JOURNAL OF MATERIALS SCIENCE 20 (1985) 2001–2004

# Mechanical properties of a new type of apatite-containing glass–ceramic for prosthetic application

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A new type of apatite-containing glass–ceramic in the system $MgO–CaO–SiO_2–P_2O_5$ can form a tight chemical bond with bones and has a high mechanical strength. The cause for its high mechanical strength was examined by comparing mechanical properties of the glass–ceramics which have an identical chemical composition and different microstructures. It was found that the mechanical strength of the apatite-containing glass–ceramics is considerably increased by the precipitation of β-wollastonite crystals due to an increase in fracture surface energy resulting in an increase in fracture toughness.

## 1. Introduction

Alumina ceramics are already widely used as materials for bone and joint replacement because of their good biocompatibility and high mechanical strength. However, they do not form a tight chemical bond with bones, and their fixing within a body needs a mechanical interlocking with the bone. Such interlocking is liable to become loose over a long period.

Glasses in the system $Na_2O–CaO–SiO_2–P_2O_5$ called Bioglass [1] and glass–ceramics in the system $Na_2O–K_2O–MgO–CaO–SiO_2–P_2O_5$ called Ceravital [2] as well as hydroxyapatite ceramics [3–6] are known to form a chemical bond with bones. Their mechanical strengths hitherto reported are, however, not sufficiently high.

Recently, the present authors found that some glass–ceramics in the system $MgO–CaO–SiO_2–P_2O_5$ can form a tight chemical bond with bones and have a fairly high mechanical strength [7]. In this study, the cause for their high mechanical strength was investigated in terms of their microstructure.

## 2. Experimental techniques

### 2.1. Preparation of samples

A batch mixture of the nominal composition of MgO 4.6, CaO 44.9, $SiO_2$ 34.2, $P_2O_5$ 16.3, $CaF_2$ 0.5 in weight ratio was melted in a platinum crucible at 1450° C for 2 h. The melt was poured on to a stainless steel plate and pressed into plates 2 to 6 mm thick. From the resultant glass plates, four kinds of samples which have different microstructures were prepared. The first one, designated G, was prepared by annealing glass plates at 750° C. The second one, designated A, was prepared by heating glass plates up to 870° C at a rate of $60° C h^{-1}$ and holding them at the temperature for 4 h. The third one, designated A-W, and the fourth, designated A-W-CP, were prepared by heating glass powders compacting up to 1050 and 1200° C, respectively, at a rate of $60° C h^{-1}$ and holding them at the respective temperatures for 4 h. The glass powder compacts were prepared by crushing glass plates into powders of particle size below 5 μm and pressing the powders with 1 wt% paraffin into rectangular bars 25 mm × 25 mm × 100 mm under a hydrostatic pressure of 200 MPa. At least five pieces were prepared for each sample. The following experiments were done for specimens cut from these pieces.

It has already been confirmed by a biological study using rabbits that all of the four samples

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described above can form a tight chemical bond with bones [8].

## 2.2. Analysis of microstructure

The kind and content of crystals precipitated in the samples were determined by powder X-ray diffraction analysis. In the determination of crystal contents, relative intensities of non-crystalline scattering, (3 1 0) reflection of apatite and (2 1 1) reflection of β-wollastonite were used.

Fracture surfaces of the samples were observed under a scanning electron microscope (Hitachi Co, Model S-450) after coating with a platinum thin film.

Porosities of the samples were determined by measuring bulk and true densities using Archimedean and pycnometer methods, respectively. Pure water was employed as the immersion liquid.

## 2.3. Measurement of mechanical properties

Bending strength, $\sigma$, was measured by a three point loading method using rectangular specimens 5 mm x 5 mm x 20 mm abraded with no. 2000 alumina powders. The span length was 16 mm. A stress rate of 18 MPa $\sec^{-1}$ was employed. Six measurements were made in air and dry nitrogen gas atmosphere, respectively, for each sample.

Fracture toughness, $K_{IC}$, was measured by the double torsion method [9] schematically shown in Fig. 1. The specimen was a plate 3 mm x 20 mm x 70 mm having a groove 0.5 mm wide and 1 mm deep at the centre of the bottom. The $K_{IC}$ was calculated using the following equation.

$$K_{IC} = PW_m \left[\frac{3(1+\nu)}{Wd^3 d_n}\right]^{1/2} \quad (1)$$

where $P$ is the load to fracture the specimen, $\nu$ is Poisson's ratio and the other symbols are geometrical constants given in Fig. 1. Three measurements were made in dry nitrogen gas atmosphere for each sample.

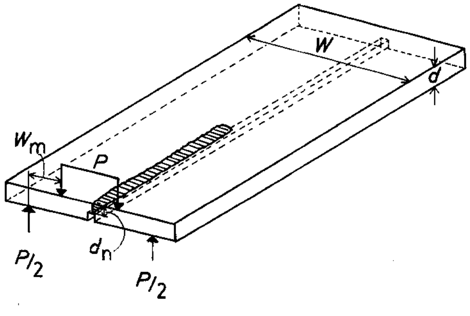

*Figure 1* The double torsion method.

Young's modulus, $E$, and Poisson's ratio were measured by a resonance method [10] using cubic specimens 4 mm x 4 mm x 4 mm. Poisson's ratio was determined from a resonant frequency using a dimensionless frequency against Poisson's ratio diagram for an isotropic solid. Young's modulus was calculated from the Poisson's ratio and shear sound velocity, $V_s$, which was also determined from the resonant frequency, using the following equation:

$$E = 2\rho V_s^2(1+\nu) \quad (2)$$

where $\rho$ is the bulk density of the specimen.

# 3. Results and discussion

## 3.1. Microstructure

The kind and content of crystals and the content of residual glass contained in the samples are shown in Table I. Sample G consisted of only glassy phase. Sample A contained oxy- and fluoroapatite ($Ca_{10}(PO_4)_6(O, F_2)$) crystals. Sample A-W contained β-wollastonite ($CaO \cdot SiO_2$) crystals besides the apatite crystals. Sample A-W-CP contained a larger amount of wollastonite crystal. A part of the apatite crystals in sample A-W-CP was converted to whitlockite ($\beta$-$3CaO \cdot P_2O_5$) crystals. The content of the glassy phase decreased in the order G > A > A-W > A-W-CP.

Porosities of samples G and A were 0% whereas those of samples A-W and A-W-CP were about 0.7%.

Scanning electron micrographs of fracture surfaces of the samples are shown in Fig. 2. It can be seen from Fig. 2 that the roughness of fracture surfaces increases in the order G < A < A-W < A-W-CP.

## 3.2. Mechanical properties

Bending strength, fracture toughness, Young's modulus and Poisson's ratio are given in Table II. It can be seen from Table II that the bending strength is considerably increased by precipitation

TABLE I Content of crystals and glassy phases in the samples

| Sample | Apatite (wt %) | Wollastonite (wt %) | Whitlockite (wt %) | Glass (wt %) |
|---|---|---|---|---|
| G | 0 | 0 | 0 | 100 |
| A | 35 | 0 | 0 | 65 |
| A-W | 35 | 40 | 0 | 25 |
| A-W-CP | 20 | 55 | 15 | 10 |

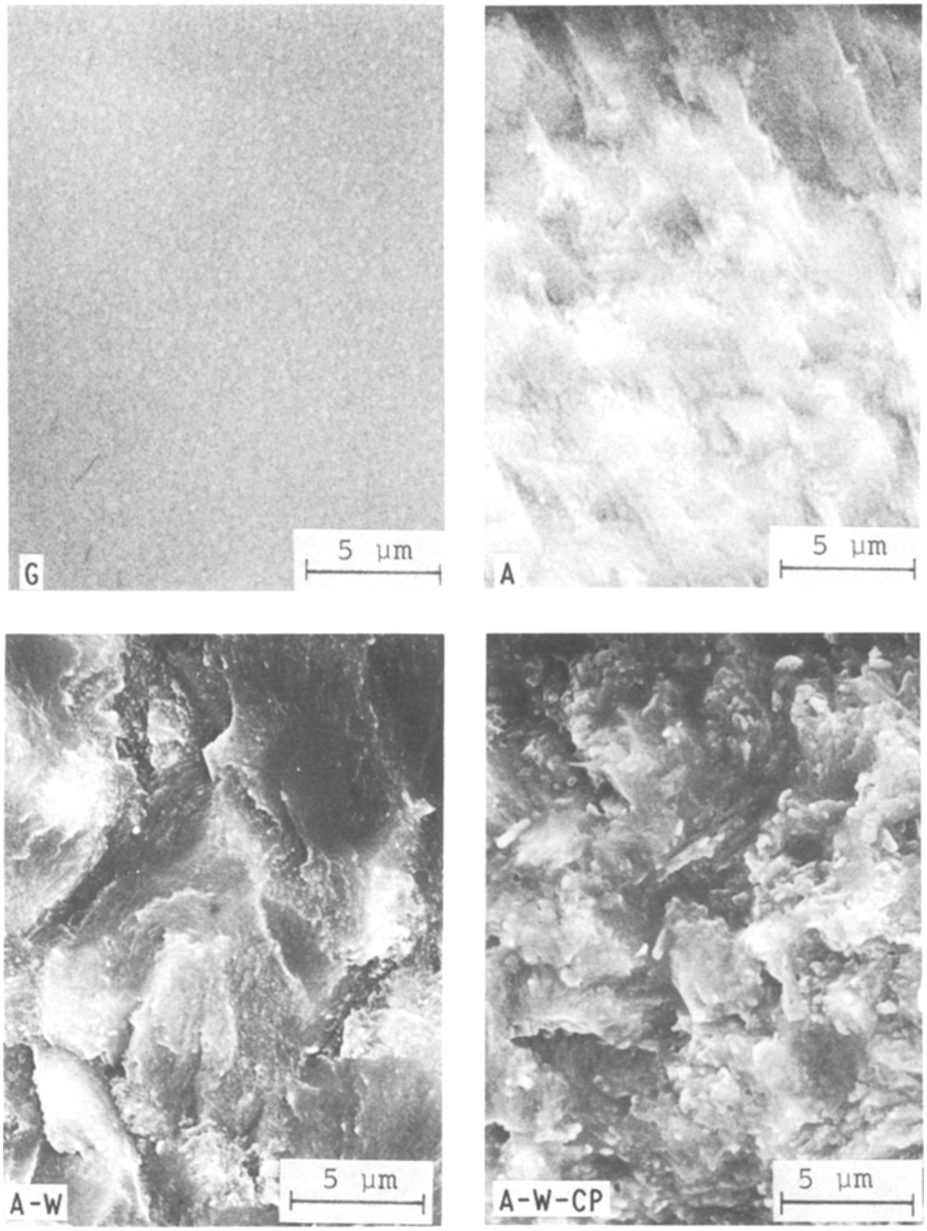

*Figure 2* Scanning electron micrographs of fracture surfaces for glass (G) and glass–ceramics (A, A-W, A-W-CP).

of wollastonite crystals. The bending strengths of samples A-W and A-W-CP are comparable to or higher than that of the strongest human bone [11].

Generally, the bending strength of brittle materials measured in dry nitrogen atmosphere is related to the fracture toughness and the critical flaw size, $c$, in the materials as follows [12]:

$$\sigma_{N_2} = \frac{K_{IC}}{Yc^{1/2}} \tag{3}$$

where $Y$ is 1.26 for semi-circular surface flaw [13]. The flaw sizes calculated from the bending strength and the fracture toughness given in Table II using Equation 3 are listed in Table III. It can be seen from Tables II and III that the higher bending strengths of samples A-W and A-W-CP are attributed to the higher fracture toughness but not to the smaller flaw sizes.

Fracture toughness is generally related to Young's modulus, Poisson's ratio and fracture surface energy, $\gamma$, as follows [14]:

TABLE II Bending strengths, $\sigma_{air}$ and $\sigma_{N_2}$, measured in air and dry $N_2$, respectively, fracture toughness $K_{IC}$, Young's modulus, $E$, and Poisson's ratio, $\nu$, of the samples

| Sample | $\sigma_{air}$ (MPa) | $\sigma_{N_2}$ (MPa) | $K_{IC}$ (MPa $m^{1/2}$) | $E$ (GPa) | $\nu$ |
|---|---|---|---|---|---|
| G | 72 ± 25 | 120 ± 20 | 0.8 ± 0.1 | 89 | 0.28 |
| A | 88 ± 12 | 141 ± 26 | 1.2 ± 0.1 | 104 | 0.27 |
| A-W | 178 ± 20 | 193 ± 12 | 2.0 ± 0.1 | 117 | 0.27 |
| A-W-CP | 213 ± 17 | 243 ± 18 | 2.6 ± 0.1 | 124 | 0.26 |

$$K_{IC} = \left[\frac{2E\gamma}{(1-\nu^2)}\right]^{1/2} \quad (4)$$

The fracture surface energies calculated from the fracture toughness, Young's modulus and Poisson's ratio given in Table II using Equation 4 are listed in Table III. It can be seen from Tables II and III that the higher fracture toughnesses of samples A-W and A-W-CP are caused by the increase in Young's modulus and the fracture surface energy. The increase in the fracture surface energy is much larger than that in Young's modulus. Therefore, it can be concluded that the higher fracture toughnesses of samples A-W and A-W-CP are attributed mainly to the higher fracture surface energies.

The higher fracture surface energies of samples A-W and A-W-CP might be caused at least partially by larger effective areas of the fracture surfaces. It can be confirmed by the roughness of fracture surfaces shown in Fig. 2 that the effective areas of the fracture surfaces of samples A-W and A-W-CP are larger than those of samples G and A. The rougher fracture surfaces of samples A-W and A-W-CP might be caused by the presence of wollastonite crystals. It is assumed that the wollastonite crystals inhibited the straight propagation of cracks, causing them to turn or branch out.

## 4. Conclusion

The high mechanical strength of the apatite-containing glass–ceramics in the system $MgO-CaO-SiO_2-P_2O_5$ is attributed to the precipitation of wollastonite crystals. It increases the fracture surface energy and thereby the fracture toughness of the glass–ceramics.

TABLE III Flaw size, $c$, and fracture surface energy, $\gamma$, of the samples

| Sample | $c$ ($\mu$m) | $\gamma$ (J $m^{-2}$) |
|---|---|---|
| G | 28 | 3.3 |
| A | 46 | 6.4 |
| A-W | 68 | 15.9 |
| A-W-CP | 72 | 25.5 |

## Acknowledgements

This research was supported by a Grant-in-Aid for Special Research, Studies on Design of Multi-Phase Biomedical Materials (No. 58211009), of Ministry of Education, Science and Culture, Japan. The authors thank Mr T. Shibuya of Nippon Electric Glass Company for the supply of the samples, and Dr K. Hirao and Professor N. Soga of Kyoto University for the resonance method.

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*Received 28 March*
*and accepted 11 July 1984*