

Experimental Binder-free Investments Reused to Cast Dental Precious Alloys

Zutai ZHANG¹, Yoshiteru AIDA², Yukimichi TAMAKI², Yasuhiro HOTTA² and Takashi MIYAZAKI²

¹Beijing Institute of Dental Research, Capital University of Medical Science, Beijing Stomatological Hospital, 4 Tian Tan Xi Li, Chongwen District, Beijing 100050, PR China

²Department of Oral Biomaterials and Technology, Showa University School of Dentistry, 1-5-8 Hatanodai, Shinagawa-ku, Tokyo 142-8555, Japan

Corresponding author, Yukimichi Tamaki E-mail: tamaki@dent.showa-u.ac.jp

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This study aimed to develop reusable dental investments. SiO₂ and MgO were selected as refractory materials to prepare three types of investment (coded as 60S-40M, 80S-20M, 100S) with 40, 20, and 0 wt% of MgO. Each type of investment was reused twice. Thermal expansion and compressive strength were examined and statistically evaluated by ANOVA. To evaluate fit of castings, full crowns were cast by using a commercial Au-Ag-Pd alloy with all investment types. Marginal fit was statistically analyzed by cement thickness. It was found that although MgO strengthened the mold, it had little influence on expansion. The strength of 60S-40M was the highest, and 100S had the greatest advantage with regard to thermal expansion. In the evaluation for clinical applicability, all investments were able to cast successfully, but their castings might be undersized. Among the experimental binder-free investments reused for dental casting in this study, 100S in particular showed to be a good candidate for repeated fabrication of precision fit castings.

Key words : Investment, Cast, Reuse

INTRODUCTION

Dental casting is a popular method in the production of restorations and prostheses. This procedure typically employs the lost wax method in which wax patterns are replaced by casting alloys¹⁾. Investment materials play an important role in mediating this procedure: at least 40 g of investment material is required to obtain even a small casting such as an inlay or crown. After divesting, these molds are thrown away as industrial waste. As for cast dentures and long-span bridges, approximately 1 kg of waste is produced from dental investments used to fabricate these prostheses. In other words, a lot of waste is produced whenever large prostheses described above are fabricated by the lost-wax casting method.

Industrial waste is increasing at an alarming rate worldwide and is fast becoming a serious environmental and social problem. To stem this escalating problem, the Japanese Ministry of the Environment recommended the construction of a sound material-cycle society. In dentistry, some reports have documented the reuse of dental materials. However, most of the reused dental materials involved metal materials and/or orthodontic tools such as wires or brackets. From the viewpoint of waste reduction, it is worthy to reuse the material with high frequency by routine laboratory use. In this connection, dental gypsum and/or dental investment should be target materials, but they are rarely examined²⁻⁴⁾.

In our previous studies⁴⁻⁷⁾, we have done some

investigations on dental investments. Pertaining to research on investment casting, there is increasing interest in the dental casting of titanium and titanium alloys⁸⁻¹³⁾. However, to date, reports are few concerning the reuse of dental investments that are used in casting titanium. One reason to account for information scarcity on the reuse of dental investments is that it is troublesome to have used investments ground to powder again. Another reason is that the binder composition of these investments changes during the casting process as a result of setting reaction or heat stress. Hence, the difficulty and reluctance of reusing commercial dental investment products may pose an obstacle to the construction of a material-cycle society. Against this background, the development of reusable dental materials should be a foremost priority and major aim.

To develop indefinitely reusable dental investments, the focus of this study was therefore on binder-free dental investments. Once reusable dental investments are available, they will definitely lead to drastic reduction in industrial waste produced by dental laboratories. Being the initial trial experiment, fundamental properties pertaining to dental investments as well as casting applicability were examined by using experimental investments composed of refractory materials only.

MATERIALS AND METHODS

Experimental investments

Silicon oxide (SiO₂; Cristobalite, average particle size:

9.1 μm ; Tatsumori Co. Ltd., Japan) and magnesium oxide (MgO; RA-F, #200 pass; Tateho Chemical Co. Ltd., Japan) were selected as refractory materials for the experimental investments. Three kinds of experimental investment (coded as 60S-40M, 80S-20M, and 100S) were produced as shown in Table 1. None were combined with binder materials such as gypsum or phosphate.

Reuse of investments

After each experimental investment, as given in Table 1, completed its first examination, pieces of fired molds were retrieved and powdered again by manual milling with a mortar and pestle. Resulting powder was used again as Second use, and then in the same way used one more time as Third use. The water/powder ratio of all experimental investments was determined as 0.3 in preliminary testing.

Specimen preparation

Dental investments are required to have a number of fundamental properties. In this study, compressive strength and thermal expansion were measured. Experimental investments were therefore mixed with water at a ratio of 0.3 for 30 seconds by hand, and then automatically by a mixing machine for a further 30 seconds under vacuum. The mixture was poured into acryl tubes (8 mm in diameter \times 15 mm in height) for the compression test, or formed into cylindrical specimens (6 mm in diameter \times 12 mm in height) using a silicone rubber mold for the thermal expansion test. Neither setting time nor setting expansion was investigated because the investments were binder-free.

Compressive strength

At 24 hours after investing, specimens in acryl tubes were directly heated in a furnace up to 900°C at a rate of 10°C/min and then heat-soaked for one hour. Following this, they were allowed to cool while still in the furnace. Compressive strength was measured using a universal testing machine (Instron MD-1125, Instron Co. Ltd., Japan) with a crosshead speed of 1.0 mm/min. Five specimens were tested for each investment, and the average value was calculated.

Thermal expansion

To evaluate thermal behavior, thermal expansion curves were obtained using a thermal dilatometer (Thermo plus TMA 8310, Rigaku Co. Ltd., Japan). At 24 hours after investing, specimens were heated up to 900°C at a rate of 10°C/min. Thermal analysis

was performed three times for each investment. Strength and thermal data were statistically evaluated by ANOVA and Scheffé's multiple comparisons test at a significance level of $\alpha=0.05$.

Casting examination

To evaluate the applicability of the experimental reusable investments for clinical use, wax patterns were produced using a commercial dental CAD/CAM system (Decsy, Media Comp., Japan). A stainless steel cone with a 15° taper was selected as the metal die. An impression of this die was made using a condensation-type silicone rubber impression material (Duplicone, Shofu Inc., Japan), and stone dies were made with a slurry composed of special stone (Shimomura Gypsum Co. Ltd., Japan). After digitization, wax patterns of a full coverage crown for the first lower molar (Fig. 1) were automatically formed by cutting tools and then cast with each experimental investment (n=3).

Since it was possible that the experimental molds were not strong enough to withstand being removed from the ready-made crucible former because of the lack of binder, a handmade crucible made of dental paraffin wax was constructed as shown in Fig. 2. A

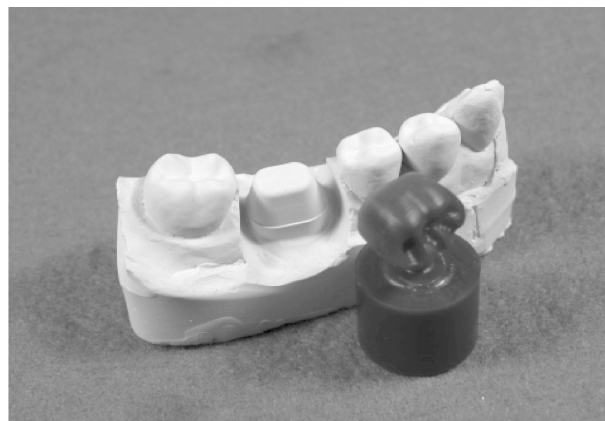


Fig. 1 Stone die and pattern prepared for experiments.

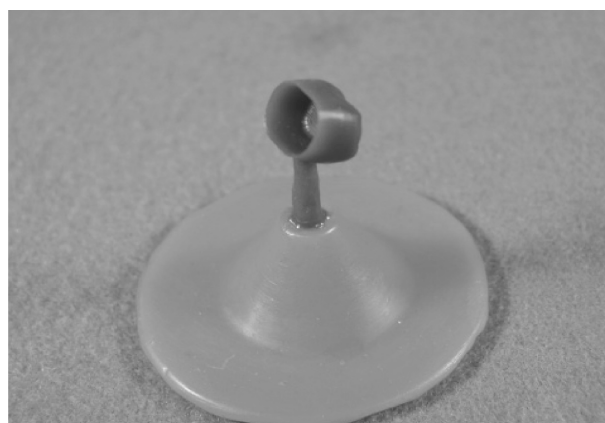


Fig. 2 Crucible former made by paraffin wax.

Table 1 Experimental investments used in this study

Code	SiO ₂ (wt%)	MgO (wt%)
60S-40M	60	40
80S-20M	80	20
100S	100	0

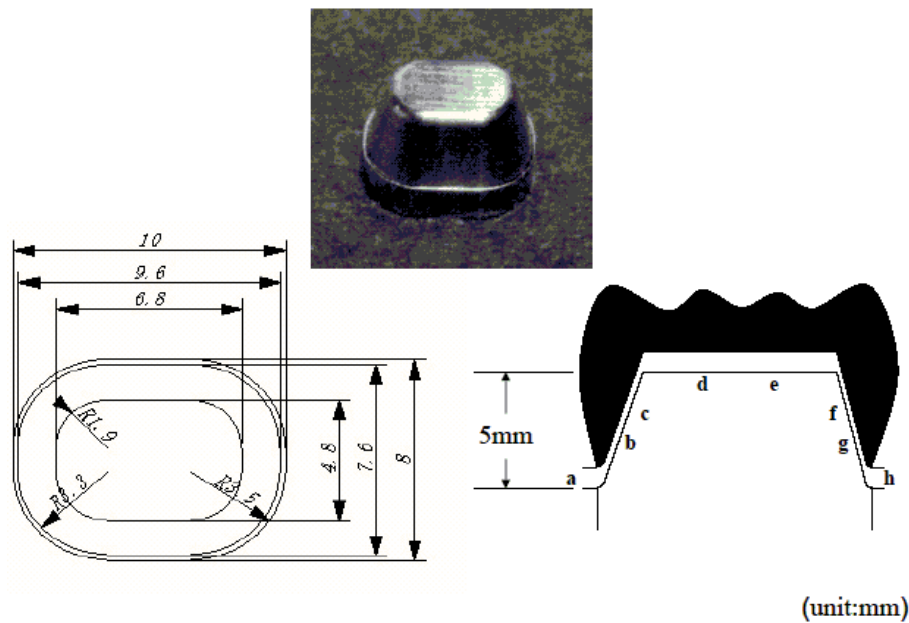


Fig. 3 Metal die used for evaluation of fit. Left: schema and dimension; Right: measuring points.

double casting liner (New Casting Liner, GC Co. Ltd., Japan) was put inside the ring (38 mm in diameter \times 45 mm in height). At 24 hours after investing, the molds were gradually heated up to 300 °C at a heating rate of 8°C/min and heat-soaked for 30 minutes. Then, they were heated again until 900 °C at a heating rate of 10°C/min. After holding at 900°C for 30 minutes, they were cooled down to 700 °C. A commercial Au-Ag-Pd alloy (Castwell MC; Au: 12 wt%, Ag: 46 wt%, Pd: 20 wt%, Cu: 20 wt%, others: 2 wt%; GC Co. Ltd., Japan) was then cast using a commercial spring-type centrifugal casting apparatus (Centrifico Casting Machine, Kerr, Japan). The spring was rolled twice prior to cast.

Cast crowns were cemented to the stone die with a zinc phosphate cement (Elite cement, GC Co. Ltd., Japan), and then sectioned in a mesiodistal direction using an automatic cutting tool (Isomet, Buehler, USA). The cement thickness of each crown was automatically measured using a digital microscope (Motic Images 2000, Shimadzu Co. Ltd., Japan). Dimensions of the metal die are shown in Fig. 3; the measurement points are indicated by letters. Tests were repeated three times by reusing each binder-free investment. Statistical evaluations of the fit at the marginal points were conducted by two-way ANOVA and Scheffé's multiple comparisons test at a significance level of $\alpha=0.05$.

RESULTS

Fired strength

Fired strength of the experimental investments

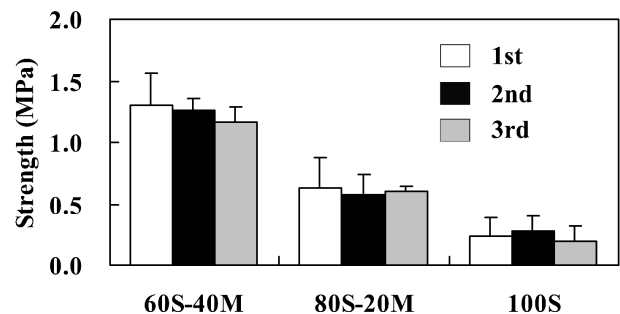


Fig. 4 Fired strengths of experimental investments for every repetition. Vertical bars indicate standard deviations.

increased with increasing MgO, as shown in Fig. 4. Values of 60S-40M, 80S-20M, and 100S were 1.30 ± 0.26 , 0.63 ± 0.25 , and 0.23 ± 0.15 MPa respectively, whereby these values differed significantly among the three investments tested. However, repeated use of investments did not seem to have any influence on fired strength.

Thermal expansion

Typical thermal expansion curves of the experimental investments tested are shown in Fig. 5. Thermal expansion depended on the amount of SiO₂ in the investments. As expected, 100S showed the largest thermal expansion among all the experimental investments (approximately 2.02%). Expansion values at 900°C are shown in Fig. 6. While there were significant differences between 100S and the other two

experimental investments, there were no significant differences in the thermal behavior of 100S after each reuse (Fig. 7).

Fit of castings

Crowns obtained from experimental 80S-20M and 100S are shown in Fig. 8. External defects were observed on the surface of one crown obtained from 100S; however, this had no influence on the fit. Significant differences in fit among the tested investments are shown in Figs. 9-11.

Crowns produced from 100S had a thinner cement layer than those from 60S-40M and 80S-20M.

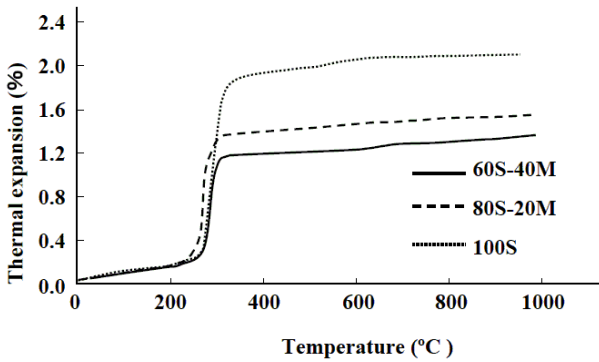


Fig. 5 Thermal expansion curves of experimental investments.

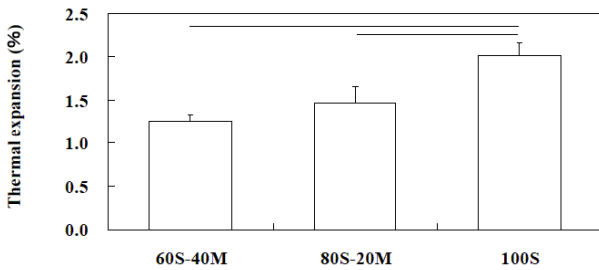


Fig. 6 Thermal expansion of experimental investments at 900°C. Vertical bars indicate standard deviations; connecting bars indicate significant differences ($p < 0.05$).

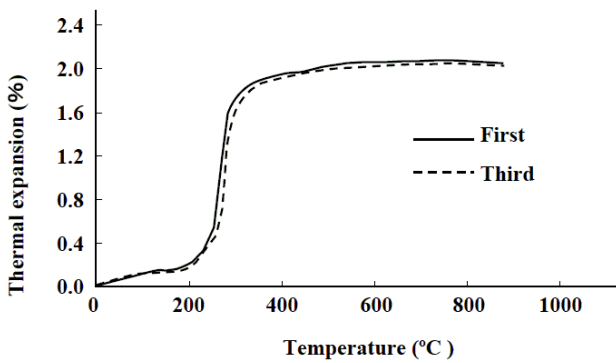


Fig. 7 Thermal behavior of 100S when reusing.

This discrepancy was particularly remarkable at both the marginal and occlusal points where values were about $100\mu\text{m}$. On the other hand, crowns produced from 60S-40M were obviously undersized, because broad layers $\geq 200\mu\text{m}$ were observed both occlusally (points d and e) and marginally (points a and h), while extremely thin layers of $30\mu\text{m}$ or less were observed axially (points b & c and f & g). Fit of the crowns obtained from 80S-20M worsened after each reuse (Fig. 10). In contrast, there was a small discrepancy in fit after each reuse with both 60S-40M and 100S (Figs. 9 and 11).

Fig. 12 shows data limited at both the marginal and

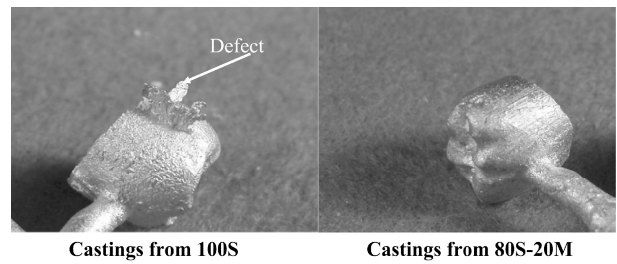


Fig. 8 Castings obtained from experimental investments.

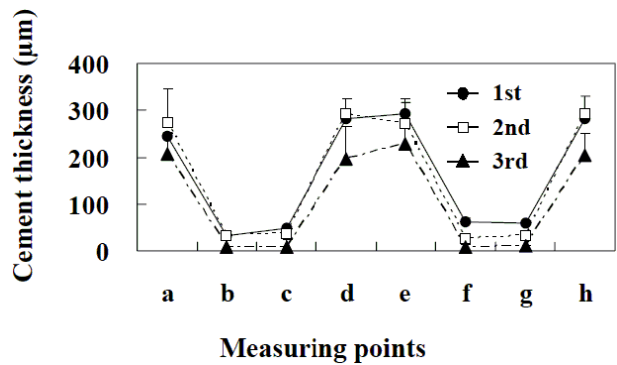


Fig. 9 Fit of castings obtained from experimental 60S-40M. Vertical bars indicate standard deviations.

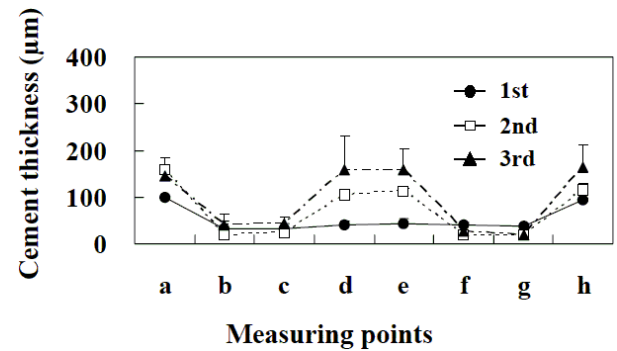


Fig. 10 Fit of castings obtained from experimental 80S-20M. Vertical bars indicate standard deviations.

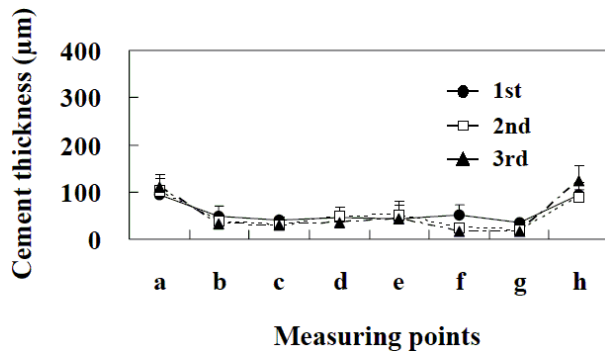


Fig. 11 Fit of castings obtained from experimental 100S. Vertical bars indicate standard deviations.

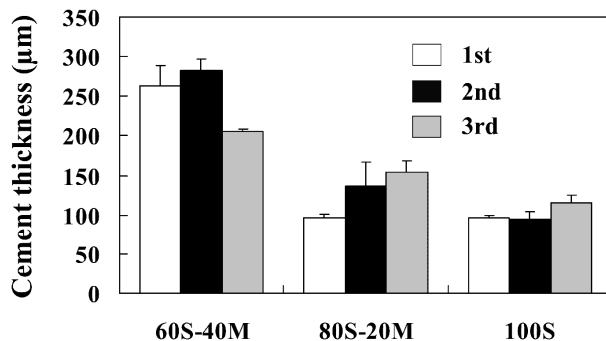


Fig. 12 Comparison of fit at marginal points. Vertical bars indicate standard deviations.

points, and as described above, values from 100S were the lowest. Based on the fit evaluation results obtained, it was found that there were significant differences among all the investments tested. However, variations in fit with each reuse were not significant.

DISCUSSION

Conventional dental investments are composed of refractory and binder materials¹⁾. Refractory materials remain stable during heat processing, but binder materials are decomposed by heat stress. Therefore, investments including such as gypsum or phosphate are both irreversible, and it is extremely difficult to reuse them. Even if possible, physical properties will surely change a lot.

Our previous research efforts^{6,7)} have focused on investment materials for dental casting, namely new phosphate-bonded investments without ammonia gas release which have been reported to be environmentally-friendly materials for laboratory use. In terms of casting method, a heat-shock casting method was also investigated to reduce the operation time⁵⁾. Of late, our research focus is on the reuse of dental investments⁴⁾. However, there are difficulties in reusing commercial products. In our previous research⁴⁾,

all investments tested had to be disposed of after each experiment. This is neither rare nor unusual in the field of dentistry, despite the public concern that industrial waste is causing severe environmental contamination.

The aim of this study, therefore, was to develop binder-free investments since it was thought that the binder material obstructed the reuse of dental investments. To design this type of investment, the crux of the matter lies in whether the mold can be successfully constructed using only refractory materials mixed with water. Without a binder, the only way to stiffen the mold is through condensation with drying and dehydration since there is no chemical reaction. Therefore, in this study, molds were left for 24 hours after mixing – by which time they were already hardened. Nevertheless, they were not strong enough to withstand being separated from a rubber crucible former. For this reason, a handmade wax crucible, as shown in Fig. 2, was prepared to prevent the mold from suffering damage prior to heating. Depressions caused by contraction with dehydration were often observed on top of the molds at 24 hours after mixing; however, they did not seem to influence performance.

Normally, the refractory material is not only stable at the casting temperature, but that it should also be able to expand to maintain the dimensional accuracy of the castings. SiO₂ is an allotrope which is frequently used as a refractory material in dental investments. Cristobalite and quartz are especially popular due to the large thermal expansion that accompanies the phase transition (from α to β) below the casting temperature. Differences between these two allotropic forms lie in the amount of thermal expansion and transition temperature. In this experiment, cristobalite was chosen in anticipation of its large amount of thermal expansion; maximum heating temperature was set at 900°C to inspect not only precious alloys, but non-precious ones too.

MgO has been used as a binder material with mono-ammonium phosphate in phosphate-bonded investments. Recently, MgO is also available as a refractory investment material for titanium castings, because it is more stable with molten titanium than SiO₂⁸⁻¹²⁾. With the aforementioned advantages cited for both SiO₂ and MgO, these two materials were therefore used as the refractory materials from which three experimental binder-free investments were prepared with the aim of developing reusable investments.

Compression test results suggested that strength was influenced by the amount of MgO. This suggestion was based on the obvious understanding that MgO particles which passed through a 200-mesh screen were coarser than cristobalite. Furthermore, on the overall, all the three investments exhibited low fired strength. In particular, 100S which con-

tained no MgO was barely able to cast at a high rotational speed because of its poor strength. As ISO has no recommended guidelines on the compressive strength of molds after firing¹⁴, we could not ascertain whether the fired strengths of experimental investments were appropriate for casting. Generally speaking, their values were too small. Nevertheless, these molds were able to successfully cast commercial dental precious alloys. In a fundamental study, set specimens without a ring were able to freely expand in all directions while heating. Heat stress due to thermal expansion might have partially occurred on the sides of the mold because the powder might not be distributed uniformly. As a result, cracks appeared on the specimen surface, thereby leading to reduced strength. On the other hand, the volume required to fabricate the casting mold should be more than that of the specimen in the fundamental study; moreover, it is usually enclosed by a casting ring, except in the case of the ringless casting method. Therefore, even with the strength of 0.5 MPa or less, the mold would be able to resist casting pressure. On the other hand, from a contrary perspective, these delicate investments could be advantageous for reuse because of the ease of milling.

Thermal expansion of investments depends on the SiO₂ content, because MgO undergoes no specific dimensional changes during heating^{7,10,11}. Therefore, 100S, which consisted of cristobalite only, expectedly showed more expansion than 60S-40M and 80S-20M. Moreover, each expansion curve was highly reproducible with reuse. These results thus indicated that MgO hardened the mold, but had little influence on expansion.

Fit of castings is undoubtedly controlled by mold expansion. The Au-Ag-Pd alloy is widely used in Japan, and commercial gypsum-bonded investments are generally chosen for casting. Although the precise shrinkage rate for the casting of this alloy is yet to be determined, it is of a certainty that it depends on casting conditions. According to data given in previous reports^{15,16}, it was estimated at about 1.5%. Judging from the results in Fig. 11, 100S must be advantageous regarding fit, which supports the results of thermal expansion shown in Fig. 5. Although 80S-20M showed good marginal fit results at first trial, it was clearly inferior to 100S thereafter. To proffer a plausible explanation for the perplexing marginal fit results of 80S-20M *versus* 100S, it was thought that more repetitions were required. Crowns produced using 100S were expected to be oversized because the degree of expansion likely exceeded the casting shrinkage rate; however, their fit was slightly tight. This might be due to a weaker compressive strength because melted metal contracts and deforms easily in lower-strength investments. On these grounds of much speculation and conjecture pertaining to marginal fit, further examinations are

indeed necessary.

With 100S, another key concern was its poor fired strength which could thwart the production of consistently sound castings. Representative castings are shown in Fig. 8. It is unclear whether these defects originated from investment cracks or casting force, but it was clear that the poor fired strength of 100S was probably one of the principal causes.

The results of this experiment suggested that 100S was most suitable as an investment mold material for casting, as well as most desirable as a reusable investment because of its low strength and high thermal expansion. However, various problems must be resolved prior to laboratory use. For example, 100S investment had a long setting time, no setting expansion, and poor strength compared with conventional dental investments. In terms of clinical use evaluation, the results of this study also suggested that it is necessary to improve the strength in order to produce stable cast prostheses for clinical use.

CONCLUSIONS

The three experimental binder-free investments could be reused to cast precious dental alloys and could therefore play an effective role in reducing the amount of industrial waste from dental laboratories. MgO made the molds strong, but had no influence on thermal expansion. In this connection, 100S (which was without MgO) was found to be most effective for repeated fabrication of precision fit castings. Nonetheless, for these investments to be used in routine laboratory work, investigations into further details such as particle components, size and distribution are necessary in future studies.

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