

Bioactive Glass-Ceramics Toughened by Tetragonal Zirconia Polycrystal

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Two types of high strength bioactive glass-ceramic composites, a composite of crystallized glass matrix /dispersed tetragonal zirconia polycrystal(TZP) grains and a composite of TZP matrix /dispersed crystallized glass grains, were developed. The former was fabricated by hot-pressing the mixture of the glass and TZP powders. The bending strength of the composite increased with increasing TZP content showing 600 to 900 MPa at 40 vol%. The latter was devised for the purposes of manufacturing such a complicatedly designed product as "tooth root" and of mass-producing by means of hot-isostatic-pressing of the pressurelessly sintered specimens the shape of which the mixture of the crystallized glass and TZP powders was molded into by an injection machine, because it was limited to the case of a lower TZP content to fabricate dense specimens by the pressureless sintering of the molds of the mixture of the glass and TZP powders. The increase in strength would be considered to result from the compressive stress field generated during the sintering process in both composites. The bioactivity and the phase transformation of TZP in simulated body fluid and in hot water were estimated.

1. INTRODUCTION

It has been reported that sintered apatite,bioglass and glass-ceramic containing apatite and wollastonite were applicable to hard issues for their excellent bio-compatibility¹⁻⁶).But their applications would be much restricted owing to their poor mechanical properties.Authors have investigated for improving the mechanical properties of the bioactive glass-ceramics by dispersing tetragonal zirconia polycrystals(TZP),since the TZP grains generate compressive stress field around them by a stress-induced phase transformation mechanism⁷⁻⁹).

In this report the previous works are summarized and the relationship between the improving mechanical properties and the bioactivity of the Bioactive glass-ceramic/TZP Composite(BTC) materials,phase transformation behavior of TZP in the composite,and manufacturing technology of the actual artificial tissues

of complicated shape will be discussed^{7, 10, 11}.

2. EXPERIMENTAL PROCEDURES

2.1 RAW MATERIALS

BTC was prepared either by hot-pressing(HP:NEMS Co.)the mixture of glass powder and zirconia powder or by HIPing(Labo HIP:Mitsubishi Heavy Industry Co.) the pressurelessly sintered body of the mold(Dr.CIP:Kobe Steel Co.or JCSS: Nippon Seiko Co.)of the mixture of crystallized glass powder and zirconia powder.The composition of $47.7\text{CaO}-6.5\text{P}_2\text{O}_5-43.8\text{SiO}_2-1.5\text{MgO}-0.5\text{CaF}_2$ (guaranteed grade:Kanto Chemical Co.)in wt% was selected as the mother glass considering the bioactivity,chemical stability and sinterability⁷.BTC related here would be classified to two types,a crystallized glass matrix/TZP dispersed one and TZP matrix/crystallized glass dispersed one.

The raw glass was prepared by melting the mixture of the composition in a platinum crucible at 1500-1550°C for 1-2h,quenching into water and pulverizing into powder of 2-3 μm in average particle size.The crystallized glass raw material for the TZP matrix composite was prepared by heat-treating the raw glass above at 1150°C. Two types of partially stabilized zirconia powders by 1.75-3 mol% yttria(TZ and LZ)were used for the raw materials of TZP.TZ powder was used for "sintered TZP particle" dispersed composite.Sintered TZP raw particles were prepared by sintering the pulverized TZ particles of the green body at 1400°C formed by pressing isostatically at the pressure of 98MPa. LZ powder was prepared for low temperature sintering,sintered well at 1200°C¹²).

2.2 SAMPLES

Three kinds of the composites developed are tabulated in table 1(notaton of the sample No.A,B,C means BTC-A,B,C,respectively).Raw materials of matrix, dispersing particles and manufacturing processes for each composite are related briefly in it.The raw powders were mixed at the prescribed ratio by ball milling with ethanol and dried.Hot-pressing,pressureless-sintering and HIPing were conducted at the temperature of 1100-1200°C which was determined in consideration of the appropriate crystallization of the glass.Namely,at this temperature range both bioactive and mechanically tough crystallized glass, containing 15% of apatite,70% of wollastonite and balanced ammount of glassy phase,was obtained for this composition.

Samples A(BTC-A)and B(BTC-B)were prepared by hot-pressing the mixture of the raw powders at about 30MPa,and sample C(BTC-C)by HIPing the pressurelessly

pre-sintered body at 200MPa in 95% argon-5% oxygen gas atmosphere¹³⁾. The green body before sintering was devised either by pressing isostatically in a rubber mold or by injection molding method which was used in case of manufacturing a complicatedly designed samples and mass-producing.

Materials thus obtained were cut, ground and polished to 0.8 μ m in roughness, especially to a mirror finish for the estimation of the phase transformation from tetragonal to monoclinic of TZP in the composite.

2.3 MEASUREMENT

Density, Modulus Of Rupture (MOR, measured by bending strength in 3 point bending), fracture toughness (K_{Ic}) were measured⁸⁾. Crystalline phases were determined by X-ray diffractometry (XRD) and by laser Raman spectroscopy, and some samples were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM)¹⁴⁾. Bioactivity may relate to the apatite formation on the surface of the sample after soaking in simulated body fluid⁴⁾. XRD intensity of apatite peak was measured before and after soaking in the fluid at 37°C for 30 days to estimate the bioactivity of the sample⁶⁾. The phase transformation behavior of TZP in the composite after soaking in distilled water at 90°C was measured by laser Raman spectroscopy^{10, 14)}.

3. RESULT AND DISCUSSION

3.1 BTC-A MATERIAL

Sintered TZP particles were used as the raw powder in manufacturing BTC-A. The particles were dispersed in glass-ceramic matrix. Relation between sintered TZP content and bending strength of BTC-A is shown by closed circle in Fig.1. The strength increased with increasing TZP content up to 60vol%, and then decreased above 70vol% suddenly. The polished surfaces of BTC-A were observed by SEM in order to discuss the reason for the degradation. As shown in Fig.2, sharp cracks were observed at the agglomerated parts of TZP particles in the composite containing 70vol% TZP⁸⁾. The degradation of the strength would be considered to occur owing to those cracks formed at the parts where those TZP did not sinter well at 1200°C, the sintering temperature of the composite. TZP particles of lower volume fraction would be dispersed well in the matrix and such agglomeration was not likely to appear.

The reason why sintered TZP for the dispersing particles is that TZ powder does not sinter well at the sintering temperature of the composite, 1200°C, determined from crystallizing behavior of the glass matrix. Toughening be observed for TZ

powder dispersed BTC instead of sintered TZP particles as shown by open circle in Fig.1. The grain size of TZ raw powder was about 10-20nm and was so small that the tetragonal phase was too stable to transform¹⁵⁾. The toughening mechanism of BTC-A is therefore considered to owe to the stress induced phase transformation of the dispersed TZP¹⁶⁾.

3.2 BTC-B MATERIAL

BTC-A has several weak points in manufacturing, the complicatedness of the preparation of the sintered TZP particles, and the degradation probability of the strength caused by the crack formation as related above, for examples. To improve these, BTC-B was developed using LZ raw powder which sintered well at 1200°C, the appropriate forming temperature of both bioactive and mechanically tough composite, instead of sintered TZP particles¹⁷⁾. Fig. 3 shows SEM(a) and TEM (b) photographs of BTC-B^{8, 10)}. The sintered bodies were dense and such a crack as observed in BTC-A of high TZP content was not found. Spherical TZP crystal grains of about 0.2μm were dispersed in glass-ceramic matrix. Thus the bending strength increased with increasing TZP content in whole range as shown in Fig. 4⁸⁾. Fig. 5 shows the relation between TZP content and fracture toughness of BTC-B. The fracture toughness increased linearly with increasing TZP as well.

3.3 BTC-C MATERIAL

It would be bothersome and would not be efficient to make up such complicatedly designed tissues as artificial joints or tooth roots from the block of hot pressed BTC. Accordingly, the manufacturing process of injection molding/pressureless pre-sintering/HIPing was investigated as follows. Mixtures of "glass" and LZ powder were molded by an isostatic pressing or an injection molding method and were pressurelessly pre-sintered at 1200°C. The same process was conducted for mixtures of "crystallized glass" and LZ powder. The relative density of the sintered body to LZ content is shown in Fig. 6¹¹⁾. The density of the former, indicated by closed circles, decreased rapidly with increasing LZ content over 20%, but that of the latter, indicated by open circles, increased on the other hand.

In the former case, the grain growth of the glass powder was observed at 800-900 °C but the densification of the composite would actually be disturbed by LZ powder in the range from 20 to 60vol% during the pressureless pre-sintering process. When the temperature went up over 900°C in the sintering process, LZ began to sinter but could not densify the composite sufficiently for shorter content of 60%. In the latter case, the crystallized glass grew up scarcely and

the sinterability of LZ powder was considered to contribute the sinterability of the composite. To obtain a high density by HIPing, the density of the pre-sintered body is needed to be more than 94% as shown in Fig. 7¹¹⁾.

As related above, the crystallized glass and the TZP for low temperature sintering must be needed as the raw materials to obtain a dense and tough BTC in this manufacturing process of the molding/pressureless pre-sintering/HIPing. Relation between TZP content and bending strength and a SEM photograph of BTC-C manufactured by this process are shown in Fig. 8 and 9, respectively¹¹⁾. Fig. 8 shows the bending strength increased with increasing TZP content in whole range, and Fig. 9 shows each crystallized glass grain was found to be surrounded by TZP grains bounded in chain.

3.4 PHASE STABILITY OF TZP IN BTC

It has been known that TZP sometimes degrades in hot water owing to the phase transformation from tetragonal to monoclinic. The phase transformation behavior of TZP in BTC-A prepared at 1100 and 1200°C was shown in Fig. 10, where the crystal grain size and the density of TZP used was 0.4 μm and 94%, respectively¹⁰⁾. The phase transformation rate of BTC-A prepared at 1200°C was much higher than that prepared at 1100°C. The authors would attempt to explain this result by a mechanical tensile stress on TZP, resulting from a thermal stress generated in the sintering process of the composite owing to the difference of thermal expansion coefficient of TZP and crystallized glass prepared at 1100 and 1200°C, which was $-0.3 \times 10^{-6} \text{deg}^{-1}$, and $1.9 \times 10^{-6} \text{deg}^{-1}$, respectively. The coefficient of crystallized glass changed because of varying quantities of precipitated α - and β -wollastonite with the temperature. A rough calculation indicated that the stress added on a TZP particle was 31-46 MPa (compressive) and 199-319 MPa (tensile) for the composite prepared at 1100 °C and 1200°C, respectively¹⁰⁾.

Fig. 11 shows the result of the similar soaking tests of BTC-A prepared at 1200 °C, using TZP of the density of 97% and the crystal grain size of 0.2, 0.3, 0.4 μm ¹⁰⁾. Fig. 10 and 11 suggest that TZP of higher density and of finer crystal grain size shows higher stability of the tetragonal phase in the composite. Therefore the phase stability of TZP in BTC-B and BTC-C would be good because of their high density of more than 98% as manufactured by means of hot-pressing or HIPing, and because of fine crystal grain size of 0.2 μm as sintered at the low temperature of 1200°C.

3.5 BIOACTIVITY OF BTC

Apatte was observed to grow thick in clusters on the surface of BTC-A containing 30 vol% TZP after soaking in simulated body fluid at 37°C for 30 days as shown in Fig.12, though it was half in quality compared with the case of the simple glass-ceramic measured by XRD⁸⁾.

4. SUMMARY

1. High strength bioactive glass-ceramic composites toughened by TZP were developed.
2. A manufacturing process of complicatedly designed artificial tissues made of the composite was devised.
3. The promotive tendency of the degradation of zirconia in the composite was analysed and was improved by controlling the phase transformation of zirconia.

Table 1 Profile of Samples

Sample No.	Raw materials		Sintering Process
	Matrix	Dispersing Particles	
A	Glass	Sintered TZP Particles	HP
B	Glass	LZ Powder	HP
C	LZ Powder	Crystallized Glass	IM/PS/HIP

notes: HP:Hot Pressing
IM:Injection Molding
PS:Pressureless Sintering
HIP:Hot Isostatic Pressing

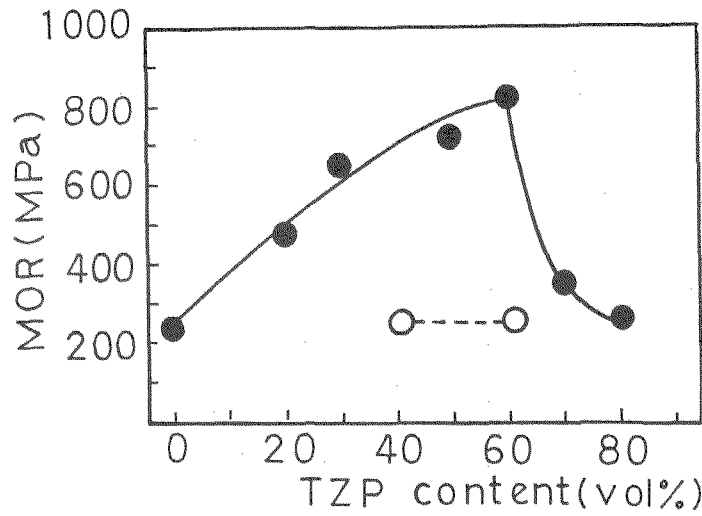


Fig.1 Relation between TZP content and bending strength of BTC-A(sintered TZP dispersed BTC:Bioactive glass-ceramic/TZP Composite)(●),and of TZ powder dispersed BTC(○).

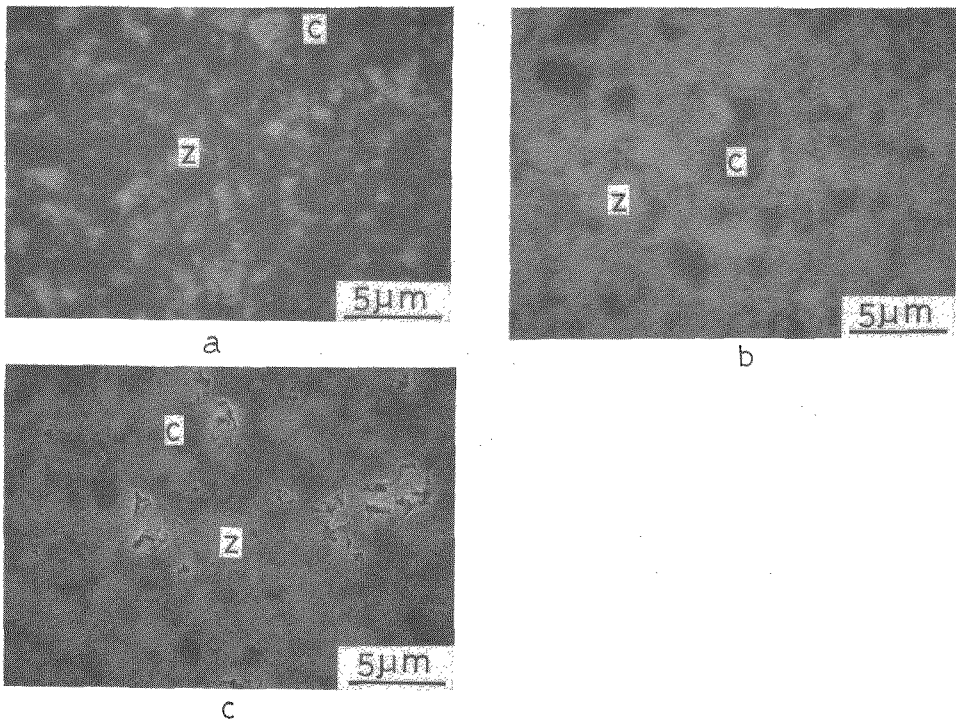


Fig.2 SEM photographs of BTC-A. TZP content is 20(a), 60(b), 70(c) vol%.

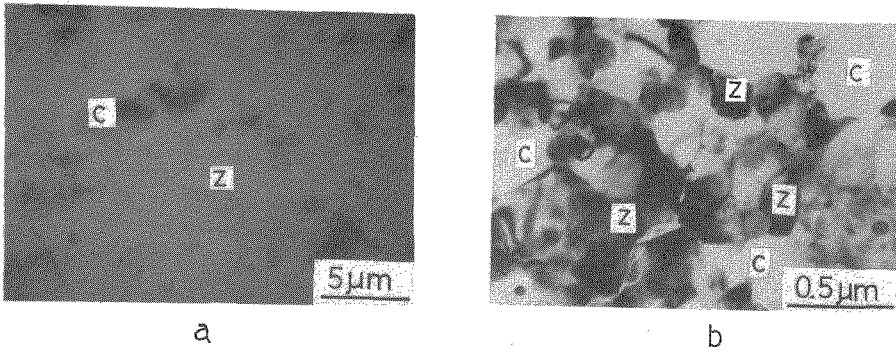


Fig.3 SEM(a) and TEM(b) photographs of BTC-B(LZ-TZP dispersed BTC).TZP content is 80 and 30 vol%,respectively.

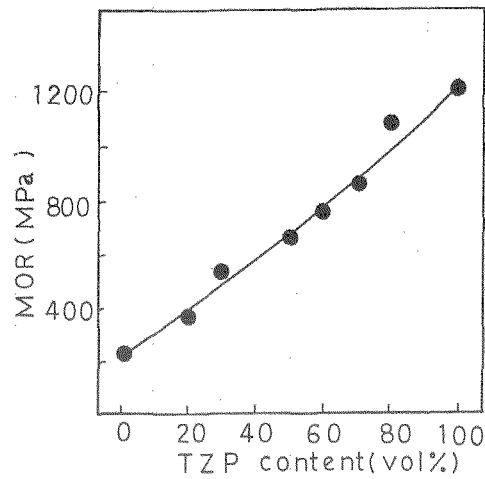


Fig.4 Relation between TZP content and bending strength of BTC-B.

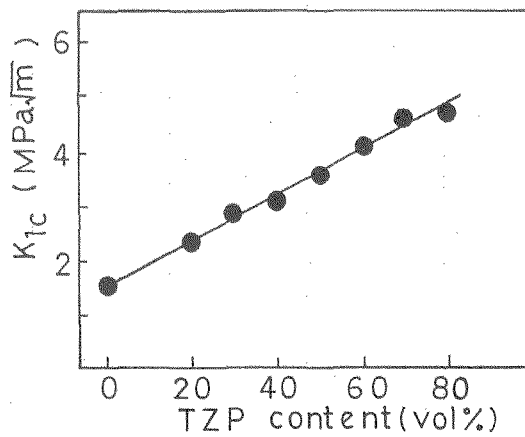


Fig.5 Relation between TZP content and fracture toughness(K_{1c}) of BTC-B.

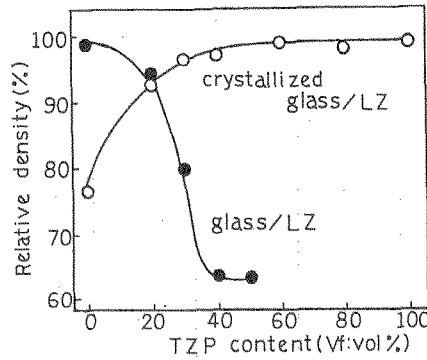


Fig.6 Relation between TZP content and density of BTC(fabricated by mixing LZ and glass(●) or crystallized glass(○) powders,molding and sintering pressurelessly).

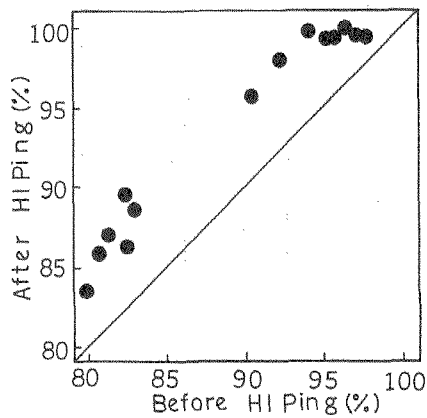


Fig.7 Effect of HIPing on densification of pre-sintered BTC.

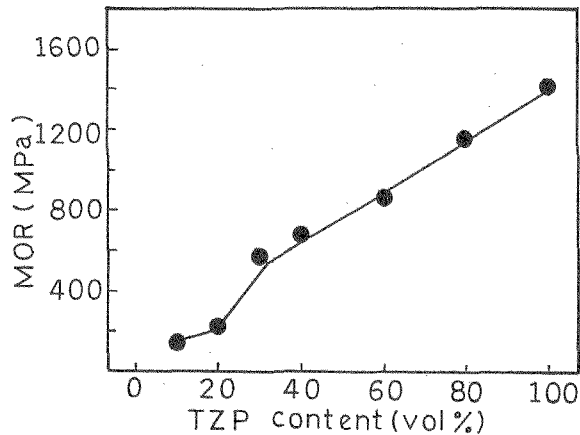


Fig.8 Relation between TZP content and bending strength of BTC-C(fabricated by mixing LZ and crystallized glass powders,molding,pre-sintering and HIPing)

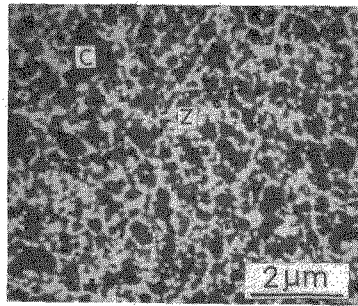


Fig.9 SEM photograph of BTC-C containing 30 vol% TZP.

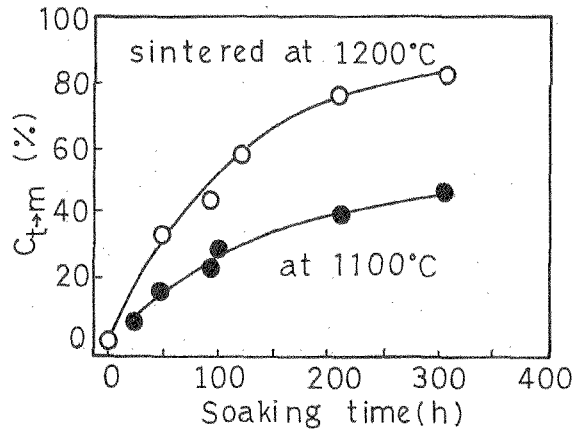


Fig.10 Phase transformation of TZP from tetragonal to monoclinic in BTC-A (hot-pressed at 1100 and 1200°C, and density of TZP is 94% and crystal grain size is 0.4 μm) after soaking in water at 90°C for 30 days.

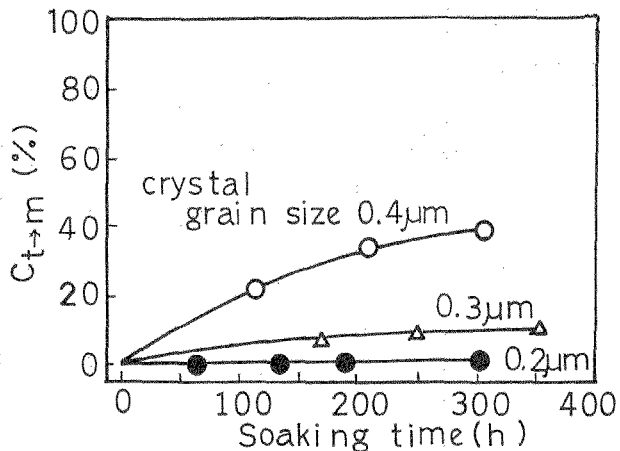


Fig.11 Phase transformation of TZP from tetragonal to monoclinic in BTC-A (density is 97% and crystal grain size is 0.2, 0.3, 0.4 μm) after soaking in water at 90°C for 30 days.

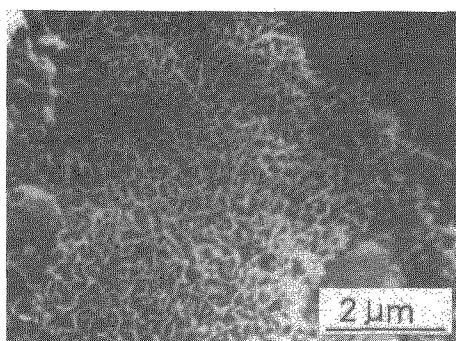


Fig.12 SEM photograph of apatite formed on the surface of BTC(containing 30vol% TZP)after soaking in simulated body fluid at 37°C for 30 days.

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