Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 2037–2042
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Sintered feldspar glass–ceramics and glass–ceramic matrix composites

E. Bernardo [a,*], J. Doyle [b], S. Hampshire [b,c]

[a] *Dipartimento di Ingegneria Meccanica, Settore Materiali, Università di Padova, Via Marzolo 9, 35131 Padova, Italy*
[b] *Materials Ireland Research Centre, University of Limerick, Limerick, Ireland*
[c] *Materials and Surface Science Institute, University of Limerick, Limerick, Ireland*

Received 9 May 2007; received in revised form 9 July 2007; accepted 26 July 2007

Abstract

Sintering with simultaneous crystallization of fine glass powders allowed the preparation of dense glass–ceramics based on unusual feldspar crystals (constituted by microcline and orthoclase, $KAlSi_3O_8$), at a very low temperature (750 °C) and with limited processing times. Al_2O_3 platelets, added to the glass powders, caused a remarkable improvement of bending strength (exceeding 100 MPa), microhardness (approaching 9 GPa) and fracture toughness (approaching 2 MPa $m^{0.5}$), even for limited concentrations (which varied from 5 to 15 vol%). Due to the simple and low cost manufacturing technique, the glass–ceramic matrix composites obtained could find applications in the construction industry.

Keywords: A. Sintering; C. Mechanical properties; D. Glass ceramics; Ceramic matrix composites

1. Introduction

Sintering with concurrent crystallization (“sinter-crystallization”) of fine glass powders (typically < 40 μm) has recently been reported as a way to obtain glass–ceramics with unusual crystal phases [1,2]. Alkali feldspar crystals (tectosilicates summarized by the formula $M_2O{\cdot}Al_2O_3{\cdot}6SiO_2$, i.e. $MAlSi_3O_8$, where M = Na or K), like albite ($KAlSi_3O_8$), sanidine and orthoclase ($KAlSi_3O_8$), known to give excellent glasses but unable to crystallize in practical periods of time [3], have been successfully developed by exploiting the tendency of powdered glass to devitrify during appropriate heat treatments. In addition, the precipitation of feldspathoid crystals (tectosilicates with different Al_2O_3/SiO_2 ratio than that of feldspars, corresponding to $M_2O{\cdot}Al_2O_3{\cdot}2SiO_2$, i.e. $MAlSiO_4$, or $M_2O{\cdot}Al_2O_3{\cdot}4SiO_2$, i.e. $MAlSi_2O_6$), like leucite ($KAlSi_2O_6$), [3] nepheline ($NaAlSiO_4$) [4] and trikalsilite ($(K,Na)AlSiO_4$), [1,2] has been shown to be more rapid, with sintering, than in traditional processing (nucleation and crystal growth).

In fact, crystallization is favoured at the surface of glass particles, since nuclei may form without being fully impeded by the surrounding material, taking into account the volume variation from glass to crystal. This condition has been exploited, since the early 1970s, for the preparation of marble-like glass–ceramics, starting from glass granules with dimensions of 1–7 mm (in this case, a very pleasant marble-like appearance is given by the formation of a crystal layer at the surface of former glass fragments, joined by viscous flow sintering) [3,5]. By maximizing the specific surface, i.e. the number of nucleation sites per unit volume, fine glass powders greatly enhance the crystallization, so that low sintering temperatures and short processing times are possible, with no nucleation agent added to the glass formulation. Many sinter-crystallization experiments have been conducted just at the glass crystallization temperatures, with holding times not exceeding 3 h [6–9]. In addition to the economic advantages in the conversion of glass into glass–ceramics conferred by lower processing temperatures and shorter times, sinter-crystallization has other advantages in the preparation of the starting glass, since it is not necessarily refined (i.e. maintained at very high temperatures for long times, just to remove gas bubbles in the glass mass) prior to milling to fine particles; on the contrary, the glass melts may be rapidly cooled (in air, water, etc.), thus favouring the rupture into small fragments to form frits. All these processing benefits are particularly profitable when applied to glasses made by employing waste raw materials: the use of wastes may only be significant when the obtained glasses

---

* Corresponding author. Tel.: +39 049 8275510; fax: +39 049 8275505.
E-mail address: enrico.bernardo@unipd.it (E. Bernardo).

0272-8842/$34.00
doi:10.1016/j.ceramint.2007.07.027

are converted into marketable products (like glass–ceramics for construction applications) employing a low cost manufacturing technique [10].

Besides ease of processing and the formation of unusual crystal phases, the sinter-crystallization of fine glass powders has a notable advantage in the preparation of glass–ceramic matrix composites; in fact, micron-sized powders may be homogeneously mixed with a secondary particulate phase. This phase may lead to significant improvements of the mechanical properties of the glass–ceramic matrix.

A typical reinforcement for sintered glasses is represented by low-cost Al_2O_3 platelets, generally employed as abrasive material. The reinforcing action is mainly related to the introduction of residual stresses in the matrix, caused by the glass/alumina thermal expansion mismatch [11–13]. The principle of reinforcement of glasses has been successfully transferred to glass–ceramic matrices: the first experiences focused on the sintering of Ba–Mg alumino-silicate glass/alumina mixtures (at 930–980 °C), which was later subjected to a nucleation/crystal growth treatment (12 h at 1200 °C) [14]; more recent works have been dedicated to the more economic simultaneous sintering and crystallization of glass powders in the presence of a secondary phase (3–5 h at 930–940 °C) [4,15]. In this case it has been shown that achieving highly dense glass–ceramic matrix composites depends on the viscosity of the glass matrix upon crystallization. If the viscosity is low, the densification may occur in short time scales, despite the well known increase of viscosity provided by elongated or plate-like inclusions [16]: for example, a glass–ceramic matrix based on nepheline crystals (a feldspathoid), originating from an "inverse glass" (a glass with a significant content of network modifiers) [4] allowed the achievement of denser composites than those produced from a glass–ceramic matrix based on the C–M–A–S system [15].

In this paper glass–ceramic matrix composites have been prepared from an appropriate glass containing Al_2O_3 platelets by sinter-crystallisation which resulted in dense glass–ceramics and unusual precipitation of potassium feldspars. The presence of the reinforcing phase did not significantly alter the sinter-crystallization process, leading to composites with significantly improved mechanical properties, even for low platelet additions.

2. Experimental

The starting glass, whose composition is reported in Table 1, was prepared from oxide powders (99.9% purity) which were blended by ball milling for 2 h. The blended powders were packed into a sintered mullite crucible and melted in standard electrically heated furnace at 1420 °C. The crucible and contents were then removed from the furnace and the molten glass was poured into cold water, yielding a glass frit. The frit was dried overnight in an oven at 110 °C, dry ball milled and sized to grains $<45\ \mu m$. The powdered glass was subjected to differential thermal analysis (DSC g404, Netzsch Gerätebau GmbH, Selb, Germany), with a heating rate of 10 °C/min, in order to identify glass transition and crystallisation temperatures (Table 1).

Table 1
Chemical composition of the starting glass

	Composition (wt.%)
SiO_2	77.46
Al_2O_3	6.39
K_2O	5.58
Na_2O	3.97
CaO	1.08
Li_2O	4.59
MgO	0.57
B_2O_3	0.18

α-Alumina monocrystals (platelets) were chosen as the reinforcement (Microabrasives Co., Westfield, MA). The platelets were hexagonal-shaped, with major axes between 5 and 10 μm and axial ratio (thickness/average diameter) ≈ 0.2. The density of α-alumina was taken as $3.99\ g\ cm^{-3}$ [17].

Fine glass powders were first uniaxially pressed in a cylindrical steel die (diameter = 31 mm) at room temperature, by using a hydraulic press operating at 40 MPa, without any binder to form discs. The glasses were then sintered in air at different temperatures for 2 h, with a heating rate of 10 °C/min, leading to dense samples with a white coloration. Also holding times of 0 h (corresponding to the cooling of samples just after the reaching the sintering temperature), 1 and 4 h were tested.

Larger rectangular (50 mm × 35 mm) samples, pressed at 40 MPa, were prepared by using both pure glass powders and glass/alumina mixtures, corresponding to 5, 10, and 15% concentrations by volume, after addition of 5 wt.% distilled water and homogenization in a dry ball mill for 1 h. The obtained green tiles, after drying at 500 °C for 3 h, were sintered for 2 h at 750 °C, with a heating rate of 10 °C/min.

The bulk density of the sintered compacts was measured by the Archimedes' principle. At least 10 fragments were analysed for each sample. The true density of the composite materials was evaluated by means of a gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA). The theoretical densities were calculated from the density of the constituents by applying the rule of mixtures.

Beam samples of about 3 mm × 2 mm × 30 mm, for bending strength determinations were cut from larger sintered tiles. All samples were carefully polished to a 3 μm finish, by using abrasive papers and diamond paste. The edges of the bars were bevelled by using fine abrasive papers and diamond paste. Four point bending tests (24 mm outer span, 8 mm inner span) were performed by using an Instron 1121 UTS (Instron Danvers, MA), with a crosshead speed of 0.2 mm/min. Each data point represents the average of at least 10 individual tests. The Young's modulus (E) was measured by means of non-destructive resonance frequency testing (GrindoSonic Mk5, Leuven, Belgium).

Polished samples were employed for Vickers indentation tests, which yielded the hardness (H_v), at low load (5 N), and the indentation fracture toughness (K_{IC}), at high load (20 N). The fracture toughness was calculated by using the equation of Anstis et al. [18], starting from the measured length of the cracks emanating from the corners of the Vickers indents.

Fragments of beam samples (un-reinforced glass–ceramic and composites) were subjected to dilatometric analysis (Netzsch Gerätebau GmbH, Selb, Germany). The morphology of sintered samples was characterized by Scanning Electron Microscopy (Philips XL 40 SEM and Philips XL 30 ESEM). Powdered samples were investigated by X-ray diffraction (Philips PW 3710), employing Cu Kα radiation (0.15418 nm). The diffraction patterns were analysed by using data from PDF-2 database (International Centre for Diffraction Data—ICDD, Newtown Square, PA), coupled with Match! program package (Crystal Impact GbR, Bonn, Germany).

3. Results and discussion

Fig. 1 shows the differential thermal analysis of the starting glass. The transition temperature T_g can be observed at about 590 °C; a slight crystallization peak is shown at about 840 °C.

Preliminary sintering treatments on discs were performed in the temperature range 700–850 °C, for a holding time of 2 h. This choice was supported by some recent sinter-crystallization experiments, starting from fine glass powders, demonstrating that surface crystallization is almost complete in 2–3 h [1,2,4]. Fig. 2a illustrates that crystallization commenced between 700 and 750 °C, about 100 °C below the crystallization temperature (see the slight peaks for 2 h at 700 °C). It can be noted, in addition, that there was no significant increase in crystallization as the sintering temperature increases from 750 to 850 °C (as shown by the intensity of the peaks in the diffraction patterns) nor any decrease of residual porosity (estimated to be about 3%). This means that fine glass powders effectively result in enhanced crystallization, despite the low "driving force", corresponding to the observed slight crystallization exothermic peak, and a low sintering temperature. As for the sintering temperature, a certain "stabilization" was observed for the sintering time at 750 °C: as illustrated by Fig. 2b crystallization was practically complete after 2 h. The crystallization conditions appear particularly interesting, since 750 °C is far lower than the temperatures of crystallization of many silicate glass–ceramics (900–1000 °C) [3].

The analysis of the diffraction pattern revealed that two potassium feldspar polymorphs are formed, with the same reference chemical formula $KAlSi_3O_8$ (i.e. $K_2O\cdot Al_2O_3\cdot 6SiO_2$): these crystals correspond to orthoclase (PDF #75-1190, monoclinic) and microcline (PDF#83-1604, triclinic). SEM analysis demonstrated (see Fig. 3) that these crystals had a "fibrous" morphology and a diameter of about 4–5 μm.

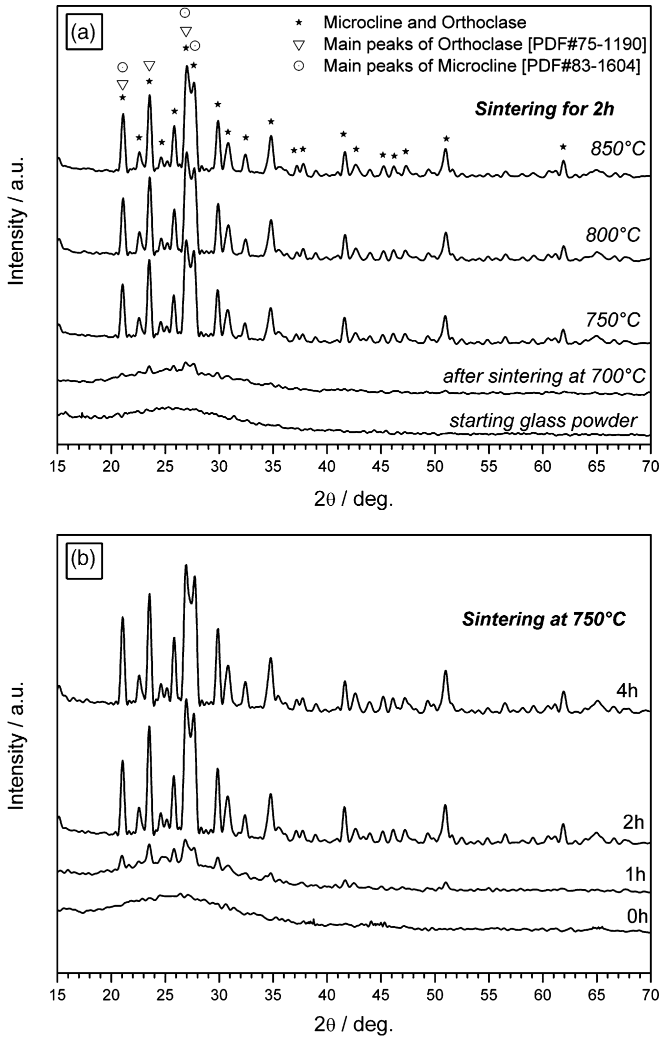

Fig. 2. Progression of crystallization and crystal size as function of (a) sintering temperature and (b) holding time.

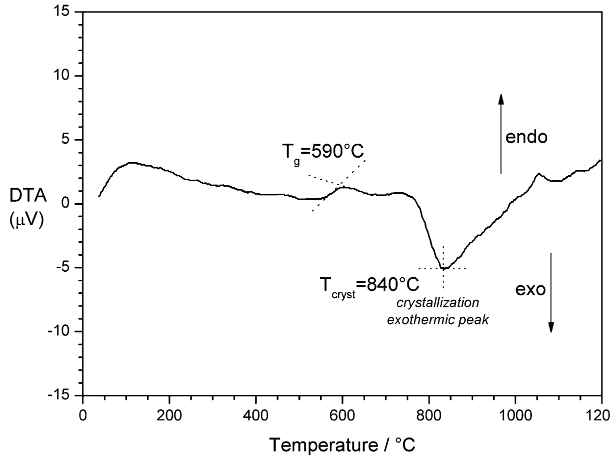

Fig. 1. Differential thermal analysis plot of the starting glass.

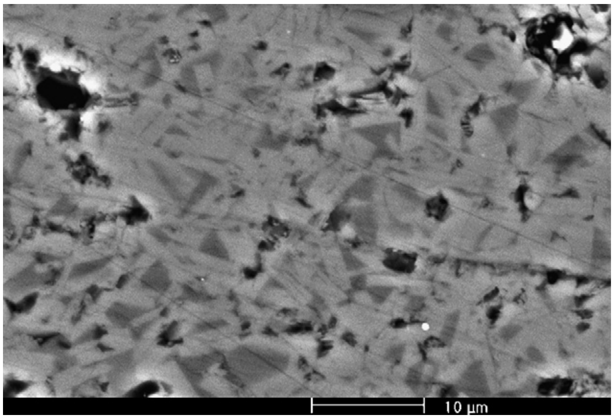

Fig. 3. Typical microstructure of feldspar glass–ceramic sintered at 750 °C for 2 h.

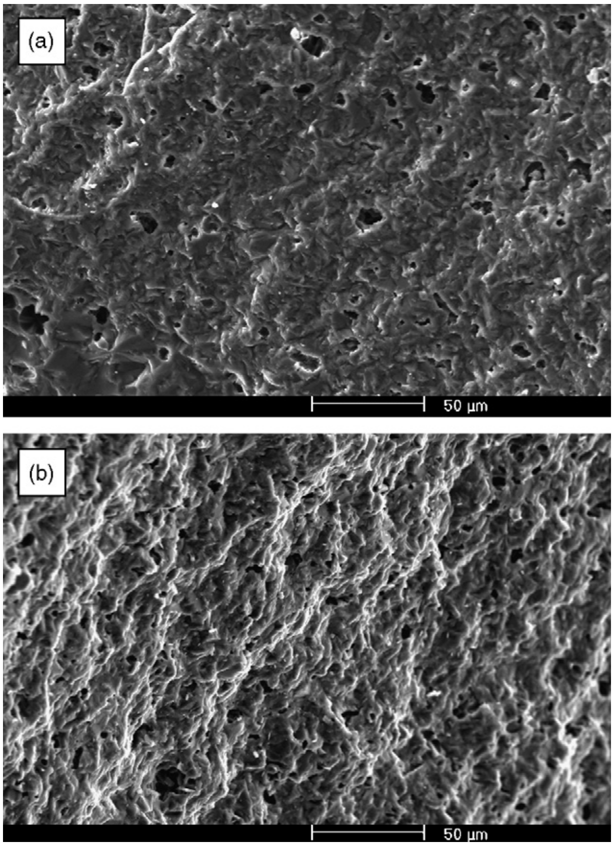

Fig. 4. SEM micrographs of fracture surfaces of glass–ceramic matrix composites: (a) unreinforced glass–ceramic matrix; (b) composite with 15 vol% Al_2O_3.

Because of their identical chemical compositions, the feldspar phases could not be distinguished from each other. From image analysis (by means of ImageJ program package) [19] the crystallinity was estimated to be about 80 vol%; in addition, from semi-quantitative analysis (by means of Match! program package) microcline phase was revealed to be dominant, being about 57 wt.% of the total crystal phase. Fig. 4a shows large pores (with dimensions of 5–10 μm) which are due to incomplete sintering since the rapid crystallization results in a significant increase of viscosity which inhibits densification by a viscous flow mechanism. Many small irregular micropores are also visible; these pores are probably formed as a result of density and thermo-elastic variations occurring during crystallization, as recently reported by Karamanov and Pelino [20] (the ‘‘free’’ volume change occurring by local volume contraction upon crystal formation cannot be compensated by the viscous flow of residual glass, which becomes more and more viscous with increasing crystal formation, so that microporosity is developed).

Unlike leucite (a potassium feldspathoid), whose crystallization (via surface nucleation) has already been reported in the literature [3], potassium feldspar crystals are very unusual (to the authors' knowledge, no glass–ceramic material have been reported, based on these phases). As for other feldspars (sanidine and albite) [1,2], the sintering approach, starting from fine glass powders, appears the only way for achieving crystallization in practical periods of time.

On the basis of the previous observations, the sintering at 750 °C, with a holding time of 2 h, was considered the optimum condition for crystallization, and it was employed for the preparation of glass–ceramic matrix composites. The preparation of tiles allowed an evaluation of the mechanical properties also for the un-reinforced matrix. From Table 2, we can observe that this material exhibited interesting mechanical properties, with a bending strength of 77 MPa, a Vickers hardness of 7.2 GPa and an indentation fracture toughness of 1.5 MPa $m^{0.5}$. These features make the glass–ceramic matrix stronger than commercial sintered glass–ceramics (wollastonite-based ‘‘Neoparies’’ possess a bending strength of about 50 MPa and a Vickers hardness of about 6 GPa).

The introduction of Al_2O_3 platelets did not modify substantially the densification of the matrix (as shown by the porosity values in Table 2). This is particularly encouraging since, as reported above, non-sintering inclusions may retard densification by dramatically increasing the viscosity of the system [16]; the relatively low viscosity of feldspar glasses, rich in alkali oxides, is probably the cause of the observed good sintering ability.

The reinforcement resulted in an overall improvement of the mechanical properties, summarized in Table 2. In particular, the measured elastic moduli were compared to those calculated by means of the Mazilu–Ondracek equation [21], as follows:

$$E_{\mathrm{comp}} = E_{\mathrm{m}}\left\{1 - \frac{\pi}{A}\left[1 - \frac{1}{9(1 + 1.99/B\{E_{\mathrm{m}}/E_{\mathrm{p}} - 1\})} - \frac{1}{3(1 + 1.68/B\{E_{\mathrm{m}}/E_{\mathrm{p}} - 1\})} - \frac{1}{9/5(1 + 1.04/B\{E_{\mathrm{m}}/E_{\mathrm{p}} - 1\})}\right]\right\} \tag{1}$$

where E_{comp}, E_{m}, E_{p} are, respectively, the moduli of the composite, the matrix ($E_{\mathrm{m}} = 380$ GPa–Table 2) and the inclusion

Table 2
Density and mechanical properties of the obtained sintered products

Al_2O_3 platelet vol. fraction (%)	Density (g/cm^3)	Porosity (%)	Young's modulus (GPa)[a]	Bending strength (MPa)	Vickers hardness H_V (GPa)	K_{IC} (MPa $m^{0.5}$)
0	2.38 ± 0.03	3.2	62.0	77 ± 15	7.2 ± 0.4	1.5 ± 0.2
5	2.48 ± 0.06	2.2	67.8 [66.2]	100 ± 7	8.1 ± 0.4	2.0 ± 0.2
10	2.53 ± 0.03	3.2	72.2 [72.2]	109 ± 11	8.5 ± 0.6	1.9 ± 0.2
15	2.57 ± 0.04	4.4	78.0 [80.2]	119 ± 3	8.9 ± 0.6	1.9 ± 0.2

[a] Data fitting by Mazilu–Ondracek's equation given in square parentheses.

phase ($E_p = 380$ GPa) [17]. A and B are factors to be calculated as follows:

$$A = \frac{(4\pi/3V_f)^{2/3}(z/x)^{-1/3}}{\sqrt{1+([(z/x)^{-2}-1]\cos^2\alpha)}};$$

$$B = \left(\frac{4\pi}{3V_f}\right)^{1/3}\left(\frac{z}{x}\right)^{1/3}\sqrt{1+\left(\left[\left(\frac{z}{x}\right)^{-2}-1\right]\cos^2\alpha\right)} \qquad (2)$$

where V_f is the volume fraction of the reinforcement, (z/x) the axial ratio and α is the average angle between the rotational axis of platelets and the stress direction. The equation refers to the hypothesis of full densification; applied to the present data, which refer to an approximately constant porosity content, the equation fits the experimental data for ($z/x = 0.2$), a typical value for Al_2O_3 platelets, and α equal to about 80°. This corresponds to platelets practically parallel to the stress direction, reasonably due to the alignment of the reinforcing phase (mixed with glass powders) in the die upon uniaxial pressing (prior to the sintering treatment). This fact is consistent with recent observations for platelet-reinforced glass matrix composites [22].

The increase of bending strength, with Al_2O_3 platelet content, was substantial despite the fact that the samples containing 15 vol% Al_2O_3 were the most porous; their strength approached 120 MPa, with an improvement of more than 50% in comparison with the matrix. The composites could be consequently compared to strong glass–ceramics for building applications (for example the well known Slag-Sitalls, whose bending strength is in the range of 90–130 MPa [3,23,24]). The remarkable Vickers hardness of about 9 GPa (reached with the same platelet content), however, is much higher than that of any commercial glass–ceramics product, and it could be a key point for the usage of composites in applications requiring high wear resistance.

The values for indentation fracture toughness for all the composites reached 2 MPa $m^{0.5}$, compared with 1.5 MPa $m^{0.5}$ for the matrix alone. As observed in the literature [25], the fracture toughness is greatly enhanced by crack deflection, i.e. by the introduction of residual stresses in the ceramic matrix, especially with low reinforcement additions, depending on the shape of the inclusions (spherical, plate-like or fibre-like); for plate-like inclusions, the toughening effect reaches a maximum level at a volume fraction equal to or higher than 5%, and then remains constant, as observed. In our case, the thermal expansion coefficient of the matrix ($8.0 \times 10^{-6}\ K^{-1}$) was lower than that of alumina ($8.9 \times 10^{-6}\ K^{-1}$), so that cracks would be expected to deviate around the platelets, without reaching them. The larger contraction of alumina, upon cooling, causes compressive stresses in the matrix only at the contact points with the Al_2O_3 platelets which are balanced by tensile stresses in the reinforcing particles. This was the effective situation, as illustrated by Fig. 4b, since no platelet is directly visible, and the roughness of fracture surfaces greatly increased in the composites, compared to the un-reinforced matrix (Fig. 4a).

4. Conclusions

A powder technology approach was employed for the manufacturing of sintered glass–ceramics and alumina platelet reinforced glass–ceramic matrix composites. The feasibility of producing potassium feldspar-based glass–ceramics at very low temperature (750 °C) with a short treatment time (2 h) was demonstrated. The introduction of reinforcing Al_2O_3 platelets did not modify substantially the densification of the matrix, but led to an overall improvement in the mechanical properties, particularly the bending strength and the Vickers microhardness. Although preliminary vitrification of feldspar minerals and glass grinding are expensive, it should be considered that no refinement of glass is required since the vitrification may be conducted with the same low cost plants employed for the preparation of glass frits, in powder form, easily ground due to the internal stresses caused by sudden cooling. The subsequent sintering is conducted at very low temperatures compared to equivalent strong materials for building applications such as commercial glass–ceramics and traditional porcelain stoneware tiles.

Acknowledgements

EB would like to thank Prof. Giovanni Scarinci (Dipartimento di Ingegneria Meccanica, settore Materiali, Università di Padova) for a very fruitful and stimulating discussion, Dr. Claudio Furlan (CUGAS, Università di Padova) and Mr. Davide Stocco for experimental assistance. SH and JD wish to acknowledge our colleagues in Materials Ireland Research Centre, University of Limerick for technical assistance.

References

[1] E. Bernardo, R. Castellan, S. Hreglich, Sintered glass–ceramics from mixtures of wastes, Ceram. Int. 33 (2007) 27–33.
[2] E. Bernardo, R. Castellan, S. Hreglich, I. Lancellotti, Sintered sanidine glass–ceramics from industrial wastes, J. Eur. Ceram. Soc. 26 (2006) 3335–3341.
[3] W. Höland, G. Beall, Glass–ceramic technology, in: The American Ceramic Society, Westerville, OH, USA, 2002.
[4] E. Bernardo, F. Andreola, L. Barbieri, I. Lancellotti, Sintered glass–ceramics and glass–ceramic matrix composites from CRT panel glass, J. Am. Ceram. Soc. 88 (2005) 1886–1891.
[5] M. Tashiro, Crystallization of glasses: science and technology, J. Non-Cryst. Sol. 73 (1985) 575–584.
[6] I. Gutzow, R. Pascova, A. Karamanov, J. Schmelzer, The kinetics of surface induced sinter-crystallization and the formation of glass–ceramic materials, J. Mater. Sci. 33 (1998) 5265–5273.
[7] T.J. Clark, J.S. Reed, Kinetic processes involved in the sintering and crystallization of glass powders, J. Am. Ceram. Soc. 69 (1986) 837–846.
[8] R. Müller, E.D. Zanotto, V.M. Fokin, Surface crystallization of silicate glasses: nucleation sites and kinetics, J. Non-Cryst. Sol. 274 (2000) 208–231.
[9] M.O. Prado, E.D. Zanotto, Glass sintering with concurrent crystallization, CR Chim. 5 (2002) 773–786.
[10] P. Colombo, G. Brusatin, E. Bernardo, G. Scarinci, Inertization and reuse of waste materials by vitrification and fabrication of glass-based products, Curr. Opin. Solid State Mater. Sci. 7 (2003) 225–239.

[11] A.R. Boccaccini, M. Bücker, J. Bossert, K. Marszalek, Glass matrix composites from coal fly ash and waste glass, Waste Manag. 17 (1997) 39–45.

[12] E. Bernardo, G. Scarinci, Sintering behavior and mechanical properties of Al_2O_3 platelet-reinforced glass matrix composites, Ceram. Int. 30 (2004) 785–791.

[13] E. Bernardo, G. Scarinci, S. Hreglich, Development and mechanical characterization of Al_2O_3 platelet-reinforced glass matrix composites obtained from glasses coming from dismantled cathode ray tubes, J. Eur. Ceram. Soc. 25 (2005) 1541–1550.

[14] A.R. Boccaccini, D.H. Pearce, P.A. Trusty, Pressureless sintering and characterization of Al_2O_3-platelet-reinforced barium–magnesium aluminosilicate glass–ceramic composites, Composites 28A (1997) 505–510.

[15] G. Brusatin, E. Bernardo, G. Scarinci, Sintered glass–ceramics from waste inert glass, in: Proceedings of IV International Workshop VARIREI (valorization and recycling of industrial residues), L'Aquila, Italy, 2003.

[16] A.R. Boccaccini, On the viscosity of glass composites containing rigid inclusions, Mater. Lett. 34 (1998) 285–289.

[17] E. Dorre, H. Hübner, Alumina, Springer Verlag, Berlin, Heidelberg, 1984

[18] G.R. Anstis, P. Chantikul, B.R. Lawn, D.B. Marshall, A critical evaluation of indentation techniques for measuring fracture toughness: I, direct crack measurement, J. Am. Ceram. Soc. 64 (1981) 533–538.

[19] http://rsb.info.nih.gov/ij/.

[20] A. Karamanov, M. Pelino, Sinter-crystallisation in the diopside–albite system: part I. Formation of induced crystallisation porosity, J. Eur. Ceram. Soc. 26 (2006) 2511–2517.

[21] A.R. Boccaccini, D. Eifler, G. Ondracek, Determination of the Young's modulus of platelet reinforced composite materials, Mater. Sci. Eng. A207 (1996) 228–233.

[22] E. Bernardo, R. Castellan, S. Hreglich, Al_2O_3-platelet reinforced glass matrix composites from a mixture of wastes, J. Mater. Sci. 42 (2007) 2706–2711.

[23] Z. Strnad, Glass–Ceramic Materials, Elsevier Science Publishers, Amsterdam, 1986.

[24] P.D. Sarkisov, The modern state of technology and application of glass–ceramics, in: Glass'89, Survey Papers of the XVth International Congress on Glass, Leningrad, (1989), p. 411.

[25] K.K. Chawla, Ceramic Matrix Composites, Chapman & Hall, London, 1993.