原　　著

Developmental Study of Functional Glass Ceramics

Part 1 Strength Evaluation

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ABSTRACT

An apatite-based glass ceramic, 20 wt% CaO/10 wt% P_2O_5/10 wt% MgO/10 wt% Al_2O_3/50 wt% SiO_2, was developed for a dental purpose, which had three different crystals of hydroxyapatite, β-tri-calcium phosphate and diopside within the glass matrix, Their crystals were formed by a thermal treatment at test temperature of 890° C for 2 hr. As an investment mould, the mixed compositions of ethyl silicate (a bonding agent) and silica particle (a refractory material) were also developed in order to crystallize thermally glass ceramic within the investment mould. Mechanical properties of apatite-based glass ceramic were examined by diametral tensile strength, compressive strength, bending strength, Charpy impact energy and bending fatigue fracture strength. This study showed that the formation of hydroxyapatite was important in considering their increases of mechanical strength and also the fracture mechanism would be deduced by the apperance of *eigenstrain* in the inclusion within the ceramic composite during plastic deformation.

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INTRODUCTION

Conventional feldspathic and aluminous porcelains enchanced their esthetic performance[1], and all-ceramic restoration gave more superior strengths than the lower strengths of feldspathic porcelains[2]. Generally, all-ceramic crownns was much less than that of porcelain-fused-to metal crowns[3,4]. Recently, newly-designed apatite-based glass ceramics were developed preliminarily[5–10]. Thus, it is necessary to determine mechanical properties of apatite-based $20CaO/10P_2O_5/10MgO/10Al_2O_3/50SiO_2$ glass ceramic in order to consider fracture mechanism theoretically, because ceramming and cooling treatments of dental ethyl silicate-bonded cristobalite/quartz investment and and glass ceramic are carried out within the investment mould[11]. New dental cast investments have been developed for casting of castable glass cetramics and titanium or titanium alloys[12–15]. To apply apatite-based glass ceramic to dental cast crowns or inlays, mechanical properties to have appropriately higher strengths to fracture were needed. Generally, the strengths were evaluated by diametral tensile strength, compressive strength[15–18], and thus bending strength, Charpy absorption energy and bendding fatigue strength were measured for more accurate strength evaluation of glass ceramics, especially toughness evaluation of apatite-based glass ceramic, as reported early as fracture toughness by the present authors and others[19–21]. From these recent works, mechanical strength evaluations were carried out as a developmental study of a newly-designed apatite glass ceramic developed by the present authors[5,6].

MATERIALS AND METHODS

1. Apatite-based glass ceramic

The glass ceramic used was a newly - designed apatite - based $20CaO/10P_2O_5/10MgO/10Al_2O_3/50SiO_2$ glass ceramic[5-10], which was melted within a platinum crusible by high-frequency melting method because of the melting temperature (around 1000° C)[6]. The glass pellet (cylindrical ingot; 10 gram weight) was melted and produced by Nippon Electric Glass Co (Shiga, Japan), as described latter.

2. Ethyl silicate-bonded investment

A developed dental material in this study was an ethyl silicate-bonded investment, which was composed of ethyl silicate and silica[11-17]. The basic compositions (α cristobalite/α quartz = 55/45 (wt%)) of cast investment (Nippon Electric Glass Co) were clarified by X-ray diffraction equipment; XD-D1, Shimadzu Co, Kyoto, Japan). The cristobalite and quartz had respectively 15 and 5 μm as a median particle size (SALD-2000, Shimadzu Co). The sol-gel reaction proceeded between two mixure solutions of $Si(OC_2H_5)_4$ (14.5 ml) and H_2O/NH_4OH (aqueous solution; 1.0 ml). The liquid/powder (L/P) ratio used was 0.32. The hardened (set) investment was placed in a burnout furnace heated to 910° C with a holding time of 30 min before casting (Jelenko Accu-Therm II 500, J. Morita Co, Kyoto, Japan).

3. Casting procedure

The casting was first carried out by a standard procedure (mould-fill of molten glass was achieved by pressurization with air and suction through the investment), employing glass pellet (Nippon Electric Glass Co), the casting machine (PROTOTYPE II, J. Morita Co) and ceramming furnace (PROTOTYPE I, J. Morita Co), according to each casting and ceramming schedule, as reported by Matsui[5], Wakasa et al[6] and Nomura et al[8]. As-cast samples were obtained according to each mechanical strength test. The ceramming of as-cast samples was treated by setting it to ceramming furnace (heated until 500°C and kept) after casting, and then heated to test temperature of 890°C for 2 hr.

4. Mechanical strength evaluations

Mechanical strengths measured were diametral tensile strength, compressive strength, bending strength at fracture, and also Charpy impact energy and bending fatigue fracture strength were determined. Diametral tensile test of cylindrical sample (5 mm diameter (d) and 10 mm height (t)) was carried out at a cross-head speed of 0.5 mm/min. The value was determined by $2L_d/\pi d\ t$ (L_d = load at fracture at diammetral tensile test). The compressive strength value of cylindrical sample (diameter (d) = 3 mm, and 6 mm height) was calculated by $4L_c/\pi d^2$ (L_c; load at fracture; cross-head speed of 2 mm/min). A three-point bending test of sample specimen (10 (w) × 65 × 2.5 (t) mm: span length (s) = 50 mm) was carried out at cross-head speed of 1 mm/min, and bending strength and bending elasticity were calculated by $3L_m\ s\ /(2\ w\ t^2)$ and $L_e\ s^3/(4\ w\ t^3\ \delta)$, respectively ($L_m$ = maximum load at bending test, and L_e = load at proportional limit and δ = a deflection at the proportional limit at bending test). These tests were carried out using a Tensile Testing machine (AUTOGRAPH; Shimadzu Co).

Charpy impact test was carried out using a Charpy Impact Tester (Charpy Type, Shimadzu Co), and bending fatigue strength was carried out using a Fatigue Testing Machine (EHF-FBI-10L, Shimadzu Co). Sample dimension of Charpy impact test was produced by making a U-notch (2 mm width and 2 mm depth) for bending test sample. Fatigue test sample was done by a bending test sample (stress cycle = sin wave, stress speed = 10 Hz, and stress ratio = 1 (minimum loading)/10 (maximum loading)). Absorption energy and impact value were measured according to an earlier report[23]. Also, bending fatigue strength and the times to reach fracture were measured until fracture at air. SI units were used for mechanical strength evaluations.

5. Hydroxyapatite content

To determine the hydroxyapatite content within amorphous glass, the mixtures of hydroxyapatite (hydroxyapatite standard sample; Mitsubishi Kougyou Cement Co, Tokyo, Japan) and as-cast glass developed in this study were produced. Using the calibration curve of their powder mixtures including different hydroxyapatite contents to amorphous glass (as-cast) which was measdured by X-ray diffraction analysis (XD-D1, Shimadzu Co), the content was calculated by the main peak ratio of cerammed samples.

RESULTS

Table 1 indicates diametral tensile strength of cerammed specimen samples which were treated at 890° C for 2 hr. After cooling to room temperature, the values measured ranged from 13.1 to 54.0 MPa. Table 2 and 3 indicate compression strength and bending strength of cerammed (treated at 890° C for 2 hr) samples for compression test and bending test, respectively. The compressive strength values ranged from 782.0 to 1111.7 MPa. The bending strength had a range of 62.7 to 124.5 MPa, showing that bending elasticity ranged from 8.25 to 9.58 GPa.

Table 4 and 5 indicate Charpy impact test and bending fatigue tests of cerammed samples (treated at 890° C for 2 hr), respectively. The impact absorption energy had a value of 0.60 to 0.75 kg • m, and the impact value 0.75 to 0.94 kg • m/cm^2. The bending fatigue strength ranged from 68.6 to 88.2 MPa, and the times to fatigue fracture ranged from 5.62×10^3 to above 4×10^6.

Figure 1 shows stress/strain curves of diametral tensile strength (σ_D), compressive strength (σ_C) and bending strength (σ_B) of cerammed glass ceramic (890° C × 2 hr), showing that a linear strength increase was found for each curve. Figures 2 and 3 show standard peaks of hydroxyapatite and the calibration of hydroxyapatite

Table 1 Diametral tensile strength of cerammed specimen samples which were treated at 890° C for 2 hr. See text for sample dimension.

Sample	Diametral tensile strength (MPa)
1	54.0
2	42.5
3	13.1
4	25.7
5	52.3

Table 2 Compressive strength of cerammed (890° C for 2 hr) samples for compression test samples.

Sample	Compressive strength (MPa)
1	784.9
2	782.0
3	1069.2
4	1111.7
5	934.9

Table 3 Bending strength and bending elasticity at bending test (890° C for 2 hr).

Sample	Bending strength (MPa)	Bending elasticity (GPa)
1	124.3	8.87
2	124.5	8.41
3	90.2	8.48
4	62.7	9.58
5	83.3	8.25

Table 4 Charpy impact test of cerammed samples (890° C for 2 hr). The impact absorption energy and impact value were calculated.

Sample	Absorption energy (kg • m)	Impact value (kg • m/cm^2)
1	0.75	0.94
2	0.64	0.80
3	0.64	0.80
4	0.75	0.94
5	0.75	0.94
6	0.64	0.80
7	0.60	0.75
8	0.64	0.80
9	0.66	0.83
10	0.60	0.75

Table 5 Bending fatigue strength and the times to fatigue fracture at bending fatigue test of cerammed samples (890° C for 2 hr).

Sample	Stress (MPa) Max	Min	Times to fracture
1	68.6	6.9	2.26×10^5
2	68.6	6.9	3.03×10^4
3	68.6	6.9	$>4.0 \times 10^6$
4	71.5	7.2	3.04×10^6
5	71.5	7.2	$>4.0 \times 10^6$
6	75.5	7.6	5.62×10^3
7	75.5	7.6	3.35×10^6
8	75.5	7.6	3.39×10^5
9	78.4	7.8	7.91×10^5
10	88.2	8.8	8.03×10^3
11	88.2	8.8	1.17×10^4
12	83.3	8.3	$>4.0 \times 10^6$
13	86.2	8.6	$>2.5 \times 10^6$

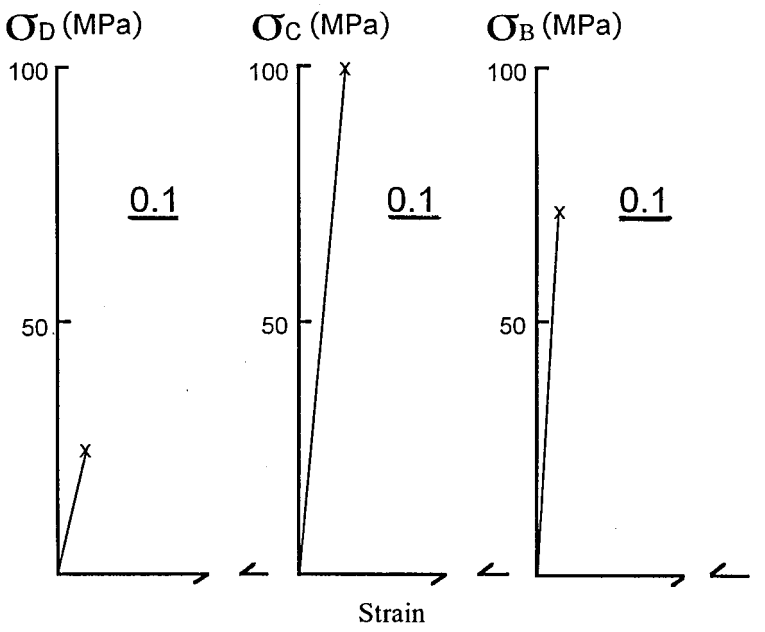
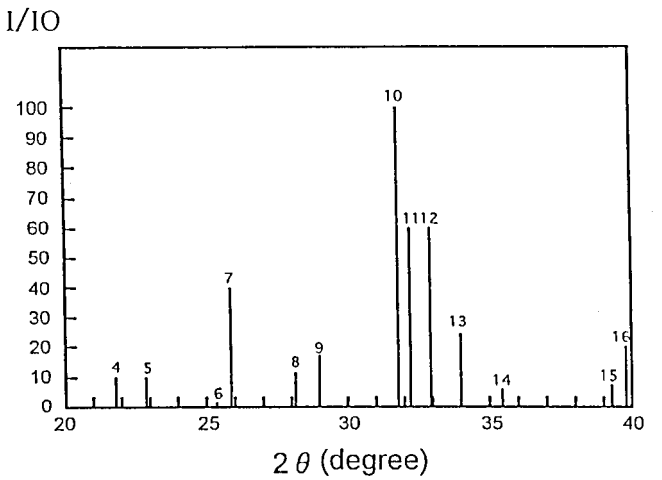


Figure 1 Stress/strain curves of diametral tensile strength, compressive strength and bending tests of cerammed glass ceramic (890°C × 2 hr). See text for key.



No	2θ	d	I/I0
4	21.82	4.07	10
5	22.90	3.88	10
6	25.35	3.51	2
7	25.88	3.44	40
8	28.13	3.17	12
9	28.96	3.08	18
10	31.77	2.81	100
11	32.19	2.78	60
12	32.90	2.72	60
13	34.05	2.63	25
14	35.48	2.53	6
15	39.20	2.30	8
16	39.82	2.26	20

Figures 2 Standard peaks of hydroxyapatite by means of X-ray diffraction patterns.

within of cerammed samples (890°C for 2 hr). The hydroxyapatite content within amorphous glass was calculated by the main peak ratio of cerammed samples, and the content was 7.5 wt%.

DISCUSSION

The dental cast investments for titanium and castable glass ceramics have been developed because of the simple procedures involved, and it is still developed for the construction of high fusing base metal alloys and castable glass ceramics[12-17]. These types of investment are

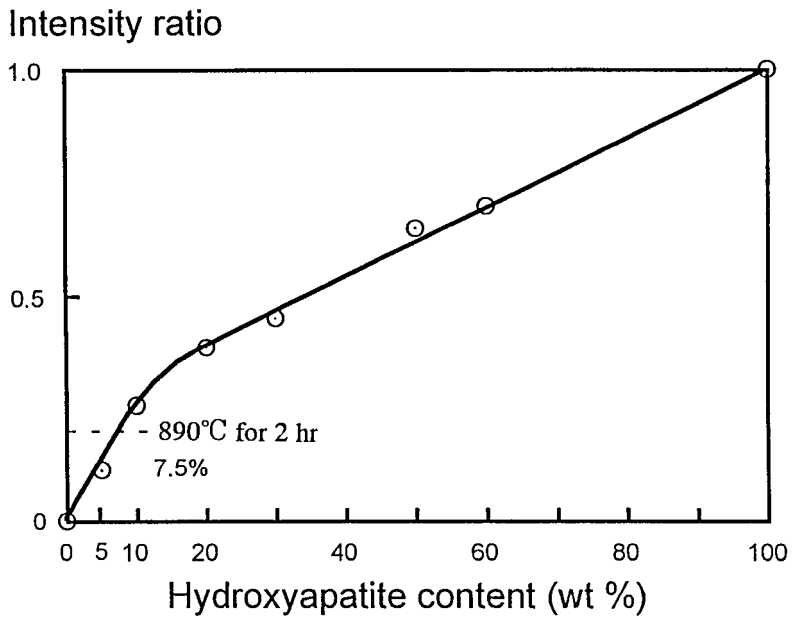


Figure 3 The calibration curve to determine the hydroxypatite content within amorphous glass (as-cast) matrix, using the main peak ratio of cerammed samples.

ethyl silicate-bonded investment (α cristobalite and α quartz)[15-17], MgO-included investment[12-14] and ethyl silicate-bonded investment including MgO and phosphate-bonded investment with fairly more porosity within the investment mould[12-14]. In this study, ethyl silicate-bonded investment was composed of mixture solution (ethyl silicate) and a catalyst (ammonium carbonate), and thus a colloidal sol of polysilicic acid was produced as a binder. As a standard casting procedure, the investment mould including as-cast glass sample after casting was placed in the furnace, according to ceramming schedule, immediately after setting, because the dimensional change of glass ceramics was affected by cast shrinkage of castable glass ceramics[24, 25]. That is, the thermal changes of investment and glass ceramic occurred within the mould, and the cast glass crown has lower thermal change than did the cast glass inlay. This type investment was designed to make silica gel around the silica particles to apply to casting of the higher fusing metal alloys, as reported by Wakasa and Yamaki[12]. In the ceramic crown, the total expansion compensated the shrinkage value of glass ceramic.

A ceramming of apatite-based glass ceramic was carried out within the investment mould after casting, according to temperature schedule, as reported early[6]. The as-cast samples were kept within the mould, and heated to 500° C and heated to 890° C for 2 hr, because glass ceramic had different crystallized structures, hydroxyapatite, diopside and β-tricalcium phosphate[6, 7, 9, 10]. The compressive strength of enamel and dentine had,respectively, 38.4 and 29.7 MPa, and the bending strength 9.8 (enamel) and 50.0 MPa (dentine)[26]. Compared with these results, this study showed that greater strength values of the apatite-based glass ceramic (ceramic composite) were obtained associated with the crystals within amorphous glass matrix during ceramming treatment. Thus, Eshelby's inclusion problem was applied in this study[27-29]. That is, the hydroxyapatite as an inclusion within amorphous glass matrix was important to consider mechanical strengths, as indicated in Figure 4. The crack will form around spherical hydroxyapatite, similar to the analogous to the crack formation around silica filler within the resin matrix[28]. According to the equation, proposed by Yoshida et al, the critical crack length, $2a_c$, was determined to be about 0.06 μm around the inclusion as follows.

$$(a_c)^{1/2}\,\varepsilon_P = (3/2)\{\pi(1-\nu)/2(1+\nu)\}^{1/2} \cdot (\Gamma/E)^{1/2}$$

where ε_P = strain at fracture, ν = Poisson ratio (0.3), Γ =

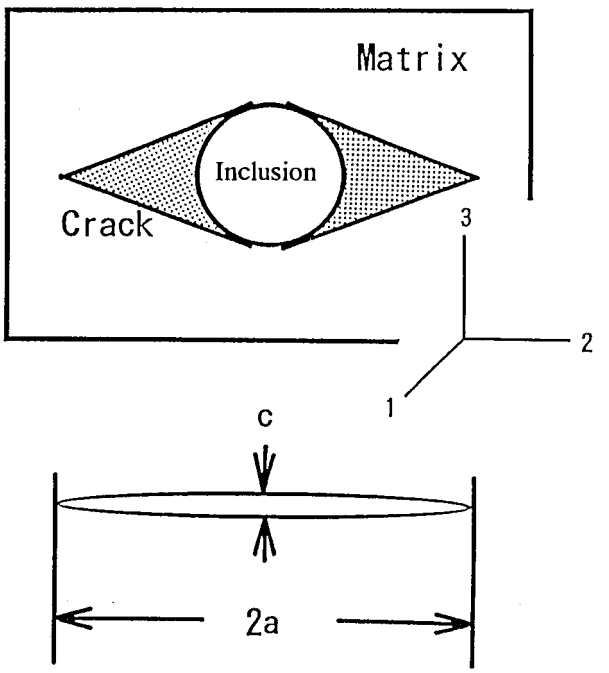


Figure 4 Fracture mechanism around the inclusion as an inclusion. The crack length can be estimated according to the equation proposed by Yoshida et al[29].

surface energy (380×10^{-3} J/m^2)[30], and E = elastic modulus of matrix of ceramic composite (10 GPa)[30].

This distribution of the inclusion is important in evaluating compressive strength (Table 2), because the crack occurred around the inclusion (Fig 4). The scattering of the compressive strength will be dependent upon the difference of the propagation of the cracks (rapid or slow) around the glass matrix after the nucleation of cracks. In modeling the mechanical strengths of the ceramic composite, this study predicted the fracture mechanism which was considered as the apperance of inhomogeneous strain between glass matrix and the inclusion (hydroxyapatite crystal). This corresponded to *eigenstrain* within the inclusion after plastic deformation[27,28]. The crack occurred only around the inclusion and propagated within the ceramic composite, and thus led to a fracture after yielding. This ceramic composite exhibited a fracture after a linear increase of mechanical strengths at each mechanical tests used in this study. Thus, this study suggests that it is necessary to reduce the crack propagation after the formation of crack around the hydroxyapatite crystal in the strengthened matrix of newly-designed ceramic composite.

SUMMARY

Dental apatite-based glass ceramic, $20CaO/10\ P_2O_5/10MgO/10Al_2O_3/50SiO_2$ with three different crystals (hydroxyapatite, β-tri-calcium phosphate and diopside within the glass matrix) was developed in this study. These crystals were formed by a thermal treatment at test temperature of 890° C within the investment mould, whose compositions were ethyl silicate (a bonding agent) and silica particle (a refractory material). Mechanical strengths of apatite-based glass ceramic were examined by diametral tensile strength, compressive strength, bending strength, and especially, Charpy impact energy and bending fatigue fracture strength. This study showed that the formation of hydroxyapatite was important in evaluating their increases of mechanical strength, suggesting that the fracture mechanism would be considered by *eigenstrain* in the inclusion within amorphous glass matrix during plastic deformation.

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