Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 37 (2011) 1169–1174

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Microstructure and mechanical properties of dental 3Y-TZP ceramics by using CaO–P_2O_5 glass as additive

Wen-Fu Ho [a], Hsueh-Chuan Hsu [b,c], Yun-Fen Peng [c], Shih-Ching Wu [b,c,*]

[a] Department of Materials Science and Engineering, Da-Yeh University, Changhua 51591, Taiwan, ROC
[b] Department of Dental Technology and Materials Science, Central Taiwan University of Science and Technology, Taichung 40601, Taiwan, ROC
[c] Institute of Biomedical Engineering and Materials Science, Central Taiwan University of Science and Technology, Taichung 40601, Taiwan, ROC

Received 23 February 2010; received in revised form 8 October 2010; accepted 15 November 2010
Available online 25 December 2010

Abstract

This study investigated the effects of glass frits on the sintering and mechanical properties of dental 3Y-TZP ceramics. The glass frits, which consisted of MgO, CaO, Al_2O_3, SiO_2, and P_2O_5, were selected to lower the sintering temperature of zirconia via liquid phase sintering.

The results of the experiment showed that these glass frit additives neither destroy the stability of the high temperature t-phase nor induce grain growth. All the mechanical properties and the relative densities were strongly correlated with the addition of glass frits. At lower sintering temperatures, the presence of glass additives resulted in an increase in mechanical properties. At higher sintering temperatures, the presence of glass additives decreased the mechanical properties.

Keywords: A. Sintering; C. Mechanical properties; D. Glass; D. ZrO_2

1. Introduction

Compared with metal and resin dental restorations, the use of ceramic materials in dental applications is highly desirable due to their excellent chemical durability, wear resistance, biocompatibility, aesthetics, and even environmental friendliness [1–3]. The increasing use of CAD/CAM machining techniques has solved the shrinkage problem, which occurs in all-ceramic dental crown and bridge applications during the sintering process. A variety of CAD/CAM systems have been applied to the process of fabricating dental restorations [4,5].

Several kinds of all-ceramic dental materials have been investigated and used, including glass–ceramics, feldspathic porcelain, alumina-based core, glass-infiltrated core materials, zirconia core ceramic, and others [6]. Most of these materials have limitations in their applications because of their brittleness with the exception of zirconia. Yttria stabilized tetragonal zirconia polycrystal (Y-TZP) is gaining recognition as a candidate material in dentistry, owing to its high levels of mechanical strength and toughness, which arise from the effect of the transformation-toughening phenomena associated with the martensitic tetragonal to monoclinic phase transformation [7,8]. However, zirconia ceramics are usually fabricated via solid state sintering at high temperatures of around 1500–1600 °C [9,10], which is a relatively expensive fabrication method that inevitably increases production costs.

In order to lower the sintering temperature, additives are deliberately introduced. A variety of additives are effective in the sintering of ZrO_2, such as Fe_2O_3, SiO_2, Al_2O_3, Bi_2O_3, B_2O_3, CuO, Mn_2O_3, or TiO_2 [11,12]. All these studies have introduced small amounts (1–5%) of these additives and all of these additives attain a comparable density at lower temperatures. In most cases, the presence of additives results in improved densification of the ceramics via liquid phase sintering. However, these improvements in sintering were generally at the expense of mechanical properties. There also are some reports concerning the effects of glass additives, such as CAS-, LAS-, and other oxide glasses [13–16], in zirconia ceramic sintering. This shows that some additives do improve the densification and lower the sintering temperature.

---

* Corresponding author at: Department of Dental Laboratory Technology and Materials Science, Central Taiwan University of Science and Technology, No. 666, Buzih Rd., Beitun District, Taichung City 40601, Taiwan, ROC.
Tel.: +886 4 22391647x7413; fax: +886 4 22392922.
E-mail address: scwu@ctust.edu.tw (S.-C. Wu).

0272-8842/$36.00 © 2010 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2010.11.027

The CAD/CAM machining of zirconia for use in dental crown and bridge applications is different from its use in engineering applications. The shape of dental restoratives is complex in comparison with typical industrial products and is dependent on personal requirements. For the sake of processing ease and dental margin accuracy, zirconia ceramic restoratives are manufactured through a two-step heat-treatment process called presintering and sintering. Zirconia powder slurry is presintered at a relatively low temperature to produce zirconia blocks. The design and fabrication of ceramic restoratives use a compact machine set with sophisticated CAD software to compensate for the shrinkage that will occur in sintering. Finally, the shaped zirconia restoratives are sintered at a higher temperature to produce a high strength dental product [17].

Glass additives, especially biocompatible $CaO–P_2O_5$ containing glass, can lower dental zirconia sintering temperatures. In addition, the viscosity of the glass additives during the first stage of presintering heat-treatment may improve the uniformity and density of dental zirconia ceramic blocks. In this study, $MgO–CaO–Al_2O_3–SiO_2–P_2O_5$ glass powders [18] were introduced as additives to lower the sintering temperature of Y-TZP, with the aim of developing ceramics as dental materials. The microstructure and influences of varying amounts of glass additives on the mechanical properties were evaluated.

2. Experimental

2.1. Glass preparation

An $MgO–CaO–Al_2O_3–SiO_2–P_2O_5$ glass, denoted by A-A, was used as an additive. A-A glass (41.4 SiO_2, 35 CaO, 12 P_2O_5, 8.6 Al_2O_3, 3 MgO in wt%) was obtained from high-purity SiO_2, Al_2O_3, MgO, $CaCO_3$ and $Ca_3(PO_4)_2$ powders. The powders were weighed, mixed, and melted in a Pt crucible for 2 h at 1450 °C. The produced glass was quenched in cold water and then crushed in an agate mortar. It was then ball milled in deionized water for 72 h with ZrO_2 balls. When the milling was completed, the glass particles were sieved through a #500 mesh to obtain uniform and smaller particles. After sieving, the glass particles were dried in an oven at 80 °C for 12 h, then disaggregated in an agate mortar to obtain the A-A glass frits. These glass frits had an average size of 1.5 μm, as analyzed by a Malvern Zetasizer Nano ZS apparatus (Fig. 1).

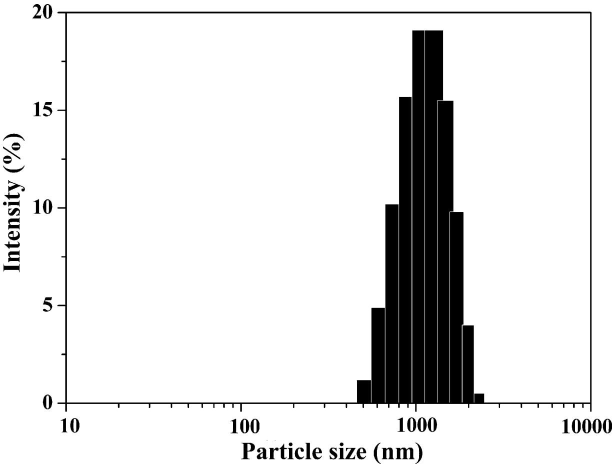

Fig. 1. Particle size distribution of the original glass powder.

2.2. Materials processing

High purity commercial 3 mol% $Y_2O_3–ZrO_2$ powder (CERAC, USA) and A-A glass frits were used as raw materials. The 3Y-TZP powder with 0, 1, 3, 5, 10 wt% of A-A glass frits as additives were mixed by ball milling using a polyethylene pot and high purity ZrO_2 sintered balls, then sieved through a 32 μm screen. The mixtures were compacted into 25 mm × 6 mm × 4 mm rectangular bars and 13 mm diameter cylindrical pellets by uniaxial pressing at 100 MPa. These compacts with a relative green density near 50% of theoretical density were sintered at 1200–1500 °C in a $MoSi_2$ furnace for 2 h, with a heating rate of 10 °C/min, and then, cooled in the furnace.

2.3. Characterization

The bulk density was measured by the Archimedes method. X-ray diffraction (XRD) for phase analysis was conducted using a diffractometer (XRD-6000, Shimadzu, Japan) operating at 30 kV and 30 mA. Ni-filtered Cu Kα radiation with a step width of 1°/min was used in this study.

The polished surface of sintered samples was thermal etched at 1200 °C for 15–60 min with a heating rate of 20 °C/min. A field emission scanning electron microscope (FE-SEM; JSM-7401F, JEOL, Japan) was used for examining the microstructure.

The bending strength was measured using a desktop mechanical tester (AG-IS, Shimadzu, Japan) at a cross-head speed of 0.5 mm/min. The samples were rectangular bars, with a span of 15 mm. Hardness was determined using a Vickers indentation hardness tester (INDENTAMET 1100 SERIES, RUEHLER, USA). In each sample, 10 indentations were measured, under a load of 2000 gf and a holding time of 30 s. Fracture toughness, K_{IC}, was analyzed using single edge notch specimens in accordance with the ASTM standard (ASTM C-1421, three-point flexure tests).

3. Results and discussion

3.1. Sintering behavior

Fig. 2 shows the X-ray diffractogram patterns of the original zirconia powders and the samples sintered at 1200 °C, with different glass contents as the sintering additive. Analysis of the X-ray diffractogram patterns indicates that the original zirconia powders existed as both $t-ZrO_2$ and $m-ZrO_2$. After sintering, only the $t-ZrO_2$ phase was evident. In fact, all the specimens sintered at other temperatures including 1300 °C and 1400 °C also showed only the $t-ZrO_2$ phase. The $t-ZrO_2$ to $m-ZrO_2$ transformation in pure zirconia during cooling is a reversible athermal martensitic transformation, with a finite amount of volume expansion of about 4%. This leads to the need to add

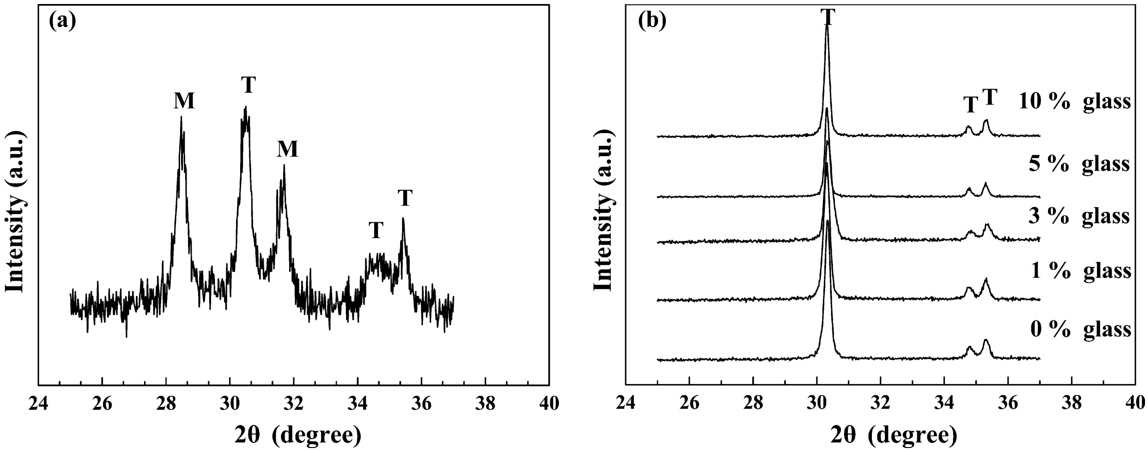

Fig. 2. XRD spectra. (a) Original ZrO_2 powders and (b) specimens sintered at 1200 °C with different amounts of glass additive (M: monoclinic phase; T: tetragonal phase).

several dopants, such as Y_2O_3, MgO, CeO_2, and CaO, to stabilize the high temperature t-phase in the sintered microstructure. This process enhances the toughness because the energy associated with crack propagation is dissipated both in the t-ZrO_2 to m-ZrO_2 transformation and in the overcoming of the compression stresses due to the volume expansion. Several previous studies indicated that the glass additives induced the monoclinic content [11,16]. Habibe even reported a slight increase in the monoclinic content as a function of increasing additives, which was independent of the sintering temperature [19]. This tetragonal-monoclinic phase transformation promotes a volume expansion, resulting in microcracking and a decreasing in the mechanical strength. However, the glass frit additives did not destroy the stability of the high temperature t-phase in this study. Intergranular crystallization was not detected in the sintered samples, either indicating that the intergranular phase composed originally of glass were still amorphous or the crystalline fractions were not enough to be detected by the diffractometer.

Fig. 3 shows the scanning electron microscope images of 3Y-TZP with glass frits. Fig. 3(a)–(e) show the specimens sintered at 1200 °C with varying glass contents of 0%, 1%, 3%, 5%, and 10%, respectively. In Fig. 3(a), the grains still appear loose, indicating that the pure 3Y-TZP has not been well sintered at this temperature. The proper sintering temperature for 3Y-TZP is considered at approximately 1500 °C [20]. The specimen with 1% glass additive in Fig. 3(b) shows better sintering conditions, indicating that the glass frit effectively promoted the sintering process at this lower (1200 °C) temperature.

These SEM images (Fig. 3(a)–(e)) showed that the glass frits were well-wetted into the crystalline grain. The intergranular spacing increased with increasing amounts of glass additives. The grain shape gradually changed from a polygon to a rounder shape indicating the dissolution of the ZrO_2 grains and a change in sintering behavior of the specimens. The addition of glass frits forms a viscous flow at this sintering temperature. In liquid phase sintering theory [21], viscous flow thoroughly wets the solid particles, resulting in substantial capillary pressure in the narrow channels between the particles. This aids densification by rearranging the particles to produce better packing and by providing a rapid diffusion path between the particles in which mass transfer occurred through a dissolution-reprecipitation mechanism. Though there is no reprecipitation evidence, these SEM images show that the glass frit additive formed a viscous flow during the sintering process.

Fig. 3(c), (f), (g), and (h) show the SEM images of 3Y-TZP with the same 3% glass additive at different sintering temperatures. Grain growth is obvious and the larger grain sizes occurred in conjunction with an increase in sintering temperature. The grain size was around 0.2 μm at 1200 °C and 0.8 μm at 1500 °C. The increase in grain size was clearly dependent on the sintering temperature. In fact, the mechanical properties of TZP depend on the t-phase retained at room temperature, and the fraction of t-phase retained at room temperature is dependent on both the grain size and the yttria content [7]. A critical grain size exists which is linked to the yttria concentration. Grains must reach a certain size before spontaneous T–M transformation of the grains takes place. This transformation would be inhibited in a fine-grained structure. 3Y-TZP material is composed of tetragonal grains with a size in the order of hundreds of nanometers [9]. The grain size in this study, however, attained the order of hundreds of nanometers even at a 1500 °C sintering temperature. This appears to match the X-ray diffractogram patterns and the fact that only the t-phase was observed in this study.

3.2. Densification and mechanical properties

Fig. 4 shows the relative densities of the sintered specimens as a function of sintering temperature and glass content. Calculations of these relative densities were based on the theoretical value of 6.10 g/cm^3 for 3Y-TZP and the experimental data of 2.79 g/cm^3 for A-A glass. Densification was greatly enhanced by the addition of glass at a 1200 °C sintering temperature. At 1200 °C, the relative density of pure 3Y-TZP without any glass additives was only 68.3%, but that of specimens with 1% glass additives was 85%, and with 5% glass additives, the density reached a maximum value of 94.8%.

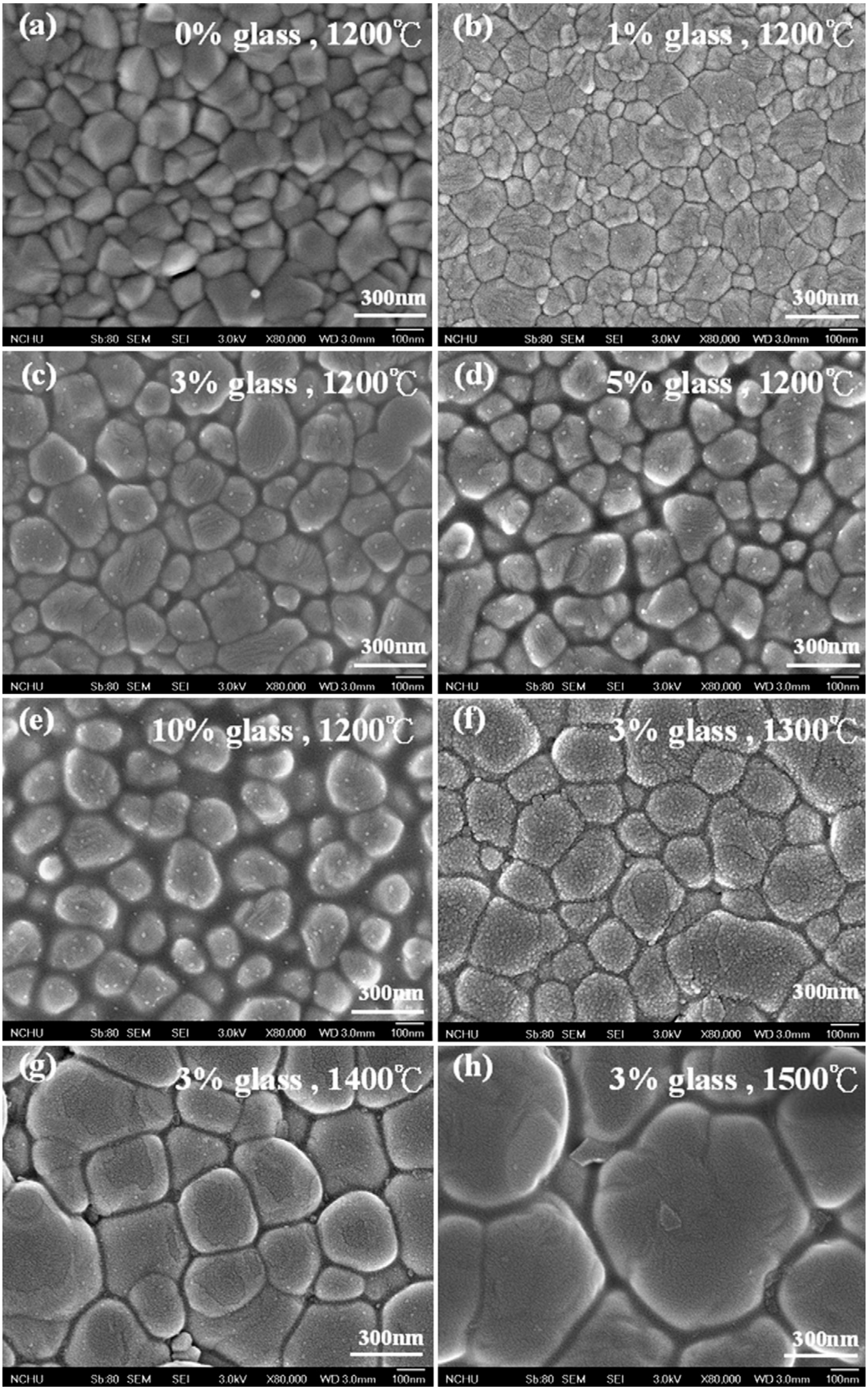

Fig. 3. SEM micrograph of 3Y-TZP ceramics with different glass contents and sintering temperatures.

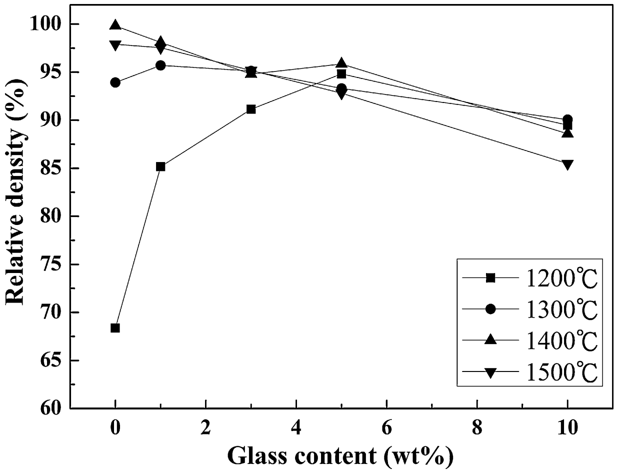

Fig. 4. Relative density as a function of glass content.

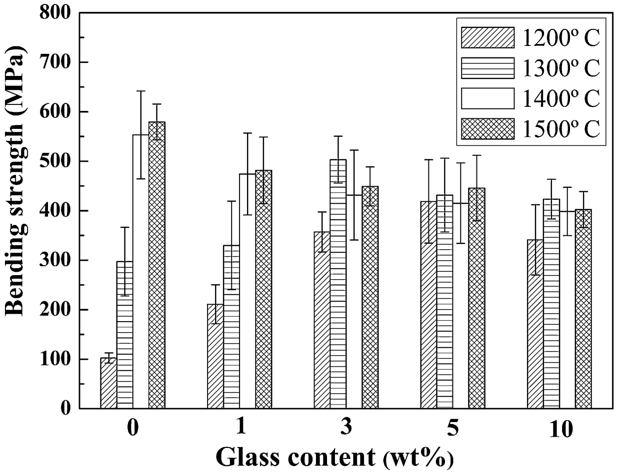

Fig. 6. Bending strength of the sintered samples as a function of glass content.

Similar behavior occurred for sintering at 1300 °C, except that the highest relative density occurred in the specimen with 1% glass additive.

Specimens sintered at 1300 °C presented better densification than those sintered at 1200 °C. However, the addition of glass frits wetted the crystalline grain and accelerated densification. The increase in the sintering temperature reduced the liquid viscosity, and particles joined easily. Therefore, the addition of glass could be effective in lowering the sintering temperature, as seen in the relative densities figures. The fact that all the values with 10% glass additives seem to have lower relative densities is possibly due to the existence of the intergranular glassy phase. The intergranular glassy phase causes a lower theoretical density than that calculated in this study.

Figs. 5 and 6 show the hardness and bending strength of 3Y-TZP as a function of the sintering temperature and additive content. The hardness and the bending strength strongly correlated with the variation of relative densities. The bending strengths were 102.4, 211.0, 357.2 MPa with 0, 1, and 3% glass additives, respectively, when sintered at 1200 °C. The bending strength achieved a maximum value of 418.8 MPa with 5% glass additives. When the specimen was sintered at 1300 °C, the highest bending strength occurred with 3% glass additives, reaching 503.1 MPa.

When sintering at 1400 and 1500 °C, the bending strength decreased with the glass content. This indicates that adding A-A glass frits lower the bending strength at these sintering temperatures. The ISO 6872 document for dentistry—ceramic materials, divides dental ceramics into six classes, according to their intended clinical use [22]. Each class has a different mechanical requirement. Therefore, choosing the appropriate glass additive content and sintering temperature will result in the bending strength that is required. Except for Class 6, which is for prostheses involving four or more units, adding A-A glass frits with appropriate heat treatment would still satisfy the requirements of Class 1–Class 5 dental ceramics.

Fracture toughness shows a relationship similar to that of hardness and bending strength (Fig. 7). For sintering at 1400 °C, the fracture toughness decreased with the glass content. On the other hand, the fracture toughness increased with 0, 1, and 3% glass additives, respectively when sintered at 1200 °C. It reached a maximum value of 5.32 MPa $m^{1/2}$ with 5% glass additives. For sintering at 1300 °C, the maximum fracture toughness value was 7.73 MPa $m^{1/2}$, which occurred in the specimens with 1% glass additives.

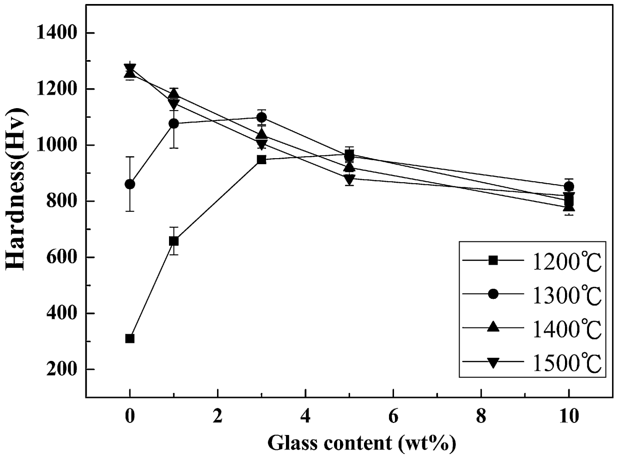

Fig. 5. Hardness of the sintered samples as a function of glass content.

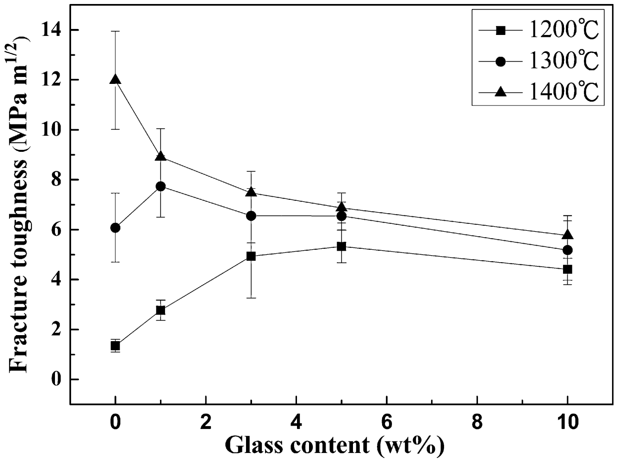

Fig. 7. Fracture toughness of the sintered samples as a function of glass content.

The results of these mechanical properties showed two significant effects associated with the presence of glass additives. At lower sintering temperatures, the presence of glass additives resulted in an increase in mechanical properties, while at higher sintering temperatures, the presence of glass additives decreased the mechanical properties. The increase in mechanical properties at lower sintering temperatures (1200 °C and 1300 °C) could be attributed to enhanced densification of the glass-containing specimens; the more glass additives contained, the better the densification. Once the specimens were sintered to nearly theoretical density, the presence of glass additives decreased the mechanical properties. The reduction in the mechanical properties appears to be correlated with increasing levels of grain boundary phase in specimens.

4. Conclusions

In this work, the addition of A-A glass frits effectively promoted the sintering process of 3Y-TZP ceramics. These glass frit additives did not destroy the stability of the high temperature t-phase and did not induce grain growth. The 3Y-TZP ceramics sintered at 1200 °C with 5% A-A glass resulted in good mechanical properties, in terms of a bending strength of 418.8 MPa, a hardness of 967.9 HV, and a fracture toughness of 5.32 MPa $m^{1/2}$. In the 3Y-TZP ceramics sintered at 1300 °C, the best mechanical properties appeared in the specimens with 3% A-A glass, which had a bending strength of 503.1 MPa, and a hardness of 1098.9 HV. The high correlation among various mechanical strengths and relative densities indicates that the addition of A-A glass frits effectively promotes the sintering process.

Acknowledgement

The authors would like to thank the support by a grant from the National Science Council, Republic of China (Project No. NSC 98-2221-E-166-006).

References

[1] B.I. Ardlin, Transformation-toughened zirconia for dental inlays, crowns and bridges: chemical stability and effect of low-temperature aging on flexural strength and surface structure, Dent. Mater. 18 (2002) 590–595.

[2] T. Kosma, C. Oblak, P. Jevnikar, N. Funduk, L. Marion, The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic, Dent. Mater. 15 (1999) 426–433.

[3] H.M. Ashkanani, A.J. Raigrodski, B.D. Flinn, H. Heindl, L.A. Mancl, Flexural and shear strengths of ZrO_2 and a high-noble alloy bonded to their corresponding porcelains, J. Prosthet. Dent. 100 (2008) 274–284.

[4] T. Miyazaki, Y. Hotta, J. Kunii, S. Kuriyama, Y. Tamaki, A review of dental CAD/CAM: current status and future perspectives from 20 years of experience, Dent. Mater. J. 28 (2009) 44–56.

[5] J. Tinschert, D. Zwez, R. Marx, K.J. Anusavice, Structural reliability of alumina-, feldspar-, leucite-, mica- and zirconia-based ceramics, J. Dent. 28 (2000) 529–535.

[6] A.J. Raigrodski, Contemporary materials and technologies for all-ceramic fixed partial dentures: a review of the literature, J. Prosthet. Dent. 92 (2004) 557–562.

[7] C. Piconi, G. Maccauro, Zirconia as a ceramic biomaterial, Biomaterials 20 (1999) 1–25.

[8] N. Nakanishi, T. Shigenmastu, Martensitic transformations in zirconia ceramics, Mater. Trans. 33 (1992) 318–323.

[9] F.F. Lange, Transformation toughening. Part 3: experimental observations in the ZrO_2–Y_2O_3 system, J. Mater. Sci. 17 (1982) 240–246.

[10] A.H. Heruer, Transformation toughening in ZrO_2-containing ceramics, J. Am. Ceram. Soc. 70 (1987) 689–698.

[11] Y.H. Sun, Y.F. Zhang, J.K. Guo, Microstructure and bending strength of 3Y-TZP ceramic by liquid-phase sintering with CAS addition, Ceram. Int. 29 (2003) 229–232.

[12] X.W. Huang, J.C. Yu, F. Ding, Effect of the addition of CaO–MgO–SiO_2 glass on the sintering and mechanical properties of Al_2O_3/3Y-TZP composites, J. Mater. Sci. 41 (2006) 5029–5032.

[13] X.J. Sheng, H. Xu, Z.H. Jin, Y.L. Wang, Preparation of glass-infiltrated 3Y-TZP/Al_2O_3/glass composites, Mater. Lett. 58 (2004) 1750–1753.

[14] J.R. Kim, D.W. Kim, I.S. Cho, B.S. Kim, J.S. An, K.S. Hong, Low temperature sintering and microwave dielectric properties of $Ba_3Ti_5Nb_6O_{28}$ with ZnO–B_2O_3 glass additions for LTCC applications, J. Eur. Ceram. Soc. 27 (2007) 3075–3079.

[15] C. Santos, R.C. Souza, N. Almeida, F.A. Almeida, R.R.F. Silva, M.H.F.V. Fernandes, Toughened ZrO_2 ceramics sintered with a La_2O_3-rich glass as additive, J. Mater. Process. Technol. 200 (2008) 126–132.

[16] C. Santos, R.C. Souza, A.F. Habibe, L.D. Maeda, M.J.R. Barboza, C.N. Elias, Mechanical properties of Y-TPZ ceramics obtained by liquid phase sintering using bioglass as additive, Mater. Sci. Eng. A 478 (2008) 257–263.

[17] P.F. Manicone, P.R. Iommetti, L. Raffaelli, An overview of zirconia ceramics: basic properties and clinic applications, J. Dent. 35 (2007) 819–826.

[18] S.C. Wu, C.L. Wang, M.H. Hon, Effects of Ca/P ratio on the crystallization of MgO–CaO–Al_2O_3–SiO_2–P_2O_5 glass–ceramics, J. Ceram. Soc. Jpn. 103 (1995) 99–103.

[19] A.F. Habibe, L.D. Maeda, R.C. Souza, M.J.R. Barboza, J.K.M.F. Daguano, S.O. Rogero, C. Santos, Effect of bioglass additions on the sintering of Y-TZP bioceramics, Mater. Sci. Eng. C 29 (2009) 1959–1964.

[20] M. Mazaheri, A. Simchi, F. Golestani-Fard, Densification and grain growth of nanocrystalline 3Y-TZP during two-step sintering, J. Eur. Ceram. Soc. 28 (2008) 2933–2939.

[21] A. Lupulescu, M.E. Glicksman, Diffusion-limited crystal growth in silicate systems: similarity with high-pressure liquid-phase sintering, J. Cryst. Growth 211 (2000) 49–61.

[22] ISO 6872, Dentistry-Ceramic materials, 2008.