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# Dental magnesia-based investments for cast titanium crown: setting and fitness

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Titanium crowns were cast using experimental magnesia-based investment mixed with hydrolysed sol. Ten types of hydrolysed sol were used, adding a catalyst to each sol whether the setting (hardening) of the magnesia investment powder appeared within 3 h after mixing. A penetration test using a Vicat needle to measure needle depth as setting was carried out after mixing of the investment powder, showed that the penetration depth decreased gradually with increasing holding time at room temperature. Setting time was shown to be more or less than 3 h or dependent on the gelation. The total magnitude of expansion (setting + thermal) ranged from 0.5 to 0.9% using the selected mixtures. Titanium cast crowns were made in the range 0.02–1.3 mm (occlusal) and 0.03–1.5 mm (cervical), depending on the expansion value of the particular magnesia-based investments mixed with the hydrolysed sols.

## 1. Introduction

During dental casting of crowns of pure titanium mixing sols and a catalyst are needed for the investment moulding procedure. Vacuum–argon pressurized casting with arc melting, and centrifugal casting with induction melting have been used to cast pure titanium for crown materials [1–5]. The investment mould has been shown to influence the surface characteristics of cast titanium due to chemical reaction at the mould–metal interface. The investment composition affected the surface roughness, and was dependent on the mould temperature and the environmental atmosphere [6–10]. Additionally, castability was improved by selecting the investment composition. Dental magnesia-based investment or phosphate-bonded investment were generally applied to high fusing metals and alloys [11]. In the case of Ni-based alloys, the addition of other metal elements was attempted in order to minimize adhesion oxides between the alloy and the investment mould [12], and a phosphate-bonded investment with an appropriate expansion value was used clinically for cast crowns [13]. This study examines how well mixed magnesia-based investments are hardened with ten types of mixing sols, and attempts to determine the fit of cast titanium crowns in the original investment moulds.

## 2. Materials and methods

The ten types of mixing solutions tested are detailed in Table I. They were hydrolysed sols used to make magnesia-based silicate-bonded investments with a standard liquid-to-powder (L/P) ratio of 0.32 ml/g. Magnesia powder was used as the investment powder (M-1, magnesia cement contained 96 wt % MgO; coarse grain size = 5 μm; Nippon Kagaku Togyo Co., Osaka).

The wax patterns were obtained from a metal die of upper surface diameter, 8.90 mm, lower side diameter, 9.89 mm and height, 9.92 mm [14]. The fit of a cast crown was evaluated by the clearance between the margins of the crown and duplicated stone models at occlusal and cervical sites [15, 16]. The values were measured using the longitudinally cut die. Cementation was done with polycarboxylate cement (Hy-BOND cement; Shofu Inc., Kyoto).

The metal tested was pure titanium (KS-50, Kobe Steel Co., Kobe, Japan), which contained Fe = 0.06 wt %, H = 0.002%, C = 0.007%, $N_2$ = 0.01% and $O_2$ = 0.14% mean values (melting temperature, 1683 °C). The crown samples were cast by vacuum–argon pressurized casting after arc melting (CYC-LARC Prototype; J. Morita Co., Kyoto), as previously reported [17]. Casting was performed under conditions of argon pressure = 14.7 MPa, melting current = 190 A, melting time = 30 s.

The magnesia investment contained silica gel as the binder. Each sol in Table I was accelerated by 10% aqueous ammonium carbonate giving a sol-to-aqueous ammonium carbonate ratio of 16/1 [15]. The total expansion was defined as the sum of setting and thermal expansions, according to a previous report [15].

## 3. Results

Setting (hardening) of magnesia investment was observed as indicated in Table I symbol S indicates a setting time of less than 3 h; L a setting time of more than 3 h. The setting of the powder mixed with mixing solutions was thus examined. Mixing

TABLE I Mixing solutions for cast magnesia investment and an indication of setting time (S or L)

| Code | | Composition | Setting time |
|---|---|---|---|
| A | | N-butylsilicate/20, 80 %CH; 10/1 | L |
| B | | N-propylsilicate/20, 80CH; 10/1 | L |
| C | | Ethylsilicate 28/20, 80CH; 10/1 | S |
| D | D1 | Aluminosilicate/$H_2O$; 2/1 | L |
| | D2 | added 0.1; 5%NHP | L |
| | D3 | 10%NHP | L |
| | D4 | 15%NHP | L |
| | D5 | 20%NHP | L |
| | DD1 | Aluminosilicate(1) added 0.1; 10%NHP | L |
| | DD2 | 15%NHP | L |
| E | E1 | $AlPO_4/H_2O$; 100/0 | L |
| | E2 | 80/20 | L |
| | E3 | 50/50 | L |
| | E4 | 20/80 | L |
| F | F1 | $AlPO_4$ (1) added 0.1; 5%NHP | L |
| | F2 | 10%NHP | L |
| | F3 | 15%NHP | L |
| G | | Ethylsilicate 28/40, 60, 80CH; | |
| | | 10/1 | L |
| | | 10/0.8 | L |
| | | 10/0.6 | L |
| H | | Ethylsilicate 28/40CH; | |
| | | 10/1 | L |
| | | 10/0.8 | L |
| | | 10/0.6 | L |
| I | | Ethylsilicate 28/80CH = 10/1 | |
| | I1 | added 0.1; 10%AA | S |
| | I2 | 30%AA | S |
| | I3 | 50%AA | S |
| J | | Ethylsilicate28/HCl/$H_2O$/ Ethanol; 45/1/4/50 | S |

CH = $CH_3COOH$; NHP = $NH_4H_2PO_4$, AA = acrylic acid.

solutions for each mixed investment with each sol were coded as shown in Table I. As an example, acrylic acid (AA) was added to the code I sample (symbol L), and setting time in code I was less than 20 min (symbol S). Setting time is the time that elapses from the beginning of mixing until the investment hardens; the setting reaction depends on the rate of the exothermic reaction. The addition of acrylic acid to the sol accelerated the setting reaction compared with the code C sample. Setting time of less than 3 h was also observed for code J, in which a HCl mixture was added to ethylsilicate sol.

The depth of Vicat needle penetration as a function of holding time after mixing with magnesia investment powder is shown in Table II and Figs 1 and 2. With increased L/P ratio the setting reaction was slower (see code I2 as an example) (Fig. 2). In Fig. 3 the setting time at which needle penetration depth was zero plotted for code I2. Setting time increased when the L/P ratio changed to 0.42 or 0.48 as compared with that at 0.38 or the code J investment.

Ten types of investment samples (Table I) were used for the casting of titanium, although some types of investment resulted in a setting time of more than 3 h.

TABLE II Depth of penetration at various holding times for a number of samples. Powder = magnesia; mixing solution = code DD1, E1, F1, F2, F3, and L/P ratio = 0.32

| Code | | Penetration depth (mm) at holding | time (h) |
|---|---|---|---|
| D | DD1 | 10.2(0.1) | at 3 |
| E | E1 | 8.3(0.2) | at 3.5 |
| F | F1 | 2.5(0.1) | at 3.5 |
| | F2 | 5.1(0.3) | at 4 |
| | F3 | 6.2(0.1) | at 4 |

Numbers in parentheses are standard deviations.

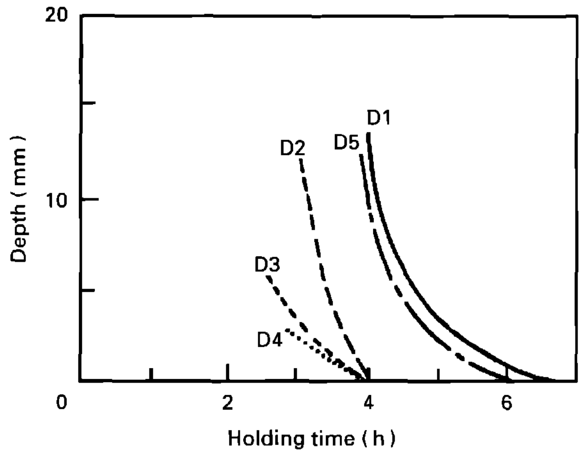

*Figure 1* Change of penetration depth with holding time. Powder = magnesia; mixing sol = code D1 to D5.

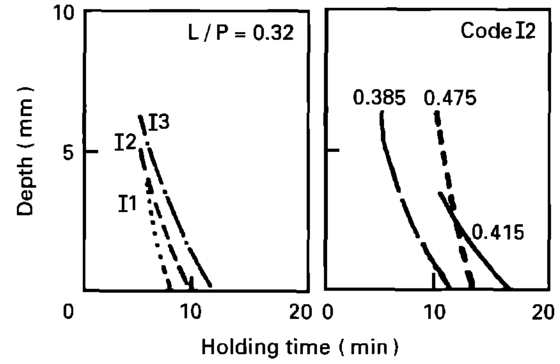

*Figure 2* Change of penetration depth. Powder = magnesia, L/P ratio = 0.385, 0.415, 0.475.

Of the investments tested the samples indicated in Table III were available as investment-mixing solutions during titanium casting. Total expansion values (setting and thermal expansion) were between 0.5 and 0.9%, indicating that setting expansion was − 0.1% for the investment samples indicated in Table III. Fit was calculated measuring the clearance between the titanium crown and a duplicated stone model from the stainless steel die. The value of fit at occlusal and cervical sites was between 1.5 and 0.02 mm (mean). Investment code J with 45/1/4/50 ratio is recommended for cast titanium crowns. More detailed work will be carried out to determine whether this sample is appropriate as an investment when different L/P ratios are used.

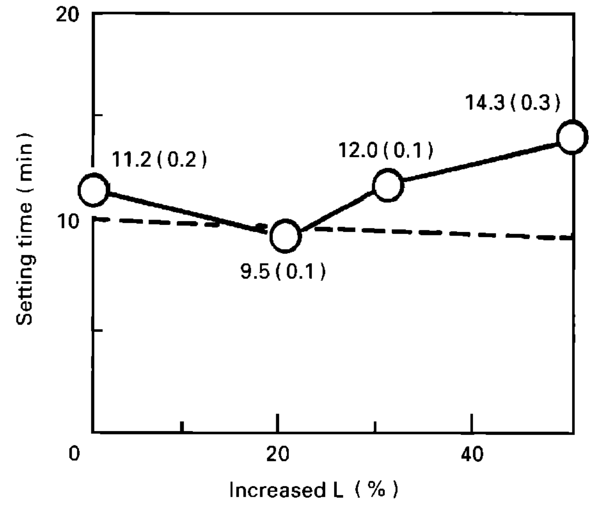

*Figure 3* Setting time for increased L of 20, 30 and 50% to mixing sol code I2 (– – – setting time of code J mixture). L/P ratio = 0.32 (0%), 0.38 (20%), 0.42 (30%), 0.48 (50%). Powder amount = 100 gram.

TABLE III Total expansion and fit values at occlusal and cervical sites when titanium was cast using vacuum-pressurized casting. Code D, F, I and J mixing solutions were used for the magnesia investment

| Code | | Total expansion (%) | Fitness (mm) occlusal site | cervical site |
|---|---|---|---|---|
| D | D1 | 0.5(0.1) | 1.0 (0.2) | 1.5 (0.2) |
| | D2 | | 1.2 (0.4) | 1.4 (0.5) |
| F | F1 | 0.5(0.1) | 1.3 (0.6) | 1.2 (0.5) |
| | F2 | | 1.1 (0.3) | 1.2 (0.4) |
| | F3 | | 1.0 (0.2) | 1.1 (0.2) |
| I | I1 | 0.7(0.3) | 0.1 (0.04) | 0.2 (0.03) |
| | I2 | | 0.2 (0.03) | 0.4 (0.01) |
| | I3 | | 0.2 (0.03) | 0.3 (0.03) |
| J | | 0.9(0.2) | 0.02(0.00) | 0.03(0.00) |

Numbers in parentheses are standard deviations.

## 4. Discussion

The fit of titanium crowns to the original die was between 0.01 and 0.14 mm using magnesia/alumina-based investments (binder = silica gel) [17]. The complete crown wax pattern fabricated on a stainless steel die was invested in phosphate-bonded investments including alumina [15, 16]. Resulting crown margins ranged from 0.0128 to 0.0498 mm. The minimum fit value of 0.02–0.03 mm was obtained using a code J sample. Code D, F and I samples were used as mixing solutions for dental magnesia-based investments.

Dental Ni–Cu–Mn-based alloys were improved by the addition of minor metal additives to obtain better castability and fit for dental purposes [12]. Titanium cast using a magnesia/alumina investment mould (magnesia/alumina = 1) showed improved castability and fit of titanium cast crowns [17]. Recent studies have shown that phosphate-bonded investments including alumina yield better surface characteristics and castability than conventional silica-based investments [18–20]. A newly formulated investment mould for casting titanium uses a magnesia-based investment including alumina and a very small amount of zirconia, bonded by silica gel [17].

In this study, magnesia-based investments were set using the sol–gel reaction of silica sol (Table I). Magnesia-based investments were hardened using a hydrolysed sol accelerated with aqueous ammonium carbonate, the gel in the sol mixture acting as the binder. The setting reaction of hydrolysed sol was different for the various sols tested; magnesia-based investment took more than 3 hours (symbol L) to harden when N-butylsilicate, N-propylsilicate and aluminosilicate were used. Considering the fit of titanium, it was deduced that the expansion value of magnesia-based investment was dependent upon the sol concentration of the mixing solution used. Sol concentration controlled setting time; as previously reported, the optimum concentration to minimize setting time was about 15% [17].

The fit value of titanium crowns cast into the set magnesia-based investment changed with increased magnitude of total expansion (Table III). The best fit is obtained using the investment mixed with code J. Results also suggest that the fit becomes a minus value (not used as a titanium crown) when the total expansion is more than 0.9%.

Magnesia-based investment for cast titanium crowns hardened with a mixed sol and catalyst showed appropriate magnitudes of total expansion. The mixing sol used to form a gel as binder is selected dependent on the total expansion of the magnesia-based investments. The mixing sols which had a setting time of less than 3 h, and 0.9% as a total expansion to magnesia-based investment, were selected. Code J solution tested in this study is recommended for this magnesia-based investment.

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