Gypsum-bonded Investment and Dental Precision Casting
(II) Investment for the Quick Casting Technique

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Part I of this study presented a hypothesis that the thermal expansion of gypsum-bonded investment should become higher under heating conditions favorable for the formation of $\alpha$-hemihydrate. The present study aimed at proving this hypothesis by simulating the rapid heating condition employed in the quick casting technique. The expansion values obtained were 1.72-1.93% after 30 min in three investments, two rapid heating and one conventional types. Under a comparable measuring pressure a common laboratory measurement (5°C/min) gave significantly lower expansions of 1.32-1.36% at 700°C for the same investments ($p<0.01$). The shrinkage observed at 350-400°C in this measurement was not observed in the rapid heating. Realistically large molds prepared from the conventional gypsum-bonded investment need to be investigated for their potentially high thermal expansion.

Key words: Rapid heating investment, High thermal expansion, $\alpha$-hemihydrate

INTRODUCTION

Dental stone and plaster are manufactured from gypsum (calcium sulfate dihydrate) by wet and dry calcination methods. The resulting two types of calcium sulfate hemihydrate are called $\alpha$- and $\beta$-hemihydrate, respectively. While the designations ‘$\alpha$’ and ‘$\beta$’ normally indicate crystallographic differences, in the case of calcium sulfate hemihydrate the designations have been used to distinguish differences in their thermodynamic properties since the classic study by Kelley et al.1). Part I of this study showed that when molds prepared from an investment marketed for the quick casting technique (hereafter, rapid heating investment) were heated either quickly or slowly, the difference in the heating speed was creating different dehydration conditions, similar to wet or dry calcination of gypsum, respectively2). While the molds were placed in a furnace preheated to 700°C to simulate the quick casting technique (hereafter, rapid heating) in the quick heating test, they were heated at a rate of 5°C/min in the slow heating test.
The above identification of wet or dry calcination was made by the measurement of mass changes occurring in the heated specimens. The unstable form of calcium sulfate anhydrite (III-CaSO₄) rehydrates to form hemihydrate, when the heated specimens are exposed to atmospheric moisture³-⁷. This is a familiar phenomenon exploited in the industry, known as 'aging', for the production of β-hemihydrate in dry calcination⁸-¹⁰. The mass increase due to the hydration of III-CaSO₄ to hemihydrate becomes less than the expected full recovery, when the stable form of calcium sulfate anhydrite (II-CaSO₄) is formed. The above rapid heating test revealed an initial stage of II-CaSO₄ formation at 200°C, while the formation of II-CaSO₄ was only after 350°C in the slow heating test; the full weight recovery to the hemihydrate level continued to this temperature in the latter heating. Powell¹¹ first demonstrated that this large temperature difference could be shown in differential thermal analysis (DTA) by a difference in the position of a relatively small exotherm due to the transformation of III-CaSO₄ to II-CaSO₄ (hereafter, III-II transition). This method was used to identify α- and β-hemihydrate in dental products¹²,¹³. The small exothermic peak gives an impression that the III-II transition is rapid but it is a slow reaction. The sluggish process can be shown more clearly by the measurement of weight recovery on heated gypsum samples¹⁴. Ridge et al. reported that estimates given by this method for the formation of II-CaSO₄ were not very different from the values obtained by X-ray diffractometry¹⁵.

Part I of this study presented a hypothesis that the thermal expansion of gypsum-bonded investment should become higher with the formation of α-hemihydrate. This assumption was derived from reports which noted expansions of gypsum specimens after autoclaving¹⁶,¹⁷. The present study aimed at proving this hypothesis by simulating the rapid heating condition employed in the quick casting technique in thermal expansion (TE) measurement.

**MATERIALS AND METHODS**

Table 1 shows three investments and their water/powder (w/p) ratios used in the present study. In Part I, R1 was used for the weight recovery measurement and K for the TE measurement. Although the latter is a conventional gypsum-bonded investment, it was included as control in the present study.

A cylindrical plastic mold was designed to produce the same specimen size (25

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Gypsum-bonded investments studied</th>
</tr>
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<tbody>
<tr>
<td>Code</td>
<td>Type</td>
</tr>
<tr>
<td>R1¹</td>
<td>Rapid heating</td>
</tr>
<tr>
<td>R²</td>
<td>Rapid heating</td>
</tr>
<tr>
<td>K³</td>
<td>Conventional</td>
</tr>
</tbody>
</table>

¹GC Corp., Tokyo, Japan
²Shofu Inc. Kyoto, Japan
³Kerr/Sybron Inc., Orange, CA, USA
mm in diameter and 50 mm high) as that used in the weight recovery measurement in Part I and to make an axial hole in the base to accommodate a thermocouple during the TE measurement. Mixing of the investments was made according to the procedures described in Part I. A 1 mm thick round disc (25 mm in diameter) cut from heat-resisting alloy (Inconel) was placed at the top of the mix before the mold was sealed with a glass plate. The specimen was aged in the mold until the TE measurement started at 30 min from the start of mixing.

As described in Part I, a fused silica push-rod was positioned on a small recess formed on the surface of the heat-resisting plate. The measuring load was 0.2 N including the mass of the metal plate (0.02 N), giving a measuring pressure of 0.5 kPa. The furnace was suspended on the metal shafts so that it could be raised quickly to the upper position manually or with the assistance of compressed air as shown in Fig. 1. This was to simulate the rapid heating employed in the quick casting technique. The furnace was preheated to 700°C. Data were collected every 5 s by a data logger (Data Taker 500, Data Electronics, Sydney, Australia). A metal-sheathed Type K thermocouple was encased in a stainless steel tube (not shown in Fig. 1), which was fixed to the stage at the bottom and to a supporting jig at the top. Unlike the measurement in Part I, the water vapor released from the specimen was not exhausted to simulate the actual investment heating condition. However, vents were made at the lower part of the silica tube (Fig. 1). Ambient laboratory conditions

Fig. 1 The apparatus used in the measurement of thermal expansion of investments under the rapid heating.
INVESTMENT FOR QUICK CASTING TECHNIQUE

Table 2  Thermal expansion values (%) of three gypsum-bonded investments obtained under the rapid heating. The specimens were placed in the furnace preheated to 700°C. R1 and R2 are rapid heating investments and K is a conventional investment.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>R1 (n=5)</th>
<th>R2 (n=5)</th>
<th>K (n=5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.5</td>
<td>0.20 (0.02)</td>
<td>0.22 (0.01)</td>
<td>0.17 (0.06)</td>
</tr>
<tr>
<td>5</td>
<td>0.25 (0.03)</td>
<td>0.44 (0.06)</td>
<td>0.34 (0.07)</td>
</tr>
<tr>
<td>7.5</td>
<td>0.38 (0.05)</td>
<td>0.89 (0.09)</td>
<td>0.76 (0.08)</td>
</tr>
<tr>
<td>10</td>
<td>0.68 (0.11)</td>
<td>1.40 (0.10)</td>
<td>1.37 (0.09)</td>
</tr>
<tr>
<td>12.5</td>
<td>1.01 (0.11)</td>
<td>1.68 (0.08)</td>
<td>1.78 (0.10)</td>
</tr>
<tr>
<td>15</td>
<td>1.34 (0.08)</td>
<td>1.79 (0.06)</td>
<td>1.82 (0.08)</td>
</tr>
<tr>
<td>17.5</td>
<td>1.48 (0.07)</td>
<td>1.85 (0.07)</td>
<td>1.84 (0.08)</td>
</tr>
<tr>
<td>20</td>
<td>1.58 (0.07)</td>
<td>1.89 (0.07)</td>
<td>1.85 (0.09)</td>
</tr>
<tr>
<td>22.5</td>
<td>1.64 (0.07)</td>
<td>1.92 (0.07)</td>
<td>1.85 (0.09)</td>
</tr>
<tr>
<td>25</td>
<td>1.68 (0.06)</td>
<td>1.93 (0.07)</td>
<td>1.85 (0.09)</td>
</tr>
<tr>
<td>27.5</td>
<td>1.70 (0.06)</td>
<td>1.93 (0.07)</td>
<td>1.85 (0.09)</td>
</tr>
<tr>
<td>30</td>
<td>1.72 (0.06)</td>
<td>1.93 (0.07)</td>
<td>1.85 (0.09)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>R1 (n=5)</th>
<th>R2 (n=5)</th>
<th>K (n=5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.23 (0.05)</td>
<td>0.29 (0.05)</td>
<td>0.25 (0.05)</td>
</tr>
<tr>
<td>300</td>
<td>0.70 (0.06)</td>
<td>1.00 (0.05)</td>
<td>0.90 (0.02)</td>
</tr>
<tr>
<td>400</td>
<td>0.94 (0.05)</td>
<td>1.36 (0.07)</td>
<td>1.30 (0.07)</td>
</tr>
<tr>
<td>500</td>
<td>1.26 (0.07)</td>
<td>1.63 (0.07)</td>
<td>1.67 (0.09)</td>
</tr>
<tr>
<td>600</td>
<td>1.60 (0.07)</td>
<td>1.85 (0.06)</td>
<td>1.82 (0.09)</td>
</tr>
<tr>
<td>700</td>
<td>1.72 (0.06)</td>
<td>1.93 (0.07)</td>
<td>1.85 (0.10)</td>
</tr>
</tbody>
</table>

were 21±1°C and 50±10% relative humidity throughout the experiment. Five measurements were made for each material.

RESULTS

Results of the TE measurement are summarized in Table 2. It includes TE values reached at various specimen temperatures. The average TE values are shown against time in Fig. 2. All specimens started expanding within 1 min and there was no negative TE segment in all investments. Average TE values of 0.25% (R1) and 0.44% (R2) were reached after 5 min, at which the specimen temperature was approaching 200°C (Table 2). The largest TE increase was between 10 and 12.5 min in R1 and between 7.5 and 10 min in R2, where the specimen temperature was around 400°C. The final TE values were 1.72% (R1) and 1.93% (R2), and about 80% (R1) and 90% (R2) of these values were reached at the midpoint of heating (15 min). The specimen temperature at this point was between 500 and 600°C. Control K gave a similar final TE value of 1.85%. Approximately 98% of this value was already reached at 15 min, forming a plateau for the remaining TE curve. The formation of a plateau was shorter with the rapid heating investments, indicating a considerable TE gain after 15 min due to the low-high inversion of quartz.
DISCUSSION

The TE curves obtained by the simulation of the quick casting technique did not have negative segments during the 30 min heating (Fig. 2). This is unique as the TE curve of gypsum-bonded investments generally show the shrinkage due to the dehydration of gypsum just after 100°C and that due to the III-II transition starting at about 350°C, although the former shrinkage can be eliminated by making the mold denser\(^2\). The final TE value was high even with control K, which exhibited the two shrinkages in Part I. The final TE values of the rapid heating investments, 1.72% (R1), 1.93% (R2), were much higher than those given by the manufacturers, 1.35% (R1) and 1.25% (R2). Similar low TE values have been reported for the two investments, 1.04-1.39%\(^8,19\). However, comparison is not easy for varied experimental factors. Jones and Wilson have commented that a high measuring load is required in horizontal furnaces and the measuring pressure is one of the most significant factors for the comparison of TE values\(^20\). The present results indicate that the production of oversized full crowns\(^9\) is quite likely with enough cushion in the ring.

The final TE value of 1.85% from control K was much higher than that (1.19%) obtained in Part I. The difference was 0.66% and in this case the measuring pressures were comparable, 0.7 kPa (Part I) and 0.5 kPa (Part II). This supports the hypothesis presented in Part I that the rapid heating of gypsum-bonded investment should lead to high TE. However, the w/p ratios used for K were different in the two experiments and this is discussed later with a supplementary experiment. As mentioned before, the hypothesis was derived from the observations made by Miura and Sasaki\(^15\) and Whyte and Brockhurst\(^17\). The former found, in their experiment on the production of \(\alpha\)-hemihydrate in the laboratory, that the cast gypsum specimens (10 mm×10 mm×60 mm) expanded about 1% after heating in an autoclave at 200°C for 4 h. Their X-ray diffraction analysis showed that the specimens were already
100% II-CaSO₄. When the temperature was reduced to 140°C, the expansion was about 0.3% with the formation of 4% II-CaSO₄. The latter researchers reported expansion values of 0.2-0.4% in gypsum specimens in an attempt of sterilizing dental models by autoclaving. These values appear to justify the degree of the enhanced expansion (0.66%) obtained in K. Shibuya et al.¹⁹) have also shown a TE difference of 0.6% between the quick heating and a slow heating (0.5°C/min) for R1 for an unknown measuring pressure.

As Table 2 shows, the specimen temperature at the mid point of heating (15 min) was between 500°C and 600°C. The low-high inversion of quartz should appear at around this point and this was apparent in the TE curves of R1 and R2, as control K containing cristobalite only was already forming a plateau at this point. The content of quartz appears to be less in R2 than R1 and the resistance to cracking may be better achieved by the wider distribution of TE with R1. The TE values of 38 commercial gypsum-bonded investments surveyed in 1930 were less than 1% and this was increased to 1.25% by replacing quartz with cristobalite in an experimental investment²²). It is interesting that we are achieving much higher TE values this time by the co-use of cristobalite and quartz in the quick casting technique. The compositional analysis of rapid heating investments will be interesting not only for the refractory but also for the binder, as the possible high TE value can be related to the amount of the latter incorporated.

The large TE difference in control K (0.66%) was obtained under the comparable measuring stresses and also for the comparable specimen sizes, 50 mm long prism with equilateral (25 mm) triangular cross section (Part I) and 50 mm long cylinder with 25 mm diameter (Part II). However, a significant experimental difference still remained in the two TE measurements. That is, while the present one was conducted under the simulation of the quick casting technique, the specimens were dried at least 24 h under ambient conditions and heated at 5°C/min under a soft vacuum in Part I. The heating was slowed to 1°C/min at 200-300°C as well. Similar dry heating conditions are common in general laboratory TE measurements, as small sample sizes suitable for commercial dilatometers are often used. The small specimens will lose most of the excess water by the time the TE measurement starts and the amount of water released from the gypsum binder is not great either. In an anticipation of obtaining a similar low TE value in K with a commercial dilatometer, a supplementary experiment was conducted on a general, small sample size. The manufacturer of K has been recommending a range of w/p ratios, 0.36 to 0.40, and thus claiming a range of TE values, 1.17% to 1.25%. The w/p ratio of 0.38 was adopted in the supplementary experiment to examine the possible elimination of the first shrinkage due to the dehydration of gypsum at 100-200°C, which was recorded in Part I, by the increased mold density. All investments studied so far, including investment G used in Part I, were included without altering their w/p ratios.

The mix was cast in a cylindrical plastic mold of 5 mm in diameter and 20 mm in height. The specimens were aged in the closed mold for at least 2 h. In order to avoid an ambiguous degree of dryness, the specimens were dried to constant mass
under ambient conditions. The TE measurements was made using a thermomechanical analyzer (TMA, Rigaku Denki Corp., Tokyo, Japan) with a cylindrical fused quartz reference having the same size as that of the specimen. The test specimen and reference were heated to 700°C at a heating rate of 5°C/min. The minimum measuring load available, 0.01 N, was used to achieve a comparable measuring stress (0.5 kPa) to that used in the present rapid heating (0.7 kPa). The TE value reached at 700°C was expressed as a percentage of the original specimen height. The results were subjected to Student t-test to compare them with the results obtained from the rapid heating experiment.

Fig. 3 shows TE curves of the four investments. The TE values at 700°C were similar in all investments, 1.36±0.04% (K), 1.45±0.05% (G), 1.32±0.05% (R1) and 1.33±0.06% (R2). While the first shrinkage due to the dehydration of gypsum at 100-200°C disappeared in K, the shrinkage due to the III-II transition at 350-400°C still remained in all investments. The increase in TE after this shrinkage was substantial with the rapid heating investments, more clearly indicating the inclusion of quartz than in the rapid heating experiment (Fig. 2). The TE values of R1 and R2 were significantly lower than those obtained in the rapid heating (p<0.01). The difference was also significant in K (p<0.01) with the increased TE value of 1.36% from the previous 1.19%. In this connection, we note that TE values of about 1.1% to 1.4% have been reported for 2 h old K under a comparable measuring pressure (0.7 kPa) and under a soft vacuum for w/p ratios of 0.30 to 0.40 \cite{23,24}.

The results of the supplementary experiment demonstrate that comparable TE values can be obtained, regardless the specimen size, if the measuring pressure and the dehydration condition are similar. In fact, the same TE value (1.45%) was obtained in the supplementary experiment and in Part I with G. The supplementary measurement gave TE differences of 0.47% (K), 0.40% (R1), and 0.60% (R2).
A systematic study of the equilibrium of the system CaSO₄·H₂O was made by Kelley et al. The phase diagram presented in this classic study gives all necessary equilibrium temperatures for the transitions of dihydrate to hemihydrate and then to III-CaSO₄. Matsuya et al. also presented a simplified equilibrium diagram. In a process where the product is formed by a dissociation reaction, the vapor pressure around the sample is an essential factor, as the partial vapor pressure around the sample becomes higher than the equilibrium vapor pressure due to the accumulation of vapor dissociating from the sample. That is, the surrounding atmosphere becomes increasingly non-equilibrium with the increase in sample mass. The equilibrium diagram indicates that the dehydration of dihydrate to hemihydrate should occur at about 40°C, if the water vapor pressure surrounding the sample can be controlled at the ambient water vapor pressure in the laboratory, 15 mmHg at 18°C. However, most of the reactions we are concerned proceed under non-equilibrium conditions. For example, β-hemihydrate is successfully manufactured at any temperature between 110°C and 200°C. In DTA the endotherm accompanied by the dehydration of dihydrate to hemihydrate usually appears at about 120-150°C. In this case, the heating is a dynamic one, where the temperature is constantly increasing. Furthermore, in the quick casting technique, large molds contain the excess water originating from the mixing water and quickly release water from the binder under a dynamic heating.

Fowler et al. investigated the hemihydrate phase growing from gypsum crystal under a microscope for a range of 0.00001 mmHg to 2500 mmHg for water vapor and 50°C to 150°C for temperature. Under a high vacuum, a vigorous evaporation of water molecules occurred from the gypsum crystal, while the water dissociated from the gypsum sample acted as a bridge between the old and the new phases and enabled the diffusion of water molecules even at atmospheric pressure; they consider that this is an important and unusual feature at high vapor pressures or in wet calcination, as the essentially solid transformation permits non-coherent nuclear growth. That is, a great mobility of the atoms in the gypsum crystal lattice enables the formation of α-hemihydrate through recrystallization, which can result in a significant increase in the crystal size due to non-coherent nuclear growth or due to the lack of superstructure. The transformation is coherent to the original crystal structure in dry calcination. Wet calcination is achieved not only at high vapor pressure (autoclaving) but also in solutions under ordinary atmospheric pressure and by a combination of solution and high pressure methods.

The expansion of about 0.15% at 120-160°C, which Shibuya et al. noted in R1 in their rapid heating experiment, can be the expansion accompanied by the formation of α-hemihydrate, although they attributed this expansion to the inversion of tridymite. A comparable expansion of 0.23% was recorded at 200°C in the present rapid heating (Table 2). In realistically large molds, the temperature in the center will stay low and keep the water or water vapor for an extended period of time. The dehydration of gypsum is an endothermic reaction and requires energy to complete the reaction. It is quite likely, therefore, that a temperature gradient is created.
between the surface and inside of the mold and the formation of $\alpha$-hemihydrate will continue for an extended period of time with a gradual increase in volume. In the site where this transformation is completed, it will soon lose the remaining water of crystallization and then transform to $\beta$-CaSO$_4$. The $\beta$-$\gamma$ transition is very much dependent on the evaporation of the last traces of water$^{14,36}$ but it is generally accepted that above 200°C the rate of this reaction can be appreciable$^{15}$. Under general dynamic heating rates employed in DTA, the exothermic peak due to the $\beta$-$\gamma$ transition appears at around this temperature in $\alpha$-hemihydrate$^{12,27}$. When the formation of $\alpha$-hemihydrate continues for an extended period of time due to the temperature gradient in large molds, the subsequent $\gamma$-$\beta$ transition will also occur for an extended period of time. The inversion of cristobalite is taking place at around 225-275°C, although it can occur in a wide temperature range of 120-275°C$^{37,38}$. These concurrent reactions make the TE curve subjected to the rapid heating complex. Nevertheless, the continued growth of $\alpha$-hemihydrate and the cristobalite inversion are effectively offsetting the shrinkage due to the $\gamma$-$\beta$ transition at these relatively low temperatures and leading to the elimination of the shrinkage, which is the most prominent shrinkage at 350-400°C$^{2,14,16,30,36}$ in general TE curves of gypsum-bonded investments.

Molds for the conventional casting techniques may not be as wet as those in the quick casting technique. However, as long as the condition favorable for the formation of $\alpha$-hemihydrate is created, a higher TE expansion than that obtained in general TE measurements could occur. Finger and Jørgensen found that immersion of a mold prepared from a gypsum-bonded investment for 3 min before heating led to a 0.1% increase of TE value$^{39}$. Jones and Wilson observed a much higher TE value of approximately 1.5% in K under a measuring pressure of 0.2 kPa for 1 and 24 h old specimens$^{20}$. Quite large specimens, 20 mm in diameter and 100 mm long, were prepared from an unknown w/p ratio. Their report also indicates that the TE value could be as high as 1.7% with this oldest investment.

Molds can be placed in a furnace preheated to 200°C for the elimination of wax patterns$^{40}$. The furnace temperature is much lower than that used in the quick casting technique, but it is high enough to produce a similar dehydration condition favorable for the production of $\alpha$-hemihydrate. It is therefore reasonable to assume a higher TE than that expected by general laboratory measurements in this special technique. In this way, the oldest investment K may have been successfully compensating for the metal shrinkage, while the manufacturer has claimed its TE values to be 1.17% to 1.25% as mentioned before. There is a need for a more realistic treatment of TE values in the assessment of casting accuracy.

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