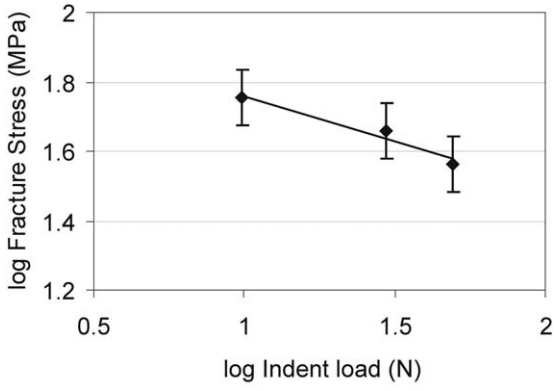

Fig. 4. Plot of log fracture stress vs. log indent load for 1000(3)C TCS bioactive glass-ceramic. The slope of the line made by the data points, ~1/3, confirmed that the fracture toughness was approximately constant over the range of indent loads used.

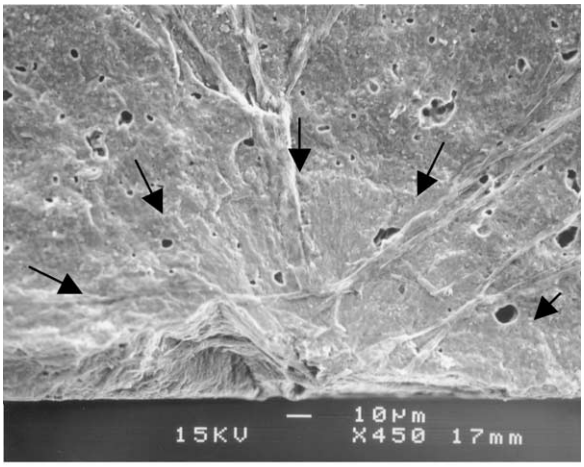

Fig. 5. Fracture surface of 1000(3)C TCS bioactive glass-ceramic (5 kg indent). The fracture origin is outlined by arrows.

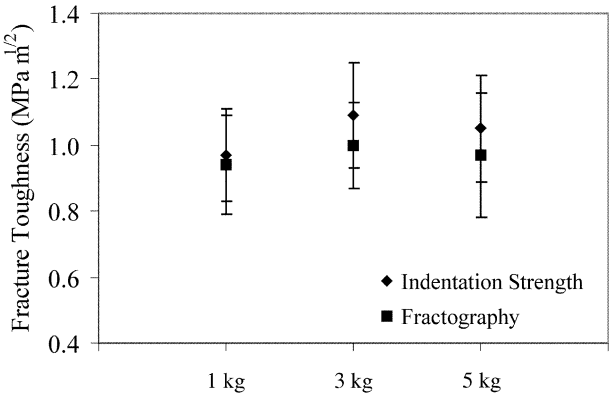

Fig. 6. Comparison of K_C determined by the indentation strength method and by fractography for 1000(3) TCS bioactive glass-ceramic. No significant difference existed between the six conditions (ANOVA, $\alpha = 0.05$).

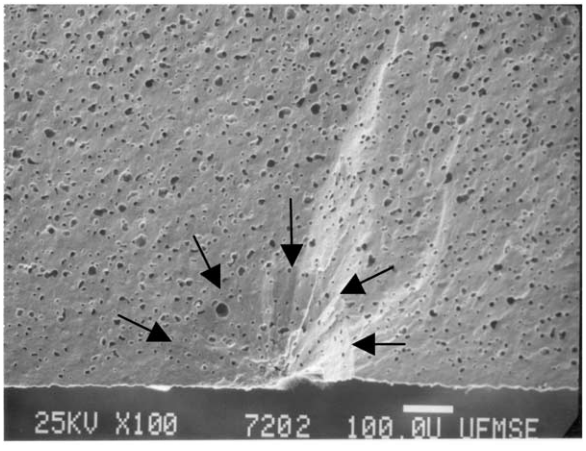

Fig. 7. Fracture surface of porous 1000(3)C TCS bioactive glass-ceramic made by the alternative processing route. The fracture origin is highlighted by arrows.

for 1, 3, and 5 kg indents, respectively, whereas the corresponding values using the fractographic method were determined to be 0.9±0.2, 1.0±0.1, and 1.0±0.1. The average critical flaw sizes for the 1, 3, and 5 kg indents were 101±18 ($n = 8$), 200±47 μm ($n = 10$), 272±42 μm ($n = 6$), respectively.

3.2. Porous TCS bioactive ceramic

Although the average strength of the indented (3 kg) porous 1000(3)C TCS bioactive ceramic was slightly less than that of the laminated samples (38±9 MPa compared with 44±9 MPa), the difference was not statistically significant (Student's t-test, $\alpha = 0.05$, $P = 0.097$). K_C values measured using the indentation strength and fractographic analysis methods agreed well, and the values were similar to those determined for the laminated samples. The indentation strength method yielded a toughness of 0.9±0.2 MPa $m^{1/2}$ ($n = 15$), and similarly, K_C was 0.9±0.2 MPa $m^{1/2}$ ($n = 12$) using fractographic analysis. The fracture origin of the porous 1000(3)C TCS bioactive ceramic is shown in Fig. 7. The average crack size (Fig. 7) was 201±38 mm ($n = 12$).

4. Discussion

Mercury porosimetry analysis confirmed that four heating schedules could be used to obtain a range of sintered porosities in TCS bioactive ceramic. The effective porosity values for 900C, 1000(3)C, and 1000(6)C TCS bioactive ceramic were 35, 7, and 2% of that for 800C (1.14 cm^3/g), respectively. Hardness increased with processing temperature and time in a manner inversely proportional to the densification (Fig. 1). Such characterization methods may therefore lend to the tailoring of bioactivity or osteoblast response in vitro, as both have been shown to be influenced by the processing history of TCS bioactive ceramic.[8,9,15]

Given that there existed a wide variation in porosity due to different processing schemes, the variation in measured flexural strength was not unexpected. The strength of 1000(3)C TCS bioactive ceramic (87 MPa) determined by four point flexure using bar samples cut from larger as-processed discs, was slightly less than that of cortical bone (100–200 MPa). However, previous work has shown that the bend strength of uncut TCS bioactive glass-ceramic biaxial flexure samples (120 MPa) is within the range of cortical bone following immersion in Tris buffer.[9] Biaxial flexure samples avoid degradation of strength due to edge chipping and machining damage.

The toughness (0.9–1.1 MPa $m^{1/2}$) of TCS bioactive ceramic, initially composed of bioactive glass 45S5 particulate, was higher than that of bioactive glass 45S5 (0.6 MPa $m^{1/2}$ [19]) and comparable to that of sintered

hydroxyapatite (~1.0 MPa $m^{1/2}$).[20–22] TCS bioactive ceramic, however, has certain inherent advantages over hydroxyapatite, viz. bioactivity and resorbability.[8,9]

The fracture toughness values calculated using the indentation strength method agree well over the range of indent loads used and the slope of the log-log plot of fracture stress vs. indent load only deviated slightly from −1/3. No statistical differences exist between the toughness values determined for different indentation loads using the indentation strength method (ANOVA $\alpha = 0.05$). Furthermore, the fractographic analysis agreed well with the indentation strength method data over the range of indents used.

The strength of porous 1000(3)C TCS bioactive ceramic was found not to differ significantly from that of normal 1000(3)C laminates. The toughness of porous 1000(3) samples (0.9 ± 0.2 MPa $m^{1/2}$ by both fracture surface analysis and by indentation strength), was comparable to that of laminated TCS bioactive ceramic as well.

It has been demonstrated that a porous TCS bioactive ceramic can be produced, with toughness equivalent to that of the parent material, without altering the original slurry composition. Such porous laminae may be used to control crack propagation (via crack deflection) and thus increase the effective fracture toughness.[23] Although increasing the pore size of porous TCS bioactive ceramic might be necessary to encourage bone ingrowth in vivo, such increases in porosity may degrade the fracture strength. Thus, an optimization of the osteoconductive and mechanical properties should be sought.

5. Conclusions

Significant densification of TCS bioactive ceramic took place within the range of sintering temperatures studied, and the hardness and effective porosity were found to be inversely proportional. The strength of TCS bioactive ceramic sintered at 1000 °C for 3 h approached that of cortical bone. The fracture toughness values of such samples, determined by two independent methods (indentation strength and fractography) were found to agree well (0.9–1.1 MPa $m^{1/2}$) over the range of indent loads used. Porous TCS bioactive ceramic could also be produced without significantly decreasing the toughness. Such layers could be used for controlling crack propagation in TCS bioactive ceramic laminates.

Acknowledgements

The authors would like to thank USBiomaterials Corporation (Alachua, Florida) and the March of Dimes Charity for support of this research.

References

1. Hench, L. L., Splinter, R. J., Allen, W. C. and Greenlee, T. K., Bonding mechanisms at the interface of ceramic prosthetic materials. *J. Biomed. Mater. Res. Symposium*, 1971, **2**, 117–141.
2. Kokubo, T., Kushitani, H., Sakka, S., Kitsugi, T. and Yamamuro, T., Solutions able to reproduce in vivo surface-structure changes in bioactive glass-ceramic A-W. *J. Biomed. Mater. Res.*, 1990, **24**, 721–734.
3. Xynos, I. D., Edgar, A. J., Buttery, L. D. K., Hench, L. L. and Polak, J. M., Gene transcription profiling of human osteoblasts following treatment with ionic products of Bioglass 45S5 dissolution. *J. Biomed. Mater. Res.*, 2001, **55**, 151–157.
4. Effah Kaufmann, E. A. B., Ducheyne, P. and Shapiro, I. M., Effect of varying physical properties of porous, surface modified bioactive glass 45S5 on osteoblast proliferation and maturation. *J. Biomed. Mater. Res.*, 2000, **52**, 783–796.
5. Chen, Z. and Mecholsky, J. J. Jr., Control of strength and toughness of ceramic/metal laminates using interface design. *J. Mater. Res.*, 1993, **8**, 2362–2369.
6. Werner, J., Linner-Krcmar, B., Friess, W. and Greil, P., Mechanical properties and in vitro cell compatibility of hydroxyapatite ceramics with graded pore structures. *Biomaterials*, 2002, **23**, 4285–4294.
7. Arita, I. H., Wilkinson, D. S., Mondragon, M. A. and Castano, V. M., Chemistry and sintering behaviour of thin hydroxyapatite ceramics with controlled porosity. *Biomaterials*, 1995, **16**, 403–408.
8. Clupper, D. C., Mecholsky, J. J. Jr., LaTorre, G. P. and Greenspan, D. C., Bioactivity of tape cast and sintered bioactive glass-ceramic in simulated body fluid. *Biomaterials*, 2002, **23**, 2599–2606.
9. Clupper, D. C., Mecholsky, J. J. Jr., LaTorre, G. P. and Greenspan, D. C., Sintering temperature effects on the *in vitro* bioactive response of tape cast and sintered bioactive glass-ceramic in Tris buffer. *Journal of Biomedical Materials Research*, 2001, **57**, 532–540.
10. Hench, L. L. and Andersson, Ö., Bioactive glasses. In *An Introduction to Bioceramics*, ed. L. L. Hench and J. Wilson. World Scientific, Singapore, 1993, pp. 41–62.
11. Filgueiras, M. R. T., LaTorre, G. and Hench, L. L., Solution effects on the surface reactions of three bioactive glass compositions. *J. Biomed. Mater. Res.*, 1993, **27**, 1485–1493.
12. Filgueiras, M. R., LaTorre, G. and Hench, L. L., Solution effects on the surface reactions of a bioactive glass. *J. Biomed. Mater. Res.*, 1993, **27**, 445–453.
13. Filho, O. P., LaTorre, G. P. and Hench, L. L., Effect of crystallization on apatite-layer formation of bioactive glass 45S5. *J. Biomed. Mater. Res.*, 1996, **30**, 509–514.
14. Peitl, O., Zanotto, E. D. and Hench, L. L., Highly bioactive P_2O_5–Na_2O–CaO–SiO_2 glass-ceramics. *J. Non-Cryst. Solids*, 2001, **292**, 115–126.
15. Gough, J.E., Clupper, D.C., Hench, L.L. Osteoblast responses to sintered and tape cast bioactive glass. *Bioceramics* (submitted for publication).
16. Clupper, D. C. and Mecholsky, J. J. Jr., Toughening of tape cast Bioglass® by lamination with stainless steel 316L. *Journal of Materials Science Letters*, 2001, **20**, 1885–1888.
17. Anstis, G. R., Chantikul, P., Lawn, B. R. and Marshall, D. B., A critical evaluation of indentation techniques for measuring fracture toughness: I, direct crack measurements. *J. Am. Ceram. Soc.*, 1981, **64**, 533–538.
18. Chantikul, P., Anstis, G. R., Lawn, B. R. and Marshall, D. B., A critical evaluation of indentation techniques for measuring fracture toughness: II, strength method. *J Amer Ceram Soc.*, 1981, **64**, 539–543.

19. Thompson, I. D. and Hench, L. L., Mechanical properties of bioactive glases, glass-ceramics and composites. *Proc Inst Mech Engrs*, 1998, **212**, 127–136.
20. Hench, L. L., Bioceramics. *J. Am. Ceram. Soc*., 1998, **81**, 1705–1728.
21. Suchanek, W., Yashima, M., Kakihana, M. and Yoshimura, M., Hydroxyapatite/hydroxyapatite-whisker composites without sintering additives: mechanical properties and microstructural evolution. *J. Am. Ceram. Soc*., 1997, **80**, 2805–2813.
22. Thangamani, N., Chinnakali, C. and Gnanam, F. D., The effect of powder processing on densification, microstructure and mechanical properties of hydroxyapatite. *Ceramics Intl*, 2002, **28**, 355–362.
23. Davis, J. B., Kristoffersson, A., Carlstrom, E. and Clegg, W. J., Fabrication and crack deflection in ceramic laminates with porous interlayers. *J. Am. Ceram. Soc*., 2000, **83**, 2369–2374.