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Experimental Paste-paste Type Phosphate-bonded Investment with Colloidal Silica Solution

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Abstract: Although silica is the most popular refractory material, it is known that inhaled silica powder can induce lung or respiratory diseases, potentially leading to cancer. The purpose of this study was to develop experimental paste-type phosphate-bonded investments fabricated with colloidal silica solutions. Paste 1 was prepared by mixing cristobalite powder of 80 g with 30 cc monomagnesium phosphate solution. To investigate the effects of colloidal silica solution within paste 2, three volumes (A: 20 cc, B: 25 cc, C: 30 cc) were prepared with 15 g of MgO each. Basic properties and fit of the casting were compared to commercial phosphate-bonded investment and evaluated. The setting times for A, B and C were statistically different. The quickest setting time was measured from U. The fired strength of U was remarkably greater than those of others. The setting expansion of U was obviously greater than those of the experimental investments. The average value of A was statistically higher than that for B. C expanded minimally while setting. The expansion percentages at 850ºC were no significant differences among experimental investments. In addition, that of U during the entire heating was remarkably low. The degree of the fit differed significantly between U and A because setting expansion of A was insufficient. Although the results are not optimal, the newly developed paste-paste type phosphate-bonded investments produced in this study still offer potential as alternative investment systems due to their excellent fluidity, manipulation and reasonable basic properties.

Key words: phosphate-bonded investment, colloidal silica solution, casting, dust-free.

Dental phosphate-bonded investments have been widely used to cast the prostheses of alloys with high melting temperatures like cobalt-chromium alloy and titanium.[1~3] These investments are typically composed of refractory (80~90%) powders and binder materials.[4] Silica (SiO_2) is the most popular refractory material, while Al_2O_3, MgO, ZrO_2 and other oxides are occasionally utilized, particularly in the casting of titanium. Both ammonium dihydrogen phosphate and magnesium oxide (MgO) are commonly used as binder materials. When mixing powder with water, the chemical reaction for the binder system that causes an investment to set is generally written as follows[5,6]:

$$NH_4H_2PO_4 + MgO + 5H_2O \rightarrow NH_4MgPO_4 \cdot 6H_2O$$

With the recent development of quick-heat type dental investments, particle size has become finer, averaging less than $10\,\mu$m. As a consequence, the fine powder can drift into the atmosphere during unpacking, measuring or mixing and can be easily inhaled. It is known that inhaled silica powder can induce lung or respiratory diseases,[7,8] potentially leading to cancer.[9] Thus, fine powders are a

major risk factor for the health care of dental laboratory workers. Therefore, development of dust-free investment materials is anticipated for the improved safety of dental professions.

Recently, experimental paste-paste type investments using MgO slurry combined with Vaseline® have been reported.[10] However, there have been some complications, including long setting times, dull fluidities and minimal setting expansions. Therefore, we aimed to develop a paste-paste type investment without the use of Vaseline®, to potentially improve these properties.

Due to the insolubility of MgO in water, we fabricated an MgO-paste by combining MgO with colloidal silica. It is well-known that colloidal silica is typically used in the formulation of commercial phosphate-bonded investments to harden the molds and increase the setting expansions. This sol-gel phase change of the colloidal solution has an important role for setting investments.

The purpose of this study was to investigate the basic properties of experimental paste-type phosphate-bonded investments fabricated with colloidal silica solutions.

Materials and Methods

1.   Preparation of two pastes

Referring to our previous reports,[11~13] monomagnesium phosphate was used in this study. The monomagnesium phosphate solution (50 wt%, Yoneyama Chemistry Co., Ltd.) and cristobalite powder (SiO_2, average particle size: approximately 9.5 μm, Tatsumori Co., Ltd.) were prepared. Preliminary tests were performed to decide suitable liquid-to-powder ratios. In this study, 80 g of cristobalite was mixed with 30 cc of the monomagnesium phosphate solution, and the mixed slurry was supplied as paste 1.

Paste 2 was composed of MgO (#220, Tateho Chemistry Co., Ltd.) and a colloidal silica solution (an exclusive liquid for phosphate-bonded investments of Snow-white, Shofu Co., Ltd.). Colloidal silica solution gelled with a time dependency with regard to the incorporated MgO. According to a previous study indicating that the amount of MgO should equal the weight % of monomagnesium phosphate in the solution tested, 15 g of MgO was incorporated into paste 2. To investigate the effects of colloidal silica solution within the paste, three volumes (A: 20 cc, B: 25 cc, C: 30 cc) were prepared with 15 g of MgO each.

2.   Experimental methods

Three types of the paste 2（A, B, C, Table 1）were mixed with paste 1 and evaluated accordingly. As a comparison, a commercial phosphate-bonded investment (U, Univest Non-Precious, Shofu Co., Ltd.) was selected and examined under the same conditions.

1)   Setting time

A paraffin wax ring (diameter: 60 mm; height: 20 mm) was prepared on a glass plate for each experimental investment. Both paste 1 and 2 were weighed and mixed as described above, and then poured into the wax ring. A Vicat needle penetration test was performed to measure the setting time according to ISO-9694. Three repetitions were performed for each experimental investment.

2)   Compressive strength

Green compressive strengths were measured after 24 h of mixing for each specimen (diameter: 10 mm; height: 20 mm) using a universal testing machine (Instron MD-1125; Instron Japan) with a cross head speed of 1.0 mm/min. Fired strengths were also tested using specimens that were heated to 850ºC at a rate of 10ºC/min, held at that temperature for 1 h and then cooled to room temperature in the furnace. Five specimens were prepared for each investment.

Table 1   Compositions of experimental paste-paste investments.

Paste 1
・Monomagnesium phosphate solution
(MgH$_2$(PO$_4$)$_2$, Yoneyama Chemical Co., Ltd.)
30 cc
・Cristobalite (SiO$_2$, Tatsumori Co., Ltd.)
80 g
Paste 2
・Magnesium oxide (MgO, #220, Tateho Co., Ltd.)
15 g
・Colloidal silica solution (SnowWhite, Shofu Co., Ltd.)
A：20 cc
B：25 cc
C：30 cc

3) Setting expansion

The setting expansion of the experimental investments was measured using a touch probe system involving an electronic gauge meter (MINICOM; Tokyo Seimitsu Co., Ltd.). A paraffin wax ring (diameter: 6 mm; height: 12 mm) was fixed to a glass slide, and the mixed investment slurry was poured into the ring. After checking the initial setting, the probe was softly placed on the top surface of the mold. Expansion measurements in the vertical direction were performed at 2 h after mixing, and each value was calculated as a rate in the height direction. Three specimens were prepared for each investment.

4) Thermal expansion

Thermal expansion curves were drawn using a thermal dilatometer (Thermo Plus TMA 8310, Rigaku Co., Ltd.). Each specimen (diameter: 6 mm; height: 12 mm) was heated to 850ºC at a rate of 10ºC/min, heat-soaked for 10 min and then cooled to room temperature. The thermal analysis was performed three times for each investment.

5) Evaluation of the casting fit

Referring to the fundamental properties, a fit test of each cast crown was performed. A MOD crown was prepared using a special metal die (Fig. 1), and wax sprue (diameter: 2.5 mm, Ready Casting Wax, GC Co., Ltd.) was planted on the pattern. A double casting liner (New Casting Liner, GC Co., Ltd.) was put inside the ring (diameter: 38 mm, height: 45 mm). Twenty-four h after investing, the molds were gradually heated to 850ºC at a heating rate of 10ºC/min and heat-soaked for 60 min. Cu-Zn alloy (K-metal, GC Co., Ltd.) was
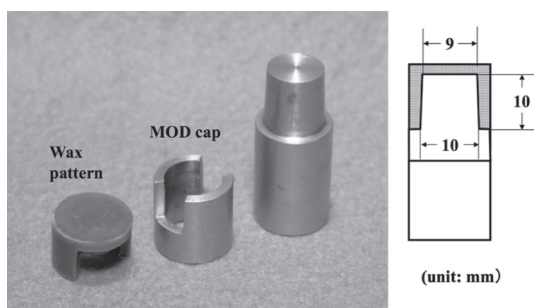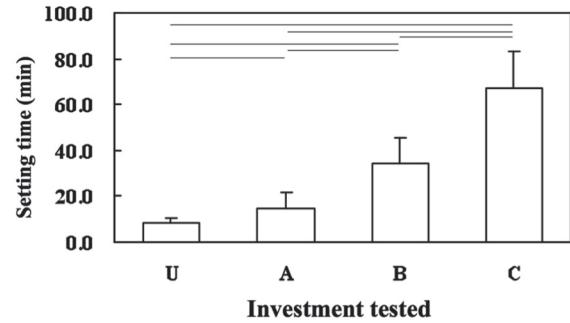

Fig. 1   MOD metal die.

Fig. 2   Setting time of investment tested. Vertical bars indicate the standard deviation and horizontal bars indicate the significant differences at the level of 5%.
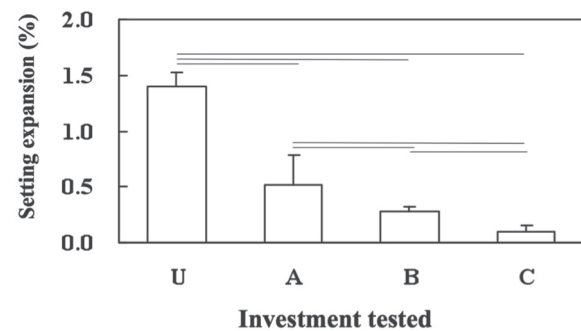

Fig. 3   Setting expansion of investment tested. Vertical bars indicate the standard deviation and horizontal bars indicate the significant differences at the level of 5%.
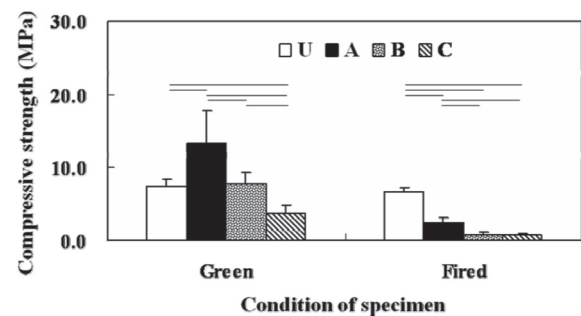

Fig. 4   Compressive strength of each investment. Green strength means the values after 24 h from mixing and fired strength means the values after firing at 850ºC. Vertical bars indicate the standard deviation and horizontal bars indicate the significant differences at the level of 5%.

then cast using a commercial spring-type centrifugal casting apparatus (Centrifico Casting Machine, Kerr Co., Ltd.). The spring was rolled twice prior to casting, and subsequently, the cast MOD crown was replaced
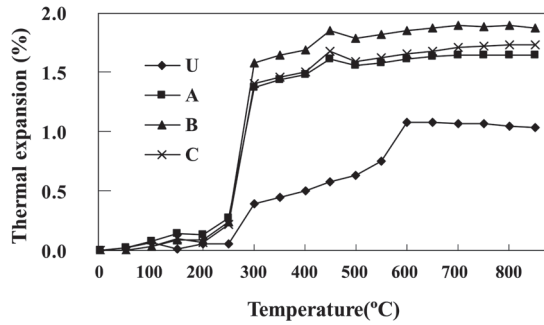
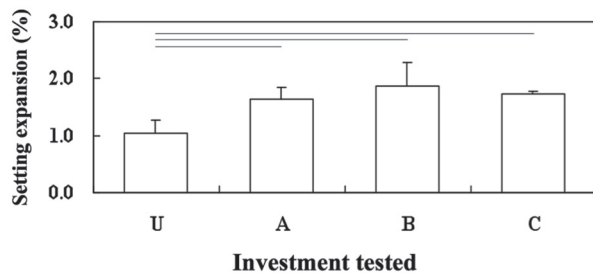Fig. 5   Typical thermal expansion curve of each investment.

Fig. 6   Thermal expansion value at 850ºC of investment tested. Vertical bars indicate the standard deviation and horizontal bars indicate the significant differences at the level of 5%.
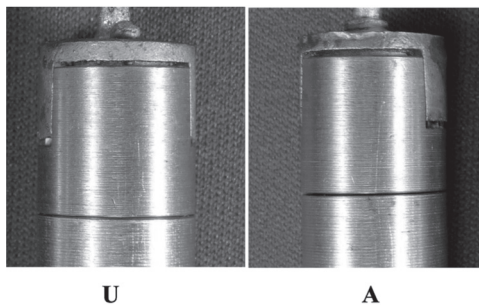

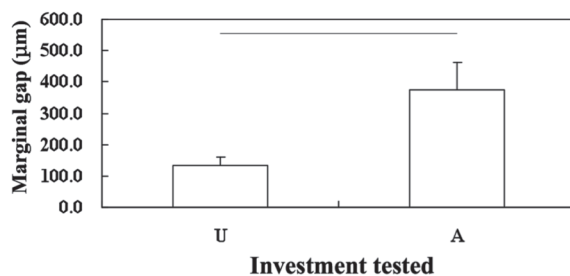Fig. 7   Fit of each MOD crown obtained from U and A.

Fig. 8   Comparison of the average gap between the die and casting induced by a commercially available (U) and experimental (A) investment. Vertical bars indicate the standard deviation and horizontal bar indicates the significant differences at the level of 5%.

onto the die. Gaps between the die and cast crown were measured at three points of the occlusal side. Three MOD crowns were fabricated, and the average values were calculated.

  6)   Statistical analysis

Data were statistically analyzed using one-way ANOVA ($\alpha = 0.05$) and Scheffe's test.

Results

The average setting times for A, B and C were 15, 34 and 64 min, respectively, and those times were statistically different for each other (Fig. 2). The quickest setting time (10 min) was measured from U.

The average green compressive strengths of A, B and C were 13.30, 7.89 and 3.80 MPa, respectively, and their average fired strengths were 2.48, 0.83 and 0.83 MPa, respectively (Fig. 3). There were obvious differences among the investments according to the amount of incorporated colloidal silica solution. Although the green compressive strength of U was nearly equivalent to B, the fired strength of U was remarkably greater than the other experimental investments.

The setting expansion of U was significantly greater than those of the experimental investments (Fig. 4). The average value of A (0.86 %) was statistically higher than that for B (0.13 %). Investment C expanded minimally while setting.

Typical thermal expansion curves of the experimental investments are shown in Fig. 5, and expansion percentages at 850ºC are shown in Fig. 6. Because thermal expansion depends on the amount of SiO_2 in the investments, there were no significant differences, as expected. However, the expansion percentage of U during the entire heating was remarkably lower than those of others.

Based on the above results, investment A was selected for the casting of the MOD crown. The fit of the MOD crown obtained from both A and U is shown in Fig. 7 and 8. The degree of the fit differed significantly between U and A. The average gap value from A was 357.6 ± 85.6 μm and was clearly undersized. Contrarily, the gap from

U was within 150 μm.

Discussion

To simplify the mixing procedure, as well as to minimize the effects of harmful dust formulation, we developed and investigated a new type of dental paste-paste investment. Because the water solubility of MgO is minimal, Vaseline®, which is an oily compound, was previously used[10] as a mixing agent for formulation of the paste; however, the high viscosity and poor fluidity of Vaseline® are not ideal for clinical applications of the investments. Therefore, paste-paste type investments without Vaseline have been anticipated to improve handling and basic properties.

We found that colloidal silica solution becomes a gel when in association with MgO; thus, we investigated suitable volumes of colloidal silica for formulation of MgO pastes. We also found that increased volumes of colloidal silica solution reduced setting times and increased compressive strengths. Additionally, smaller volumes of colloidal silica solution increased setting expansions, most likely due to lower water contents in the pastes.

The setting time, an index of manipulation, was measured. Typically, a high liquid-to-powder ratio can result in a lengthy hardening time, as well as gypsum. Conversely, a low liquid-to-powder ratio tends to result in greater setting expansion. Minimal expansion is considered disadvantageous for the fit of castings if the thermal expansion of the mold is not enough to compensate for the casting shrinkage. Compressive strength is an indicator of the mold strength. Although the strength at setting does not have a major influence on the mechanical properties of the mold, the strength value after firing becomes important to complete the casting procedure without mechanical damage. In light of our results, some casting defects may occur because the fired strengths of B and C were less than 1 MPa.[14] The fired strength of A was significantly larger than those of B and C, but was inferior to that of U.

Because thermal expansion depended on the quantity of the cristobalite, significant differences were not found among A, B and C (value range: 1.6～1.8%). On the contrary, thermal expansion of U exhibited a different thermal curve and was markedly less. Generally, both cristobalite and quartz are mixed in commercial phosphate-bonded investments as refractory materials. The transition temperature differs between quartz and cristobalite, and expansion of quartz is less than that of cristobalite. Because investments A, B and C contained only cristobalite, they exhibited different thermal expansion patterns as compared with U.

From the above-mentioned results, paste-paste type investment A was selected to evaluate the casting fit. Evaluation of fit using an MOD die is difficult because the die typically suffers from both undersized and mismatched castings. Castings obtained from A were easily removed from the mold, and no remarkable external defects were observed on the surface of the castings. Unfortunately, casting fits of A were significantly inferior to those from U, indicating that investment A does not adequately compensate for the casting shrinkage of the alloys as well as the commercial investment. We believe it is necessary to enlarge the internal volume of the mold to improve the casting fit. In our experimental paste formulations, cristobalite is contained only in paste 1. Cristobalite is a stable refractory material with a large expansion at a relatively low temperature and is not involved in the hardening response. Therefore, it may be possible to increase the thermal expansion of the mold by the addition of cristobalite into paste 2.

Although the results are not optimal, the newly developed paste-paste type phosphate-bonded investments produced in this study still offer potential as alternative investment systems due to their excellent fluidity, manipulation and reasonable basic properties. To formulate optimal paste-paste type investments available for the practical precision casting of alloys with high melting temperatures, we aim to optimize the formulations by further investigation of the paste compositions, the mixing ratio and favorable powder particle sizes.

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