

Design of Ethyl Silicate-bonded Investments for Dental Apatite-based Glass Ceramic

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ABSTRACT

Setting time and setting expansion were examined for dental ethyl silicate-bonded investment mould to cast a newly-developed apatite-based glass ceramic. The setting characteristics were important parameters to cast a glass ceramic crown by vacuum-pressurized-casting machine. The refractory fillers (investment powders) investigated were alpha cristobalite and alpha quartz, and the mixing solutions for the fillers were tested whether the hardening (setting) of the investments occurred. The results show that the hydrochloric acid mixture including ethylsilicate, ethanol and water exhibits about 10 min as a setting time of investment. The mixture (silica sol and hexahydropyridine) reported previously as ethylsilicate-amine method was not available, because setting time of investment was more than 60 min or the investment was not hardened. Using the hydrolyzed ethylsilicate in this study the ethyl silicate-bonded investment mould was applied for the casting of glass ceramic.

INTRODUCTION

Dental cast glass ceramics and nickel-based alloys have been developed as high fusing materials. The materials needed cast investment moulds for the high fusing casting in dental field. Dental investments have been improved by adding glycerol to the mixing liquid to investment powder including silica, magnesia and phosphate powders^{1,2)} and adding nitride compound to the investment

powder³⁾. The adhering oxides were related to chemical reaction of phosphate, or gypsum as a bonding agent and metal elements in nickel-based alloys⁴⁻⁶⁾. The investment mould with no phosphate, or gypsum is needed to cast apatite-based $20\text{CaO}/10\text{P}_2\text{O}_5/10\text{MgO}/10\text{Al}_2\text{O}_3/50\text{SiO}_2$ glass ceramic used in this study.

In experimental investment powder and the mixing solution the setting behaviour was measured by means of travelling microscope, because the mixed investments exhibited the setting reaction as setting time and expansion in adding the mixing solution to investment powder⁷⁾. And also the set investment expanded during heating to higher temperature (thermal expansion). As the expansion behaviour was exothermic⁷⁻⁹⁾, setting characteristics were measured after the powder was mixed by water or silica sol in gypsum-bonded or ethyl silicate-bonded investment.

Thus, the purpose of this report is to examine setting behaviour of ethyl silicate-bonded investment mixed with silica sol accelerated by a catalyst, such as aqueous ammonium carbonate or aqueous ammonia, and to use as an investment mould for casting dental ceramics.

MATERIALS AND METHODS

Tables 1 and 2 indicate the mixing solution for investment powders. The investment powders (alpha cristobalite; 55 wt% (15 μm ; median size) and alpha quartz powders; 45 wt% (5 μm)) were mixed by the hydrolyzed silica

Table 1 Mixing solution for investment powders (ethylsilicate-amine method). See text for key.

Solution	Composition
L1	98% ethylsilicate 40/2% piperidine 95% ethylsilicate 40/5% piperidine
L2	0, 25, 50 and 70% aqueous ethanol

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Table 2 Mixing solution for investment powders used in this study. See text for key.

Solution	Composition
EXP1	50% ethylsilicate 40/44% ethanol/5% water/1% 1-N HCl
EXP2	45% ethylsilicate 40/50% ethanol/4% water/1% 1-N HCl
CONT	pH-adjusted silica sol

sol liquid.

According to ethylsilicate-amine method described by Nomoto^{10,11)} and Nakano¹²⁾, L1 and L2 mixtures were tested to measure setting time (Table 1). Originally, 98% ethylsilicate 40/2% piperidine (amine) was used as a L1, and 50% aqueous ethanol as L2. A L1-to-L2 ratio used was 10/1 to 10/5. The investment powders tested were No. 5, 7 and 8 mixed silica flours. In this study L1-to-L2 ratio used was 10/1, 10/3, 10/5 and 10/10 (Table 1) and four types of L2 solutions tested were distilled water (0% ethanol), 25, 50 and 70% ethanol for L1 liquid containing 2% piperidine as an amine (hexahydropyridine, $\text{NH}(\text{CH}_2)_4\text{CH}_2$, Kishida Chem Co, Osaka). And also L1 liquid containing 5% piperidine was used for 50 and 70% ethanol (L2). The liquid-to-powder ratio was 0.50. The detail was indicated in Table 1.

In Table 2 the mixing solution used in this study was indicated. EXP1 and EXP2 have pH=1.1 and 1.2 respectively. Ethylsilicate 40 included in EXP1 and EXP2 liquid was supplied by Colcoat Co (Tokyo). The mixture which 10% aqueous ammonium carbonate (1 mL) was added to the silica sol (16, 14.5, 13 mL) was used as the liquid to mix the powder (50 gram) at a ratio of the liquid to powder (0.34, 0.31, 0.28). Hydrolyzed silica sol which was supplied by Nippon Electric Glass Co (Shiga) was used as CONT (14.5 mL as a standard fraction, pH=3.5). The accelerator was aqueous ammonia (1 mL, pH=9.4). The mixture had 8.8 as a pH value.

Setting time was measured using a Vicat needle similar to previous method¹³⁾. Setting expansion was conventionally measured by travelling microscope (Seiki Shya, Tokyo). The test sample was $10 \times 10 \times 100$ mm, whose size was made by paraffine wax (GC Co, Tokyo).

The interface between investment mould and as-cast glass ceramics developed by us¹⁴⁾ was observed by electron probe microanalyzer (EPMA; Shimadzu EPMA-8705, Kyoto). Dental casting was done using PROTOTYPE I vacuum-pressurized-casting machine (J. Morita Co,

Kyoto). Apatite-based glass ceramic $20\text{CaO}/10\text{P}_2\text{O}_5/10\text{MgO}/10\text{Al}_2\text{O}_3/50\text{SiO}_2$ (mass fraction; very small amounts of additives B_2O_3 and CaF_2 were added) was used.

RESULTS

Table 3 indicates setting when the mixture in Table 1 was applied to investment powders. The results were evaluated whether or not the investment was hardened when the hydrolyzed mixture was used after 1 day after mixing and hydrolyzing. Table 4 indicates the value of setting time when the investment powders were mixed by each mixture in Table 2.

Table 3 Setting (ethylsilicate-amine method). The symbols as n and s indicate respectively not-set and set investments.

L2	Setting L1/L2		
	10/1	10/3	10/5
0/100	n	n	n
25/75	n	n	s
50/50	s	s	s
70/30	n	n	s

L1; 98% ethylsilicate 40/2% piperidine
L2; ethanol/water

Table 4 Setting time (ethylsilicate-amine method).

L2	Setting time (min) L1/L2	
	10/5	10/10
50/50	104 (5)	n
70/30	72 (4)	100 (5)

Setting time value was indicated in Table 5 (newly designed mixing solution indicated in Table 2). Negative setting expansion was not appropriate as an investment mould, and thus the mould was placed to the burn-out furnace (910°C for 30 min) to obtain 0% setting expansion after setting (hardening), as reported by Wakasa et al^{15,16)}. Typical examples of setting expansion behaviour were shown in Fig. 1 when CONT mixing solution was used at each liquid-to-powder ratio. The others IEXP1 and IEXP2 showed the same setting as ICONT. Setting was not recorded for the investments when the mixing solution indicated in Table 1 was used (ethylsilicate-amine

Table 5 Setting time when silica sol/aqueous ammonium carbonate or aqueous ammonia was used. IEXP1 and IEXP2 were respectively mixed by EXP1 and EXP2, and ICONT by CONT solution.

Investment	Setting time (min) L/P		
	0.28	0.31	0.34
IEXP1	7.8 (0.2)	8.0 (0.3)	8.9 (0.5)
IEXP2	3.2 (0.4)	3.4 (0.2)	5.2 (0.7)
ICONT	7.5 (1.0)	10.0 (0.5)	10.2 (0.5)

L/P; Liquid/Powder ratio

method), because the setting of investment was very slow.

Fig. 2 shows EPMA observation of the interface of investment and as-cast glass ceramics, representing that the adhering oxide was not observed. The mixing solution was EXP1. The other EXP2 and CONT exhibited the same aspects as EXP1. The interface was observed after the powders were removed by ultrasonic cleansing. The interface sample was mounted using unfilled resin.

DISCUSSION

This study was summarized as follows; (1) Ethylsilicate-amine method reported previously was not useful for ethyl silicate-bonded investment, because amine was very slow

for gelation in sol-gel reaction (Tables 3 and 4), and (2) using silica sol mixture in this study, castable glass ceramic was cast into its investment mould (Fig. 2).

Mould interface observation showed that line analysis indicated that Mg, Ca and P elements in glass side distributed homogeneously there, and Si due to silica powder was found to distribute heavily in investment side. The investment powders (cristobalite and quartz) were easily removed by ultrasonic cleansing in water for 3 min¹⁷⁾.

The use of each silica sol was effective to apply to the investment mould (Fig. 2 and Table 5). Each investment powder mixed by 100% hydrolyzed silica sol set when aqueous ammonium carbonate was added to it^{14,15)}. On the contrary, ethylsilicate-amine method exhibited no quick sol-gel reaction (Tables 3, 4). As examined already¹¹⁾, the mixture of ethylsilicate/HCl/water or aqueous ammonia was needed to form silica gel.

In this study the HCl mixtures including ethylsilicate and water was utilized by adding an accelerator (aqueous ammonium carbonate) to it. Similar to aqueous ammonia as an accelerator to CONT mixture¹⁵⁾, its pH was around 9.0. After adding it to silica sol, pH value was about 8.0 and the sol-gel reaction started associated with setting (hardening) of investment powder. And also, the addition of water in HCl mixture exhibited longer period to use hydrolyzed silica sol. The expansion of mixed investment by the

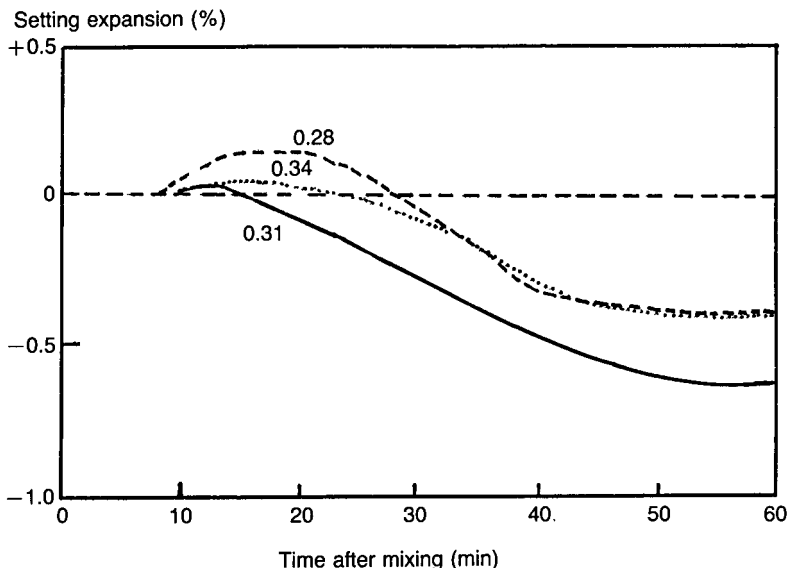


Fig. 1 Typical examples; setting expansion behaviour of investments ICONT when CONT mixing solution was used (see Table 2 for key). L/P=0.28, 0.31, 0.34.

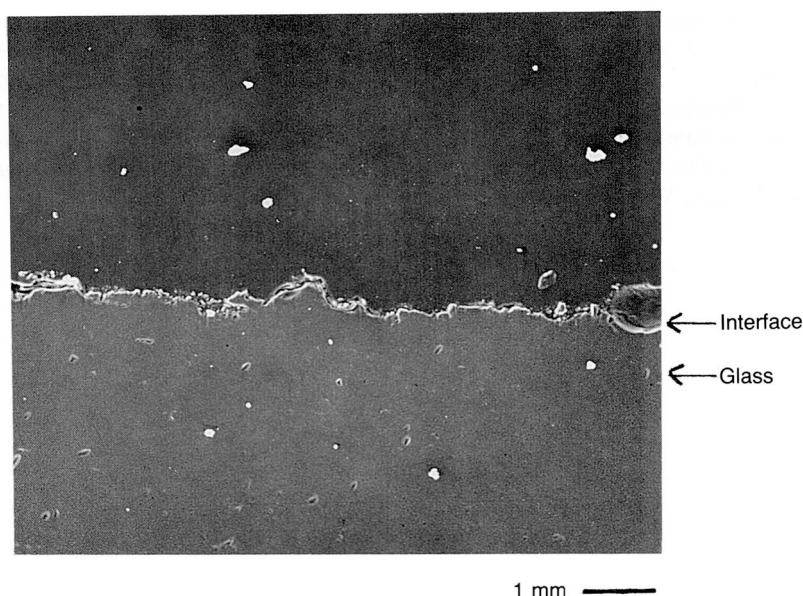


Fig. 2 Typical example; EPMA observation of the interface between mould and glass ceramic (as-cast). The mixing solution was EXP1 (Table 2).

mixture in Table 2 was enough to apply it to dental cast glass ceramic as indicated in Fig. 1.

SUMMARY

It was concluded that ethyl silicate-bonded investment mixed by HCl mixture and ammonium carbonate solution for dental ceramics had setting behaviours, because setting time was about 10 min and setting expansion was controlled by its concentration of silica sol. The results suggest that ethyl silicate-bonded investments due to 100% hydrolyzed silica sol in this study (Table 2) are applied as dental cast moulds.

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