

Cristobalite-quartz Investment for Apatite-based Glass Ceramic

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ABSTRACT

Apatite ceramic was cast within cristobalite-quartz investment mould which was mixed by the mixture of silica sol and aqueous ammonium carbonate. Immediately after hardening of the investment mould (22.4 min), a steel ring of the mould was set to burn-out furnace kept at 910°C for 30 min. For crystallization after casting, as-cast glass ceramic within the mould was treated for 2 hr at each selected temperature (800, 890 and 980°C), using the samples which were cooled to room temperature and then kept at 500°C for 2 hr. Thermal treatment at 890 (apatite and diopside) and 980°C (apatite and beta tricalcium phosphate) exhibited larger compression and diametral tensile strength values than those of as-cast sample. Little adhering layer was found based on EPMA observation of the interface between glass ceramic and investment mould.

INTRODUCTION

Apatite-based glass ceramic is cast into the investment mould using a lost wax process^{1,2}. Dental investments were improved by adding glycerol to the mixing liquid to investment powder composing of silica, magnesia and phosphate powders^{3,4}, and adding nitride compound to the investment powder⁵. The adhering layer at the interface of casting alloy, or glass ceramic and investment was affected by phosphate and gypsum as a bonding agent

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in the investment⁶⁻⁸. The cristobalite-quartz investment mould was clarified by thermal analysis⁹, because the mixed investment set with an exotherm in adding silica sol to it. Setting behaviour was measured after it was mixed with the mixture, because the expansion behaviour was exothermic associated with the temperature increase⁹⁻¹¹.

Mechanical strength of as-cast and thermally-treated glass ceramic samples which were cast into the mixed mould with hydrolyzed silica sol liquid was investigated. The reaction of silica sol and exothermic heat of the investment were also examined in relation to sol-gel reaction.

MATERIALS AND METHODS

The mould including alpha cristobalite (particle median size; 15 micron, 55 wt%) and alpha quartz powders (5 micron, 45 wt%) was mixed by each mixture (silica powders; Tatsumori Co, Tokyo). The mixture M contained aqueous ammonium carbonate (AC, Katayama Yakuhin Co, Tokyo; 1 mL) and sol E (100% hydrolyzed sol; 16 mL), and was used at a liquid (mixture)-to-powder ratio (0.34) (pH-adjusted one (E; pH=3.5) and commercial ones (H1 (HAS-1); pH=1.1 and H2 (HAS-6); pH=1.2, Colcoat Co, Tokyo). Similarly, the mixtures M1 (AC+H1) and M2 (AC+H2) were used to it. The investment mould was set to a burn-out furnace heated to 910°C, and kept for 30 min immediately after setting to make setting expansion 0% (total expansion of the mould was considered only thermal expansion when heated to 910°C; 2.1%)⁹. Apatite ceramic tested was experimental $20\text{CaO}-10\text{P}_2\text{O}_5-10\text{MgO}-10\text{Al}_2\text{O}_3-50\text{SiO}_2$, which contained a very small of B_2O_3 and CaF_2 ¹². The ceramic was cast into the mould, using vacuum-pressure casting machine (PROTOTYPE II, J. Morita Co, Tokyo).

DTA (differential thermal analysis) and TG (thermogravimetry) analyses exhibited thermal properties of heat for

gasification and combustion of each solution (DT-50, Shimadzu Co, Kyoto). The calibration was done using indium which has heat for fusion 24.4 J/g at melting temperature of 156.4°C. DSC (differential scanning calorimetry) property was measured for IE (silica sol used was E), CONT1 (H1) and CONT2 (H2) investments mixed by each mixing liquid (initial setting time (I), peak time (P), final setting time (F), heat (H)). P is the time from the beginning of mixing until a peak¹³, and F is the time from the start of mixing until DSC base line reached to the horizontal one after P from I. H is represented by heat for setting between I and F. All experiments were held at a constant temperature (20°C) (N₂ gas flow) after setting the investment sample to the pan in DSC. H value was calibrated using gallium (heat for fusion; 82.3 J/g, melting temperature; 29.9°C) for the mixed powder.

Thermal treatment (crystallization) of as-cast sample (1.5×10×20 mm) was done by keeping them at 800, 890, and 980°C for 2 hr, and apatite glass ceramic was analyzed by X-ray diffraction pattern (XD-D1, Shimadzu Co, Kyoto).

The interface between investment and glass ceramic was observed by EPMA analysis (Electron probe microanalyzer; EPMA-8705, Shimadzu Co, Kyoto).

The strength values of compression (C) and diametral tensile (D) were measured for as-cast and glass ceramic cylinder (6×12 mm) (sample size=10).

RESULTS

Fig. 1(a) and (b) (DTA and TG; heated to 800°C) show the thermal change of each solution, representing that TG had the decrease near 100°C and DTA had an exothermic heat with increasing test temperature after the endotherm for each E and AC (a), and M (b). The pH value of the mixture solution was adjusted in the range of 8.0 to 8.5 to initiate sol-gel formation.

Fig. 2 shows the exothermic heat and time curves for IE, CONT1 and CONT2 investments. The curves indicated that P was observed after the time when the exotherm started to occur (initial setting time). Table 1 indicates that heat value of silica sol liquid was low and had largest for AC solution to activate sol-gel reaction. Table 2 indicated P, F, and H from DSC curves in Fig. 2. P ranged 9.5 to 12.1 min, and F ranged 19.0 to 25.5 min.

Fig. 3 shows EPMA observation of glass ceramic sample attaching the investment powders, representing that little adhering layer was observed. The sample including

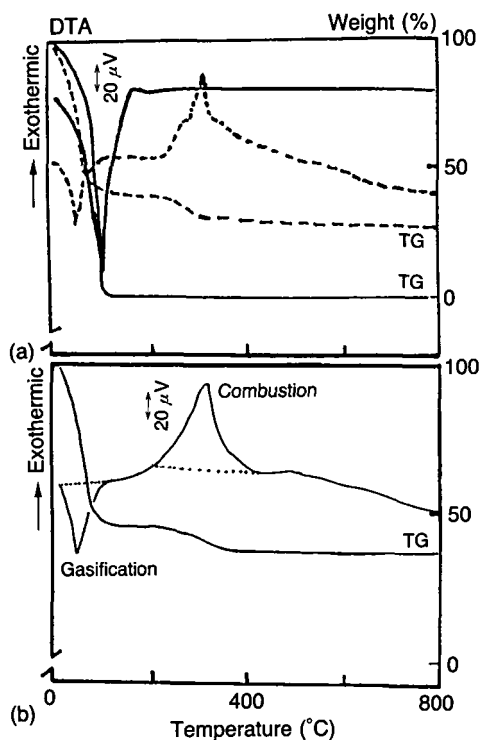


Fig. 1 Examples; DTA and TG curves of silica sol liquid E (.....), solution AC (—) (a), and the mixture (b).

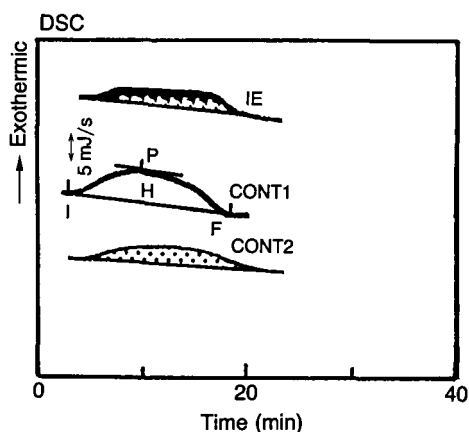


Fig. 2 Setting DSC curves of cristobalite-quartz investments (IE, CONT1 and CONT2) at isothermal temperature (20°C).

investment powders was mounted by self-curing resin. Mg, Si, Ca and P line analyses showed the finding of each metal element of the glass ceramic samples, and also Si distribution was observed at the attached investment

Table 1 DTA properties of gasification and combustion in silica sol liquid E, solution AC and the mixture M, and H1 and H2 (silica sol). Abbreviations as in text.

Reaction	Heat (KJ/g)				
	E	AC	M	H1	H2
Gasification	0.4 (0.1)	3.5 (0.2)	0.9 (0.1)	0.5 (0.1)	0.8 (0.0)
Combustion	0.4 (0.0)	—	0.4 (0.1)	0.7 (0.1)	0.5 (0.1)

Numbers in parentheses are standard deviation.

Table 2 Setting properties of peak time (P), final setting time (F) and heat for setting (H) for IE, CONT1 and CONT2 investments.

Investments	Results		
	P (min)	F (min)	H (J/g)
IE	12.1 (0.4)	22.4 (0.1)	59.0 (7.8)
CONT1	9.5 (0.2)	19.0 (0.1)	84.9 (7.2)
CONT2	11.2 (1.7)	25.5 (0.1)	78.5 (12.9)

Numbers in parentheses are standard deviation.

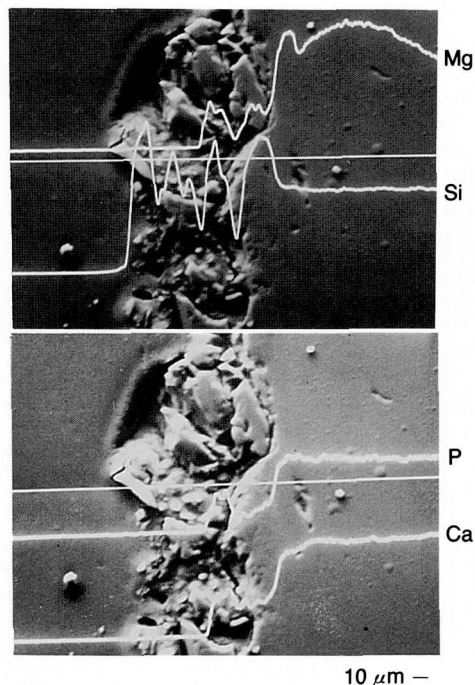


Fig. 3 EPMA observation; the interface between glass ceramic (thermally treated at 890°C) and investment mould. Analyzed line (—).

powders from Si line analysis curve. The powders at the interfaces were removed easily using ultrasonic cleanser.

Figs. 4 and 5 show X-ray diffraction patterns of the samples, representing that amorphous sample was observed for as-cast and 800°C-treated (amorphous) ones and crystal structures of apatite (Ap), diopside (Ds) and beta-tricalcium phosphate (β -TCP) for 890 and 980°C-treated ones ((a); as-cast and (b) 800°C; Fig. 4, and (a) 890°C and (b) 980°C; Fig. 5).

Table 3 indicates that C (890°C; 96.9, 980°C; 95.5 MPa) and D (890°C; 30.0, 980°C; 27.8 MPa) were larger

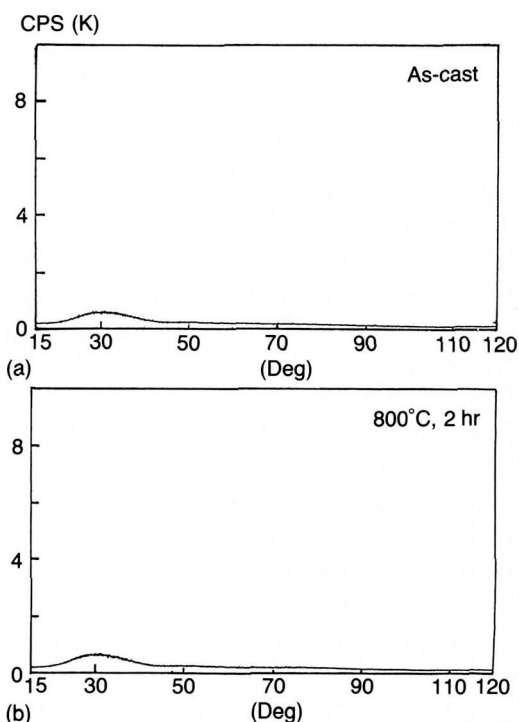


Fig. 4 X-ray diffraction patterns; (a) As-cast, and (b) 800°C for 2 hr.

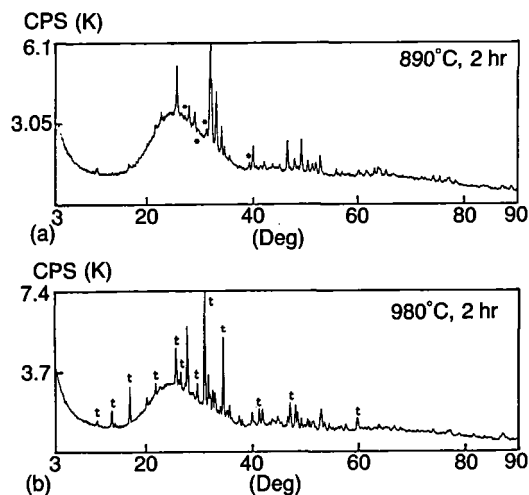


Fig. 5 X-ray diffraction patterns; (a) 890°C and (b) 980°C for 2 hr. The Ap (apatite) peak occurred at 890°C, except for the portion of the diopside peak (*) and that of the β -TCP peak (t).

Table 3 Compressive strength (C) and diametral tensile strength (D) of as-cast and glass ceramic samples.

Samples	Results	
	C (MPa)	D (MPa)
As-cast	90.9 (10.2)	26.5 (2.5)
800°C	90.2 (9.4)	23.5 (4.7)
890°C	96.9 (15.4)	30.0 (3.9)
980°C	95.5 (7.3)	27.8 (3.5)

Numbers in parentheses are standard deviation.

than those of as-cast sample (C; 90.9, D; 26.5 MPa).

DISCUSSION

Since new apatite-based glass ceramic has been developed¹²⁾, the mixed investment mould was used in this study. The investment hardened when it was mixed by the mixture of sol and aqueous ammonium carbonate (Fig. 2), because sol-gel reaction associated with the setting of the investment. The reaction occurred when pH value changed to 8.0–8.5. The initial pH value of sol was necessary to be about 1.0–3.0 before a catalyst was added to silica sol. Thus, the cristobalite-quartz investment was applied to castable apatite-based glass ceramics. As the developed apatite glass ceramic has the melting temperature (near 1160°C)¹²⁾, it is needed that adhering layer form little on the cast surface (Fig. 3). Simple

composition of the investment without magnesia and phosphate compound exhibited exothermic heat and setting in mixing the investment powder by sol-aqueous ammonium carbonate mixture. The investment powders after casting and thermal treatment were easily removed by ultrasonic cleanser within distilled water, exhibiting that little chemical reaction between investment powders and glass ceramic formed. C was in the range of the values obtained by the cylinder test sample which approximated a large porcelain veneer crown (ceramic and metaloceramic systems; 36.2 to 101.9 MPa; tensile fracture stress)^{14,15)}. The formation of crystals (Ap, Ds and β -TCP) was important with the increase of C and D values as compared with as-cast and 800°C-treated ceramic samples. No significant difference between Ap and Ds (890°C) and Ap and β -TCP (980°C) ($p > 0.05$) was found.

SUMMARY

It is concluded that cristobalite-quartz investments for dental ceramics have setting behaviour, because heat change occurred by setting between initial and final setting times of the investments. The results suggest that the investments mixed with the mixture of 100% hydrolyzed sol and AC solution are applied to casting of apatite ceramic.

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