Gypsum-bonded Investment and Dental Precision Casting (IV) Transformation of III-CaSO₄ to II-CaSO₄

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The degree of III-CaSO₄ to II-CaSO₄ transition was estimated on wet specimens, 25 mm in diameter and 50 mm high, prepared from a gypsum-bonded investment for quick casting. After 30 min from mixing the specimens were heated in a 700°C furnace until a specimen temperature of 200°C to 700°C was reached. The estimation was made by measuring mass changes of the specimens before and after heating. The transition reached 39% at 350°C. The same estimation method, when applied to a previous study, showed no transition to this temperature in dry specimens heated slowly (5°C/min). The large difference in transition found between the wet and dry specimens was attributed to the formation of α- and β-hemihydrate, respectively. At 350-450°C, the transition was 3% and 48%, respectively. The pronounced latter transition, generally identified by differential thermal analysis of gypsum, appears as the major investment shrinkage demonstrating its dry dehydration process.

Key words: II-CaSO₄ formation, α-hemihydrate, β-hemihydrate

INTRODUCTION

Specimens prepared from gypsum-bonded investment can exhibit shrinkages at different stages during the normal course of heating to 700°C, since the gypsum binder undergoes a densification process through its phase changes11. The first change is the dehydration of calcium sulfate dihydrate to hemihydrate. This is followed by the dehydration to III-CaSO₄ and then the transformation of III-CaSO₄ to II-CaSO₄ (hereafter, III-II transition). It was obvious from the beginning of investment development in the early 1930s that the largest shrinkage occurring at about 350-450°C depended on the amount of plaster incorporated in the investment powder2. Differential thermal analysis (DTA) and X-ray diffraction (XRD) of gypsum powder or cast gypsum show that the III-II transition is responsible for the large shrinkage at 350-450°C13,3-9. This major shrinkage disappears when cast investment is exposed to 700°C at 30 min after mixing20. This heating condition is widely adopted in the quick casting technique. Not only investment marketed for this new technique but also conventional gypsum-bonded investment showed this unique thermal expansion (TE) behavior leading to high TE values20. The disappearance of the major shrinkage was attributed to the formation of α-hemihydrate, as this is a recrystallization process that could result in expansion10. Calcium sulfate hemihydrate, both α- and β-forms, is formed at temperatures below 200°C. The former readily transforms to II-CaSO₄ at about 200°C, while the transformation is delayed to higher temperatures of around 350°C in the latter11. As Powell first reported this in his DTA study22. It is expected, therefore, that the III-II transition at 350-450°C responsible for the major shrinkage of cast investment be largely reduced with the formation of α-hemihydrate. However, this relationship remains obscure and requires further investigation.

Quantification of the III-II transition is relatively easy with XRD. However, since this method, as well as DTA, generally uses small samples, a large discrepancy in specimen size is inevitable between a sample prepared for XRD and a mold prepared for casting. Another option for quantification is to exploit the hygroscopic nature of III-CaSO₄ to return to calcium sulfate hemihydrate under ambient conditions5. The process is known as aging in the manufacture of β-hemihydrate and the accompanied mass increase can be measured in large specimens. The specimens need to be dried to constant mass to accurately present the rehydration process and this has been shown for cast gypsum9 and cast investment13. The present study aimed at quantifying the III-II transition for 30 min old cast investment (hereafter, wet specimens) subjected to 700°C (hereafter, rapid heating). The quantification was made also for the dry specimens investigated in the previous
study\textsuperscript{33} for comparison. Before this, DTA analysis of cast gypsum was made in an attempt of clarifying the effect of specimen size on the phase changes of gypsum. The analysis was extended to a high temperature of 1350°C to confirm the final transition of II-CaSO\textsubscript{4} to I-CaSO\textsubscript{4}.

**MATERIALS AND METHODS**

DTA specimens were prepared from a dental stone (Pattern Stone B, Investo Mfg. Co., Australia) using a water/powder ratio of 0.35. The hemihydrate powder and de-ionized water were measured to an accuracy of 0.2 g. The powder was sifted into the water in 15 sec and during the next 15 sec the mixing bowl was jarred to facilitate wetting of the powder. The powder and water were then spattered for 1 min at a rate of 3 turns/sec. The mix was then cast into a PTFE split mould of about 5 mm in diameter and 10 mm high. Specimens were kept in the mold for about 1 hr from the start of mixing. On the following day, the specimens were trimmed to a mass of 200±2 mg. They were heated at a heating and cooling rate of 20°C/min to 1350°C and then 1350°C to 800°C using simultaneous DTA-thermobalimetry (TG) equipment (Thermoflex, Rigaku Denki Ltd., Japan). The specimen was left in the furnace until room temperature was again attained. Ignited reagent grade α-alumina was used as the reference material. Peak temperature was determined on each endothermic or exothermic reaction appearing on the DTA curve. Mass changes at various temperatures were also calculated from the TG curve. Four samples were tested.

Details on the preparation of cast investment specimens (Cristoquick II, GC Dental Industrial Corp., Japan) have been described\textsuperscript{33,34}. Each specimen, 25 mm in diameter and 50 mm high, was removed from the mold after 30 min from the start of mixing and then weighed. During setting, an axial hole having a 2-degree taper, 6 mm in diameter and 20 mm high, was formed in the base of specimen to accommodate a metal-sheathed thermocouple (Type K) during heating. The specimen was then heated in a furnace preheated to 700°C until a pre-determined specimen temperature of 200°C to 700°C was reached. Only one specimen was heated each time. The specimen mass was measured, just after removal from the furnace and then until a constant was attained, to an accuracy of 0.01 g. Five specimens were prepared for each specimen temperature. Ambient laboratory conditions during the experiment were 22±1°C and 50±10% relative humidity.

In order to calculate the degree of III-II transition occurring in the present wet specimens as well as that of the dry specimens studied in the previous study\textsuperscript{33}, the amount of excess water existing in the wet specimens was first estimated from the average masses of the dry and wet specimens. These were 35.32±0.07 g (n=110) and 44.53±0.09 g (n=55), respectively. The difference of the two averages, 9.21 g, was subtracted from the mass weighed at 30 min to obtain a corrected specimen mass, where non-existence of excess water was assumed. The corrected average mass, 35.11±0.06 g (n=55), was close to that of the dry specimens. In a specimen consisting of 100% gypsum (molecular mass 172.178), the dehydration to calcium sulfate hemihydrate (molecular mass 145.154) and anhydrite (molecular mass 136.146) results in mass decreases of 15.7% and 20.9%, respectively. The expected full mass recovery is 5.2% of the original mass, if the heating produces 100% III-CaSO\textsubscript{4}. These theoretical relations were used to estimate the degree of III-II transition. Within the same specimen condition, all results were subjected to t-test to examine any significant increase in the transition rate for each temperature increase of 50°C (\(p<0.10\)).

**RESULTS**

Fig. 1 shows a typical DTA-TG curve obtained from the cast gypsum specimens. The results are summarized in Table 1. The first and second endothermic reactions starting below 200°C indicated the dehydration of gypsum to hemihydrate and then to III-CaSO\textsubscript{4}, while the TG results showed that the completion of dehydration was above 200°C. Small mass changes above 300°C indicated the existence of impurities and/or additives in the original material. The exothermic peak at about 390°C and the endothermic peak at about 1200°C showed the III-II transition and the change II-CaSO\textsubscript{4} to I-CaSO\textsubscript{4}, respectively. Only one exothermic peak appeared at about 1190°C on cooling, indicating that this was the reverse reaction of the endotherm appeared at about 1200°C on heating. No mass change was observed during cooling, although an average decrease of 1.2% was recorded during the changeover of the heating program to the cooling one.

**Fig. 1** A typical DTA-TG curve of cast gypsum on heating and cooling.
Table 2 shows mass decreases obtained from the cast investment specimens. With the mass correction described before, the average decrease at 200°C was 6.23% and this gradually increased to 6.58% at 700°C. All specimens gained mass after heating and equilibrium was reached within about 1 week. The mass recovery became smaller with the increase in the specimen temperature with a maximum at 250°C. These results are illustrated in Fig. 2 with two horizontal lines derived from the previous experiment on dry specimens\(^\text{13}\), where the lower horizontal line, \(-6.85\%\), was the average mass decrease obtained from five specimen temperatures of 500°C to 700°C under the rapid heating (n=25) and represents a best estimate for complete dehydration of this investment. The upper horizontal line, \(-5.15\%\), is the level for the expected full mass recovery of 1.70%, which is equivalent to the full recovery of 5.2% in 100% gypsum as described before. When a final equilibrium point sits above the upper horizontal line, it implies that gypsum has not completed its dehydration to hemihydrate. Once an equilibrium point starts falling from the upper horizontal line, it is then the start of II-CaSO\(_4\) formation. The distance (\(x\)) between the upper horizontal line and an equilibrium point will estimate the amount of II-CaSO\(_4\) formed. That is, the degree of III-II transition is

<table>
<thead>
<tr>
<th>Specimen temperature (°C)</th>
<th>Mass decrease on heating (%)</th>
<th>Equilibrium mass decrease after heating (%)</th>
<th>Mass recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>6.23 (0.06)</td>
<td>5.57 (0.08)</td>
<td>0.65 (0.04)</td>
</tr>
<tr>
<td>250</td>
<td>6.43 (0.23)</td>
<td>5.66 (0.24)</td>
<td>0.77 (0.03)</td>
</tr>
<tr>
<td>300</td>
<td>6.44 (0.02)</td>
<td>5.69 (0.01)</td>
<td>0.75 (0.02)</td>
</tr>
<tr>
<td>350</td>
<td>6.49 (0.03)</td>
<td>5.81 (0.03)</td>
<td>0.68 (0.03)</td>
</tr>
<tr>
<td>400</td>
<td>6.50 (0.03)</td>
<td>5.86 (0.05)</td>
<td>0.64 (0.06)</td>
</tr>
<tr>
<td>450</td>
<td>6.51 (0.12)</td>
<td>5.87 (0.11)</td>
<td>0.64 (0.03)</td>
</tr>
<tr>
<td>500</td>
<td>6.51 (0.12)</td>
<td>5.89 (0.03)</td>
<td>0.62 (0.01)</td>
</tr>
<tr>
<td>550</td>
<td>6.53 (0.08)</td>
<td>5.90 (0.07)</td>
<td>0.63 (0.02)</td>
</tr>
<tr>
<td>600</td>
<td>6.55 (0.08)</td>
<td>6.00 (0.07)</td>
<td>0.55 (0.02)</td>
</tr>
<tr>
<td>650</td>
<td>6.57 (0.07)</td>
<td>6.00 (0.04)</td>
<td>0.57 (0.10)</td>
</tr>
<tr>
<td>700</td>
<td>6.58 (0.10)</td>
<td>6.11 (0.12)</td>
<td>0.47 (0.04)</td>
</tr>
</tbody>
</table>

Values are average (standard deviation) of 5 specimens.
\(^{13}\) Cristoquick II (GC Dental Industrial Corp.)
The determination of peak temperature is difficult for small DTA peaks. This is often the case with the III-II transition of gypsum, particularly with the peak at around 350°C occurring in β-hemihydrate, although the difficulty may be overcome by various techniques including a high heating rate; the peak occurring in α-hemihydrate at around 200°C is generally more pronounced[20]. The average peak temperature was 387°C and the peak at around 200°C was not detected in the present study (Table 1, Fig.1). The result also showed the final transformation of gypsum from II-CaSO₄ to I-CaSO₄ at about 1,200°C, which was in accordance with the temperatures reported by various investigators[14]. The reverse reaction observed on cooling indicates that II-CaSO₄ is stable to ambient temperature and so occurs in nature as mineral anhydrite. I-CaSO₄ exists as a metastable phase before calcium sulfate decomposes to CaO and SO₃. The present TG result shows that I-CaSO₄ is stable well above 1,000°C until a significant mass loss of 1.2% occurs at about 1,350°C. That is, although silica is generally referred to as the refractory component, gypsum itself is potentially heat resisting up to at least 1,000°C. Gypsum-bonded investment is a century old material in dentistry but improvements for its performance are still being investigated today[3,20]. For further developments to use it at its maximum temperature, the present DTA-TG result will be of some significance. It has recently been reported that contamination of titanium occurs when it is laser-welded using a gypsum support prepared from a dental stone[20]. The present result indicates the possibility of attaining a temperature higher than 1,300°C to decompose gypsum in this welding method.

None of the wet investment specimens, including those heated to the highest specimen temperature of 700°C, reached the expected full mass decrease of 6.85% (Fig.2). This was a major finding of the present study, since the dehydration to anhydrite completed as low as 500°C in the previous dry specimens[3]. As described before, the amount of excess water was estimated and this was subtracted from the specimen mass measured at 30 min for the

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Table 3: Estimation of II-CaSO₄ formation (%) in cast investment specimens[3], either wet or dry, heated rapidly or slowly

<table>
<thead>
<tr>
<th>Specimen temperature (°C)</th>
<th>Rapid heating[2]</th>
<th>Slow heating[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>25.1 (4.9)</td>
<td>18.1 (4.0)</td>
</tr>
<tr>
<td>250</td>
<td>30.2 (13.8)</td>
<td>32.7 (0.9)*</td>
</tr>
<tr>
<td>300</td>
<td>31.6 (0.5)</td>
<td>39.5 (4.8)*</td>
</tr>
<tr>
<td>350</td>
<td>38.6 (1.7)*</td>
<td>40.2 (5.2)</td>
</tr>
<tr>
<td>400</td>
<td>42.0 (3.0)*</td>
<td>50.9 (6.3)*</td>
</tr>
<tr>
<td>450</td>
<td>42.0 (6.7)</td>
<td>54.6 (1.6)</td>
</tr>
<tr>
<td>500</td>
<td>43.8 (1.9)</td>
<td>57.3 (1.9)</td>
</tr>
<tr>
<td>550</td>
<td>44.0 (3.8)</td>
<td>58.2 (4.2)</td>
</tr>
<tr>
<td>600</td>
<td>50.1 (4.2)*</td>
<td>60.0 (2.7)</td>
</tr>
<tr>
<td>650</td>
<td>50.0 (2.5)</td>
<td>64.1 (1.6)*</td>
</tr>
<tr>
<td>700</td>
<td>57.1 (7.1)</td>
<td>71.4 (1.0)*</td>
</tr>
</tbody>
</table>

[1] Cristoquick II (GC Dental Industrial Corp.).
[5] dried to constant mass.

100% for x=1.7 and generally x/1.7.

Table 3 shows the degree of III-II transition estimated for the present wet specimens as well as for the dry specimens investigated in the previous study. The transition to II-CaSO₄ was 25% at 200°C and steadily increased to 57% at 700°C in the wet specimens. A similar transition process, ranging from 18% (200°C) to 71% (700°C), was found in the dry specimens exposed to the rapid heating. The transition process was quite different in the dry specimens heated slowly (5°C/min), as it did not start until a temperature above 350°C was attained. A large transition of 48% occurred between 350°C and 450°C. The transition at 400°C was significantly higher than that at 350°C in all specimen conditions. Even with this significant increase, the transition was only 3% between 350°C and 450°C in the wet specimens. The transition significantly increased at 650-700°C in the dry specimens heated both rapidly and slowly, giving similar final rates of 71% and 70%, respectively. This active transition at these high temperatures was not observed in the wet specimens and the final transition remained lower.
purpose of calculation in the present study. However, this water actually remained in the specimens and delayed the dehydration far from completion. The active III-II transition at 650-700°C, which was observed in the dry specimens, did not occur in the wet specimens either (Table 3). Instead, the III-II transition progressed 25% already at 200°C. This was another significant finding revealed by the comparison of III-II transition, since the transition at such a low temperature did not occur at all in the dry specimens heated slowly (Table 3).

In the dry specimens heated slowly, the III-II transition suddenly started at a temperature above 350°C and almost half of the transition (48%) was completed at 450°C (Table 3). This pronounced III-II transition over the short temperature range of about 100°C accords with the exothermic peak observed in the DTA of cast gypsum (Fig. 1). Since a finite time is required for an advancing temperature front to transverse a large sample, small samples are generally used in DTA to make a reaction completed in a short time and to detect a subsequent reaction without interference from the previous reaction. Small cast gypsum or investment specimens subjected to DTA do not contain much excess water due to their small sizes. It easily evaporates by the time the analysis is commenced. Furthermore, DTA specimens are often dried to constant mass for the simultaneous TG analysis. Therefore, the dehydration conditions of cast gypsum and investment samples in general DTA are similar to those prevailing in the dry calcination for the manufacture of \( \beta \)-hemihydrate, and this was taking place in the dry investment specimens heated slowly. Similar dry dehydration processes must have been occurring in small cast investment samples subjected to common laboratory dilatometry, as this was shown in the previous study.

The difficulty generally encountered in defining the exothermic peak accompanied by the III-II transition in \( \beta \)-hemihydrate is due to its sluggish reaction, while the relatively sharp peak observed with \( a \)-hemihydrate suggests that it has a structure with which \( 2\mathrm{CaSO}_4 \) forms rapidly\(^{21,26,27}\). Mitsuki and Kita also reported a large difference in the rate of III-II transition between \( a \) and \( \beta \)-hemihydrate\(^{28}\). The follow-up of mass recovery shown in Fig. 2 elucidates that the III-II transition in the wet specimens under the rapid heating is not as simple as that observed in the dry specimens heated slowly or that obtained from DTA analysis. A dynamic picture shown here is the mixed III-II transition at low and high temperatures. The 25% transition to \( 2\mathrm{CaSO}_4 \) at 200°C is due to the formation of \( a \)-hemihydrate, but the specimen also contains \( 3\mathrm{CaSO}_4 \) that does not transform to \( 2\mathrm{CaSO}_4 \) but rather rehydrates due to the formation of \( \beta \)-hemihydrate. The average mass recovery was highest at 250°C but similar amounts of recovery continued to 550°C (Table 2). The surface of the specimen exposed to the furnace temperature dehydrates easily and this vigorous removal of water at the surface is similar to the dry calcination of gypsum for the manufacture of \( \beta \)-hemihydrate. As the mass recoveries remained similar up to 550°C, the formation of \( \beta \)-hemihydrate at the surface appears to be fairly consistent for different specimen temperatures and thus for different heating times. The statistically significant increases in the III-II transition at 400°C, not only in the dry specimens but also in the present wet specimens, suggest the formation of a common surface layer subjected to a dry dehydration process.

Miura and Sasaki reported, in an XRD experiment of compacted \( a \)-hemihydrate powder, that a 20% transition to \( 2\mathrm{CaSO}_4 \) occurred at 190°C and this transition remained at this level even after a prolonged heating of up to 40 min\(^{29}\). They also found that this specimen expanded initially (about 0.2%) during the transition to \( 3\mathrm{CaSO}_4 \) and this did not change during the isothermal heating. The initial expansion is simply due to the increase in temperature, since no volume change is theoretically involved during the dehydration of hemihydrate to \( 3\mathrm{CaSO}_4 \) in \( a \)-hemihydrate\(^{30}\). The lack of shrinkage after this transition appears to be a characteristic of the III-II transition occurring in \( a \)-hemihydrate, although the transition is small (20%) in the compacted hemihydrate sample. The lack of shrinkage was also found in the wet investment specimens heated rapidly\(^{10}\), and the transition to \( 2\mathrm{CaSO}_4 \) in this case was much higher (42%) at 450°C, as shown in Table 3. As the starting material is not hemihydrate but dihydrate in the present study, it undergoes the process of possible expansion as a result of \( a \)-hemihydrate formation\(^{30}\). Since the dehydration was incomplete in the wet specimens, the excess water and also the water released from the gypsum binder created a condition favorable for the formation of \( a \)-hemihydrate to the highest specimen temperature. The \( a \)-hemihydrate formation is gradually progressing at an advancing temperature front to 700°C, leading to the final transition rate of 57%. Under this slow transition process, the ongoing expansion of the refractory and the expansion of \( 2\mathrm{CaSO}_4 \) already formed will effectively offset shrinkage, if any shrinkage exists during the rapid III-II transition in \( a \)-hemihydrate. In contrast, a substantial III-II transition of 48% occurred over a short temperature range of only about 100°C at 350-450°C in the dry specimens heated slowly. The transition for the same temperature range is only about 3% in the wet specimens, and this was attributed to the formation of \( \beta \)-hemihydrate at the specimen surface, as discussed before. The former large transition appears as the major investment shrinkage demonstrating its dry dehydration process\(^{10}\). It will be rare,
however, to use completely dried molds in actual dental casting. To the contrary, the slow dehydration process demonstrated in the present wet specimens appears to be further enhanced in molds confined in a lined casting ring \(^{20,31}\). This is the subject of a following report.

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