原　　　著

# Dental Use of Hydrolyzed Solution in Cast Ethyl Silicate-bonded Investment

Kunio Wakasa, Yasuhiro Yoshida*, Atsuharu Ikeda and Masao Yamaki

(Received for publication, October 3, 1994)

## ABSTRACT

This study was to apply hydrolyzed solution to cast ethyl silicate-bonded investment for high fusing materials, such as nickel-based alloys and castable glass ceramics. The mixing solution was made by hydrochloric acid (HCl) mixtures containing ethyl silicate, ethanol and distilled water, and it was conserved for 2, 4, 6 hours, and 1 and 3 days at 20°C before adding aqueous ammonium carbonate (AC) to it. With the use of the hydrolyzed solution the investment powders containing alpha cristobalite (50 wt%) and alpha quartz (50 wt%) were mixed. It hardened under each storage condition, and the heat for setting (hardening) was measured using differential scanning calorimetry (DSC). Their analytical results show that experimentally mixed investments are used as an mould of high fusing materials.

## INTRODUCTION

Nickel-based cast alloys and castable glass ceramics as high fusing materials are developed in dental field. Thus, dental investments are needed to cast high fusing ones into their moulds. On the contrary, ethyl silicate-bonded investment is used in the construction of high fusing base metal partial denture alloys[1), but it is losing popularity because of easy gelation in storing a silica sol longer. Fither silica characteristics or mixing solution for the hydrolysis related to gelation was discussed[2,3). Glycerol in mixing liquid and gypsum binders in investment powder controlled the magnitude of setting and thermal expansion of dental gypsum-bonded investment[4-6). Setting behaviour at isothermal temperature of the investment was measured by thermal analysis[2,3), because the temperature change of the investment was recorded by a thermocouple method[7-9).

The mixed investment hardened as a setting expansion after mixing the recommended liquid by a manufacturer to it. As the expansion of dental investment is exothermic, the temperature increase during setting is observed after the investment powder is mixed by the liquid[10). The investment which was mixed by hydrolyzed silica sol liquid exhibited setting behaviour in differential scanning calorimetry (DSC) analysis, illustrating that greater heat for setting than a commercial gypsum-bonded investment was obtained[11). Effect of the storage condition on the setting is not examined using a mixing solution stored for each period.

This study examined cast investment powders when mixed by HCl (hydrochloric acid) mixture including ethyl silicate and other solutions which were stored for long period at 20°C (2 hours to 6 weeks). It was examined whether the long-term storerd HCl mixture was used as the mixing solution, because the hydrolyzed ethyl silicate gelled during the storage before the use[1).

## MATERIALS AND METHODS

The solution tested was as-received ethyl silicate 28 which was composed of $Si(OC_2H_5)_4$ ($SiO_2$ content=28 wt%, pH=2.3; Colcoat Co, Tokyo). To use as the mixing solution to investment powders, ethyl silicate solution was hydrolyzed in the presence of HCl, ethanol and distilled water. Namely, the HCl mixture (ethyl silicate solution, HCl, ethanol and distilled water) was

---

Hiroshima University, School of Dentistry, Department of Dental Materials (Chairman: Professor Masao Yamaki).

* Hiroshima University, School of Dentistry, Department of Removable Prosthodontics (Chairman: Professor Yasumasa Akagawa).

Correspondence to *Dr K. Wakasa*, Hiroshima University, School of Dentistry, Department of Dental Materials, Kasumi 1 chome, Minamiku, Hiroshima City, 734 Japan.

made for dental purposes. A1 liquid (pH=2.5) had 75 wt% ethyl silicate, 1 wt% 1 N HCl, 14 wt% ethanol and 10 wt% distilled water, and A2 liquid (pH=0.8) had 50 wt% ethyl silicate, 1 wt% 1 N HCl, 43 wt% ethanol and 6 wt% distilled water. Their solutions were stored preliminarily for 2, 4, 6 hr, 1 and 3 days at 20°C. The investment powders were mixed by their HCl mixtures before measuring under DSC analysis.

The investment samples were made according to the following step. The liquids (A1 and A2) as a HCl mixture are stored for each testing period (2 hr, 3 days, and 1 to 6 weeks at 20°C). Ammonium carbonate (AC) solution as a catalyst (pH=8.1, 10 wt% concentration in distilled water; Katayama Kagaku Kougyou, Osaka) is added to them (A1 and A2) before using them, and pH of the mixing liquid changed to 8.1 (A1) and 8.2 (A2) (pH measurement, Model 751, Orion Research Inc, Cambridge, MA, USA). The investment powder including alpha cristobalite (50 wt%) and alpha quartz (50 wt%) with the median grain sizes of 32 and 4 micron (Tatsumori Co, Tokyo) is mixed with the mixing liquid.

The setting behaviour of mixed samples B1 (A1 solution was used) and B2 (A2) was measured by DSC at 20°C (DT-50, Shimadzu Co, Kyoto). Peak time (P), final setting time (F) and heat for setting (H) in mixed investments (7 samples) were recorded. All experiments under $N_2$ gas flow were carried out at 20°C. The heat for setting was calibrated by gallium (heat for fusion=82.3 J/g, and melting temperature=29.93°C)[3,10,11].

## RESULTS AND DISCUSSION

Fig. 1(a) (B1 investment) and Fig. 1(b) (B2 investment) show schematic DSC curves (isothermal temperature 20°C) when each liquid was stored for 2 hr, 3 days, and 1 to 6 weeks. At 1 to 6 weeks' storage period, pH had a small variation (pH ranged from 2.4 to 2.6 for A1 liquid, and 0.6 to 1.0 for A2 liquid), but the liquids A1 and A2 gelled at 7 weeks' storage period. Each curve had a peak with an exotherm, initial setting (I) and final setting times (F).

In Table 1 (P, F and H values in B1 and B2 for each storage period (2 hr to 6 weeks)), F was relatively greater in B1 and B2 used after 2 hr and 6 weeks than in B1 and B2 used after 1 to 5 weeks. H value was greater in 2 hr and 6 weeks than in 1 to 5 weeks, and H values ranged from 12.9 to $92.7 \times 10^{-3}$ KJ/g (B1) and from 31.6 to $94.9 \times 10^{-3}$ KJ/g (B2).

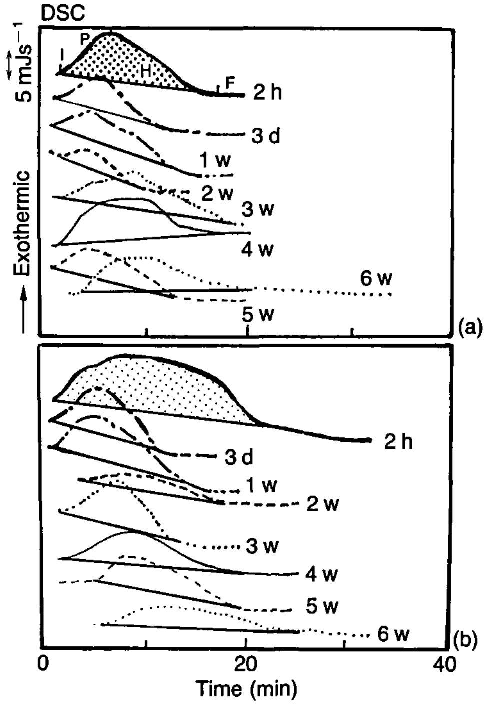

**Fig. 1** DSC curves at isothermal temperature 20°C of (a) B1 and (b) B2 investments. Stored periods of the liquids were 2 hr (h), 3 days (d), and 1 to 6 weeks (W). The heat for setting (H) was calculated by the area between initial setting (I) and final setting times (F), showing peak time (P) in DSC curves.

Setting (hardening) occurred when investment powders were mixed by HCl mixtures, because a chain of oligoner and a by-product $H_2O$ or $C_2H_5OH$ were made. As AC solution (catalyst) changed pH of the liquid to about eight, sol-gel reaction activated in the mixing solution. In this study HCl mixtures of ethyl silicate solution which contained HCl, ethanol and distilled water were effective to harden investment powders. Sol-gel reaction was controlled by the percentage of distilled water related to the hydrolysis, so setting (hardening) behaviour of the investment seemed to be influenced by it. In mixed investment sol-gel reaction activated when pH was near neutral first after adding AC solution to HCl mixtures, and the investment hardened after the reaction.

This study confirmed that the additive of aqueous ammonium carbonate to HCl mixture changed effectively its pH value and accelated gel formation. Setting of the mixed investment occurred by mixing with the liquid after the addition. The hydrolyzed mixture was stable until

**Table 1** B1 and B2 investments: DSC results of peak time (P), final setting time (F), and heat for setting (H) at each storage period (2 hr to 6 weeks). Parentheses mean standard deviation. See text for key.

| Code | Period | P (min) | F (min) | H ($KJg^{-1}$) $\times 10^{-3}$ |
|---|---|---|---|---|
| B1 | 2 h | 7.2 (0.3) | 17.6 (0.5) | 92.7 (8.8) |
| | 3 d | 6.0 (0.1) | 18.1 (0.7) | 54.7 (7.4) |
| | 1 w | 4.8 (0.4) | 16.5 (0.5) | 49.6 (3.7) |
| | 2 w | 5.3 (0.2) | 12.5 (0.1) | 12.9 (1.4) |
| | 3 w | 9.1 (0.1) | 13.9 (0.2) | 15.1 (0.3) |
| | 4 w | 9.2 (0.1) | 16.8 (0.2) | 62.4 (4.4) |
| | 5 w | 5.4 (0.1) | 13.2 (0.2) | 60.4 (1.8) |
| | 6 w | 8.5 (0.2) | 25.0 (2.3) | 60.8 (6.7) |
| B2 | 2 h | 13.6 (0.1) | 29.7 (0.2) | 83.1 (2.6) |
| | 3 d | 5.8 (0.1) | 13.3 (0.2) | 77.9 (2.9) |
| | 1 w | 5.5 (0.3) | 16.3 (0.4) | 94.9 (7.4) |
| | 2 w | 9.0 (0.3) | 24.8 (0.1) | 32.9 (6.7) |
| | 3 w | 8.0 (0.2) | 15.2 (0.2) | 31.6 (1.7) |
| | 4 w | 9.2 (0.1) | 17.6 (0.3) | 71.0 (1.8) |
| | 5 w | 10.2 (0.2) | 20.8 (0.5) | 94.1 (4.1) |
| | 6 w | 13.5 (1.0) | 30.0 (0.1) | 84.0 (2.0) |

maximum 6 weeks at 20°C, because it was not gelled before the use. In this type of investments, HCl mixture with low concentration of HCl was available effectively to hydrolyze ethyl silicate and the investment hardened as the investment mould at each storage condition tested. This result suggests that the hydrolyzed solution is used for the investment mould to cast high fusing materials.

## SUMMARY

In cast ethyl silicate-bonded investment (50/50) the hydrolyzed solution was effective to harden investment powders when stored under each period (2 h, 3 d, and 1 to 6 w). DSC analysis showed that there occurred a hardening reaction with a peak of heat during initial and final setting time. Experimental mixed investment seems to be available for apatite-based glass ceramic.

## ACKNOWLEDGEMENTS

The authours gratefully wish to express the deep appreciation to Central Research Group for the preliminary use of "Biomaterial Combined Analysis System", which was supported as Heisei 5-nen-do Hiroshima Daigaku Daigakuin Sai-sentan Setsubihi (Hiroshima University Graduate School, The latest Grant-in-Aid, 1993) from the Ministry of Education, Science and Culture, Japan.

## REFERENCES

1) Phillips, R.W.: *Skinner's Science of Dental Materials*, 9th edn, W.B. SAUNDERS Co, Philladelphia, pp. 385–412, 1991.

2) Wakasa, K. and Yamaki, M.: A modified dental cast investment for nickel base alloy: a preliminary study. *J. Mater. Sci. Letters* **10**, 1093–1094, 1991.

3) Wakasa, K., Ikeda, A., Yoshida, Y. and Yamaki, M.: Silica investment prepared by dental purposes: effect of cristobalite content on mechanical properties. *J. Mater. Sci. Letters* **12**, 1908–1910, 1993.

4) Finger, W. and Kota, K.: A modified phosphate-bonded casting investment. *Scand. J. Dent. Res.* **90**, 243–248, 1982.

5) Mori, T.: Thermal behavior of the gypsum binder in dental casting investments. *J. Dent. Res.* **65**, 877–884, 1986.

6) Mori, M., Yanagihara, T., Asai, T., Itoh, S. and Mukai, M.: Studied on investment with carbon Part 2. *Aichi Gakuin Shigaku Zasshi* **15**, 198–205, 1977.

7) Marsaw, F.A., de Rijk, W.G., Hesby, R.A., Hinman, R.W. and Pelleu, G.B.: Internal volumetric expansion of casting investments. *J. Prosthet. Dent.* 52, 361–366, 1984.

8) Nakamura, M.: Influence of various environmental temperatures on setting procedure and physical properties of cristobalite investment. *Shika Rikougaku Zasshi* **18**, 33–45, 1977.

9) Stevens, L., Okamoto, A. and Jørgensen, K.D.: Dimensional change in mould space on setting of phosphate bonded investment. *Aust. Dent. J.* **30**, 281–284, 1985.

10) Wakasa, K. and Yamaki, M.: Thermal behaviour of casting investment during setting. *J. Oral Rehabil.* in press, 1995.

11) Wakasa, K., Urabe, H., Yoshida, Y., Ikeda, A. and Yamaki, M.: Exothermic setting behaviour in dental investment and gypsum (Thermoanalytical method). *Hiroshima Daigaku Shigaku Zasshi* **26**, 263–266, 1994.