JOURNAL OF MATERIALS SCIENCE 23 (1988) 2255–2258

Preparation of zirconia-toughened bioactive glass-ceramics

TOSHIHIRO KASUGA, MASAHIRO YOSHIDA, TOMOKO UNO, KIICHI NAKAJIMA
Hoya Corporation, 3-3-1 Musashino, Akishima-shi, Tokyo 196, Japan

Bioactive glass-ceramics toughened by tetragonal zirconia polycrystal (TZP) were prepared by hot-pressing mixed powders of the $MgO-CaO-P_2O_5-SiO_2$ glass and TZP containing 20 to 80% alumina. The bending strength and the fracture toughness of the composite materials were improved compared with those of the material without TZP. These composites showed high bending strengths (400 to 500 MPa) and high fracture toughness ($\sim 2.8\,MPa\,m^{1/2}$). The existence of a crack deflection mechanism was observed by scanning electron microscopy. After soaking in simulated physiological solution at 100 °C, no phase transformation from tetragonal to monoclinic of TZP in the composites and no degradation in bending strength occurred.

1. Introduction

Alumina ceramics [1, 2] show good biocompatibility and high strength, but do not form chemical bonds with bone. Therefore, loosening is likely to occur during longterm use. Hydroxyapatite ceramics [3, 4], Bioglass^R ($Na_2O-CaO-P_2O_5-SiO_2$ system) [5] and Ceravital^R ($Na_2O-K_2O-MgO-CaO-P_2O_5-SiO_2$ system) [6] form chemical bonds with bone. However, their poor mechanical strength may limit their clinical application. Apatite- and wollastonite-containing glass-ceramics [7–9] in the system $MgO-CaO-P_2O_5-SiO_2$ can form tight chemical bonds with bone and show relatively high mechanical strength (200 to 250 MPa bending). However, some artificial hard tissues (for example, artificial dental roots for front teeth, artificial joints, etc.) require higher strength. On the other hand, zirconia ceramic, which is bioinert, is highly biocompatible [10, 11] and shows very high strength and toughness. Both bioactive and mechanically tough ceramics will be widely applicable to many other tissues. In this study, a new type of bioactive glass-ceramic toughened by the dispersion of TZP grains will be reported.

2. Experimental procedure

2.1. Preparation of composites

It has been reported [12] that the glass-ceramics containing a small amount of MgO in the system $MgO-CaO-P_2O_5-SiO_2$ could form an apatite layer on their surface in simulated physiological solution, and that the ability to form an apatite layer was not influenced by the composition of the glass-ceramics. These results suggest that the glass-ceramics in this system are capable of forming chemical bonds with bone. In this study, the composition of $47.7CaO-6.5P_2O_5-43.8SiO_2-1.5MgO-0.5CaF_2$ (wt %) was selected as the mother glass for matrices of the composites. The crystallized glass of this composition formed an apatite layer on its surface in simulated physiological solution. After implanting in the lower jaw of the dog, this glass-ceramic was found to form chemical bonds with bone tissue [13]. TZP ceramics show high strength and toughness owing to stress-induced transformation from tetragonal to monoclinic phase. It has been reported, however, that the phase transformation in zirconia ceramics during heat treatment in a wet atmosphere took place at lower temperatures and at a higher rate than that in a dry atmosphere [14–16]. This transformation causes the degradation of mechanical properties [17]. The rate of the transformation slows down with the decrease in the grain size and/or on dispersion of alumina in zirconia ceramics [18]. Biomaterials for implants are used in a wet atmosphere. Zirconia–alumina ceramics were selected to prepare composites which did not lead to the degradation of mechanical properties by the phase transformation of TZP.

A batch mixture of the composition was melted in a platinum crucible at 1500 °C for 2 h. The melt was then quenched into water. The resultant glass was pulverized into powder of particle size $< 10\,\mu m$. Zirconia powder containing 3 mol % yttria and alumina powder were used as starting materials. The zirconia and alumina powders were mixed by ball milling with ethanol. The blended powder was dried and then hot-isostatically pressed at 1400 °C for 3 h. The resultant zirconia–alumina ceramics were crushed into powder of particle size $< 20\,\mu m$ by ball milling. The compositions of the zirconia–alumina ceramics discussed are shown in Table I.

The glass powder was mixed with powdered zirconia–alumina ceramics by ball milling with ethanol. This blended powder was put into carbon dies and hot-pressed in vacuum ($\sim 10^{-3}$ Pa) to sinter and crystallize under 30 MPa at 1150 °C for 2 h.

2.2. Analysis of microstructure

The densities of the composites obtained were determined by the Archimedes method. Theoretical densities

TABLE I Compositions of zirconia–alumina ceramics

ZrO_2/Al_2O_3* ratio	Sample		
	Z20A	Z40A	Z80A
(wt %)	80/20	60/40	20/80
(vol %)	72/28	49/51	14/86

*ZrO_2 = tetragonal zirconia polycrystal containing 3 mol % Y_2O_3, Al_2O_3 = α-alumina.

of the composites were estimated from the densities of glass-ceramics, zirconia, and alumina (using 2.98, 6.10 and 3.87 g cm^{-3}, respectively). The content of the crystals precipitated in the glass-ceramic matrices and the phase of zirconia–alumina ceramics were determined by X-ray diffraction analysis. Polished and fractured surfaces of the composites were observed by scanning electron microscopy.

2.3. Measurement of mechanical properties

Strengths (σ) in air and in nitrogen were measured in a three-point bending (20 mm support span) using bevelled edge specimens (3 mm × 4 mm × 25 mm) abraded with no. 400 alumina powder. The cross-head rate was 0.5 mm min^{-1}. The fracture toughness (K_{IC}) was measured in nitrogen by a three-point loading method (20 mm support span) using chevron notch beam specimens (3 mm × 4 mm × 36 mm, with notch dimensions of α_0 = 0.375 and α_1 = 0.75). The cross-head rate was 0.05 mm min^{-1}.

2.4. Estimation of the stability of the glass-ceramic composites after soaking in simulated physiological solution

To estimate the degradation property of the composite due mainly to the phase transformation of zirconia in a wet atmosphere described in Section 2.1, the following experiment was carried out. The columnar specimens (~4 mm diameter) of the composites ground with the no. 300 diamond-wheel were soaked in simulated physiological solution at 100 °C for a few days. After soaking, three-point bending strengths of the dried specimens were measured in air with a support span of 15 mm and cross-head rate of 0.5 mm min^{-1}.

3. Results and discussion

3.1. Microstructure

All the relative densities of glass-ceramic/zirconia-alumina ceramic composites obtained were higher than 99%. Oxy- and fluoro-apatite ($Ca_{10}(PO_4)_6(O, F_2)$) and β-wollastonite (β-CaO SiO_2) precipitated in the glass-ceramic matrix. The contents of these crystalline phases in the matrix were 15 and 70 wt %, respectively. No reaction between glass-ceramic matrices and zirconia–alumina ceramics was detected by X-ray diffraction. It was observed by scanning electron microscopy that the grains of the zirconia–alumina ceramic were dispersed in the glass-ceramic matrices without intense agglomeration.

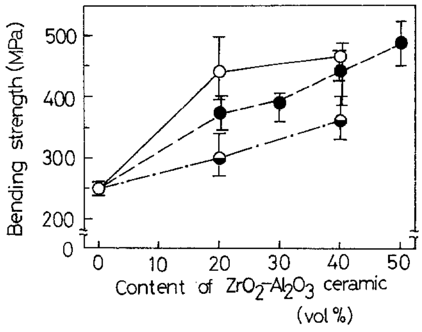

Figure 1 Relation between the content of zirconia–alumina ceramic and the bending strength of the composite. (○) Z20A, (●) Z40A, (⊖) Z80A.

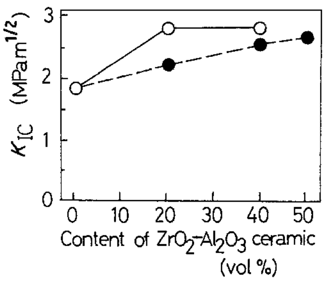

Figure 2 Relation between the content of zirconia–alumina ceramic and the fracture toughness of the composite. (○) Z20A, (●) Z40A.

3.2. Mechanical properties

Fig. 1 shows the relation between the bending strength in air of the glass-ceramic composites and the contents of the zirconia-alumina ceramics. The strength of the composite increased as the content of zirconia–alumina ceramics increased. The strengths of the glass-ceramic composites containing more than 20 vol % Z20A and containing more than 40 vol% Z40A were more than 400 MPa. This value is about twice the value of the strength of the glass-ceramic matrix (~200 MPa). Fig. 2 shows the relation between the fracture toughness and the contents of zirconia–alumina ceramics. The fracture toughness of the composites also increased as the content of zirconia–alumina ceramics increased. The fracture toughness of the glass–ceramic composite containing 20 vol % Z20A was 2.8 MPa m$^{1/2}$.

Generally, the bending strength of ceramics measured in a dry nitrogen atmosphere, σ_{N_2}, is related to the fracture toughness, K_{IC}, and the critical flaw size, c, in the ceramics as follows [19]

$$\sigma_{N_2} = K_{IC}/Yc^{0.5} \tag{1}$$

where Y is 1.26 for semi-circular surface flaw [20]. The flaw sizes calculated from the bending strength data and the fracture toughness data using Equation 1 are listed in Table II. The average flaw sizes are nearly

TABLE II Bending strength in air (σ_{air}), and nitrogen (σ_{N_2}), fracture toughness (K_{IC}) and critical flaw size (c) of the glass-ceramic and the glass-ceramic composites

Sample	σ_{air} (MPa)	σ_{N_2} (MPa)	K_{IC} (MPa m$^{1/2}$)	c (μm)
Glass-ceramic (matrix)	250	334	1.66	16
Z20A Vf 20*	440	552	2.84	17
Z20A Vf 40	463	573	2.80	15
Z40A Vf 20	375	487	2.37	15
Z40A Vf 40	443	528	2.62	16
Z40A Vf 50	488	532	2.70	16

*For example, Z20A Vf 20 is the glass-ceramic composite containing 20 vol % Z20A.

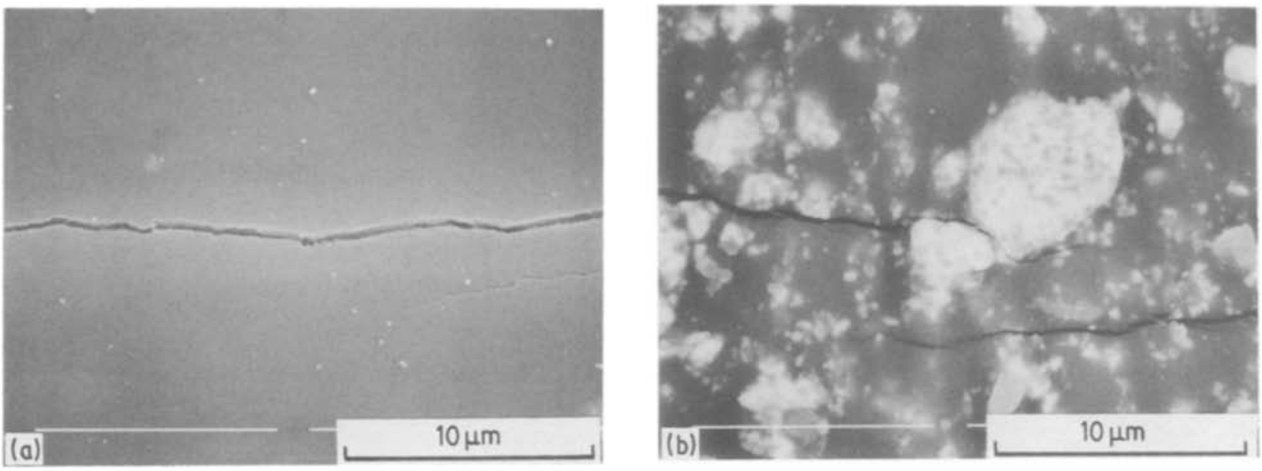

Figure 3 Vickers indentation cracks in (a) glass-ceramic and (b) composite. (a) Secondary electron imaging mode, (b) backscattered electron imaging mode. The glass-ceramic matrix appears dark and the zirconia grains bright due to their different atomic number contrast. The alumina grains appear dark in the zirconia grains.

constant for each kind of composite. The increase in σ is considered to be the result of the increase in the fracture toughness. The increase of zirconia content in zirconia–alumina ceramic was effective in increasing the bending strength of the glass-ceramic composite. According to this result, the existence of the phase transformation toughening of the material is suggested.

Figs 3a and b show the crack profiles of a Vickers indentation introduced at a load of 1 kg. The fracture path in the glass-ceramic remained planar throughout propagation, whereas that of the glass-ceramic composite containing 20 vol % Z20A demonstrated crack deflection. It is supposed that such a crack deflection mechanism could be attributed to the increase in the fracture toughness and bending strength.

3.3. Stability in simulated physiological solution

Fig. 4 shows the strengths of the glass-ceramic composites containing 20 vol % Z20A soaked in simulated physiological solution at 100 °C for a few days. The glass-ceramic composite maintained its high strength after soaking for 14 days. In the Z20A zirconia ceramic, monoclinic phase was precipitated after soaking at 100 °C for 7 days [18]. However, in this glass-ceramic composite, no phase transformation of zirconia occurred even after soaking for 14 days. This stability would be caused by the structure of this composite, that is, TZP are dispersed in the glass-ceramic matrix and are sealed against the wet atmosphere.

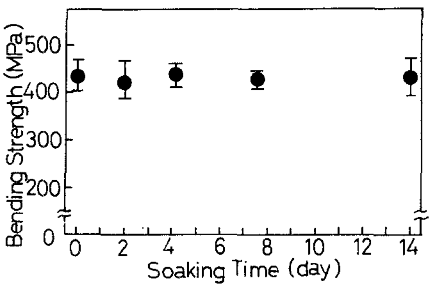

Figure 4 Bending strength after soaking in simulated physiological solution at 100 °C.

4. Conclusions

Bioactive glass-ceramic composites reinforced by zirconia–alumina ceramics were fabricated. The bending strength of the glass-ceramic composites was about twice as high as that of the matrix materials. Furthermore, the composites show bioactivity and have a high potentiality for biomaterial uses such as artificial bones or dental implants.

References

1. P. GRISS and G. HEIMKE, *Arch. Orthop. Traumat. Surg.* **98** (1981) 157.
2. *Idem, ibid.* **98** (1981) 165.
3. M. JARCO, J. F. KAY, K. I. GUMAER, R. H. DOREMUS and H. P. DROBECK, *J. Bioengng* **1** (1977) 79.
4. M. AKAO, M. AOKI and K. KATO, *J. Mater. Sci.* **16** (1981) 809.
5. L. L. HENCH, Proceedings of the 10th International Congress on Glass, Kyoto, Japan, July 1974 (Ceramic Society of Japan, Tokyo, 1974), No. 9, p. 30.
6. H. BRÖMER, K. DEUTSHER, B. BLENKE, E. PFEIL and V. STRUNZ, *Sci. Ceram.* **9** (1977) 219.
7. T. KOKUBO, S. ITO, M. SHIGEMATSU, S. SAKKA and T. YAMAMURO, *J. Mater. Sci.* **20** (1985) 2001.
8. T. NAKAMURA, T. YAMAMURO, S. HIGASHI, T. KOKUBO and S. ITO, *J. Biomed. Mater. Res.* **19** (1985) 685.
9. T. KITSUGI, T. YAMAMURO, T. NAKAMURA, Y. KAKUTANI, T. HAYASHI, S. ITO, T. KOKUBO, M. TAKAGI and T. SHIBUYA, *ibid.* **21** (1987) 467.
10. R. C. GARVIE, C. URBANI, D. R. KENNEDY and J. C. McNEUER, *J. Mater. Sci.* **19** (1984) 3224.
11. A. N. CRANIN, P. A. SCHNITMEN, M. RABKIN and T. DENISSEN, *J. Biomed. Mater. Res.* **6** (1975) 257.
12. T. KASUGA, K. NAKAGAWA, M. YOSHIDA and E. MIYADE, *J. Mater. Sci.* **22** (1987) 3721.
13. Hoya corporation, unpublished work, 1986.
14. Y. MURASE and E. KATO, *J. Amer. Ceram. Soc.* **66** (1983) 196.
15. T. SATO and M. SHIMADA, *ibid.* **68** (1985) 356.
16. K. NAKAJIMA, K. KOBAYASHI and Y. MURATA, "Advances in Ceramics", Vol. 12 (The American Ceramic Society, Ohio, 1985) pp. 399–407.
17. K. NAKAJIMA and T. MASAKI, "Zirconia Ceramics 9", edited by S. Somiya and M. Yoshimura (Uchida Rokakuho, Tokyo, 1987) pp. 27–35.

18. T. SATO and M. SHIMADA, *J. Mater. Sci.* **20**(1985) 3998.
19. R. W. DAVIDGE, "Mechanical Behaviour of Ceramics", (Cambridge University Press, London, 1979) p. 38.
20. G. R. IRWIN and P. C. PARIS, "Fracture: an Advanced Treatise, Vol. 3, Engineering Fundamentals and Environmental Effects" edited by H. Liebowitz (Academic, New York, 1971) p. 9.

Received 3 August
and accepted 23 October 1987