THE UNIVERSITY OF
SYDNEY

COPYRIGHT AND USE OF THIS THESIS

This thesis must be used in accordance with the provisions of the Copyright Act 1968.

Reproduction of material protected by copyright may be an infringement of copyright and copyright owners may be entitled to take legal action against persons who infringe their copyright.

Section 51 (2) of the Copyright Act permits an authorized officer of a university library or archives to provide a copy (by communication or otherwise) of an unpublished thesis kept in the library or archives, to a person who satisfies the authorized officer that he or she requires the reproduction for the purposes of research or study.

The Copyright Act grants the creator of a work a number of moral rights, specifically the right of attribution, the right against false attribution and the right of integrity.

You may infringe the author's moral rights if you:

- fail to acknowledge the author of this thesis if you quote sections from the work
- attribute this thesis to another author
- subject this thesis to derogatory treatment which may prejudice the author's reputation

For further information contact the University's Copyright Service.

sydney.edu.au/copyright

A STUDY OF INCREASED THERMAL EXPANSION OF GYPSUM-BONDED CASTING INVESTMENTS

Janis Anne McAloon
BDS (Hons) Sydney

DENTISTRY LIBRARY
UNIVERSITY OF SYDNEY

Thesis submitted in partial fulfilment
of the requirements for the degree of
Master of Dental Science

Department of Prosthetic Dentistry,
Faculty of Dentistry,
University of Sydney.

1989

CANDIDATE'S CERTIFICATE

This is to certify that the work presented in this thesis was carried out by the candidate in the Faculty of Dentistry, University of Sydney, and has not been submitted to any other university or institution for a higher degree.

Janis Anne McAloon, 1989

ACKNOWLEDGEMENTS

I would like to thank Professor Iven Klineberg, Head of the Department of Prosthetic Dentistry, for permitting me to use the research facilities within the department, and for his wisdom in guidance.

I will always be deeply indebted to Dr. Toshiko Mori, Director of the Biomaterials Research Unit, Department of Prosthetic Dentistry, for her selfless and diligent assistance in the preparation of this thesis. It has been an honour and a privilege to have studied under her supervision.

My sincere gratitude goes to Dr. Robin Hawthorn for persuading me to embark upon this research, and for instigating my interest in dental casting.

Thanks are also due to Dr. Erica Morey for the development of the casting experiments and for her assistance in the laboratory procedures.

としこさんの忍耐強く絶え間のない御協力に心から感謝致しております。

CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1 - LITERATURE REVIEW

1.1 Introduction

Thermal expansion, that is, an increase in length or volume upon rise in temperature, is a nearly universal property of all solids. Therefore, a dental gold alloy cast into a mould contracts on cooling. Some way of compensating this contraction must be provided if it is intended to reproduce the size of a wax pattern invested in the mould.

The concept of compensating the contraction of cast metals is found in the paper published in 1907, by Taggart, the person credited with being the first to introduce the casting process as we know it today. Taggart knew that different metals possessed different amounts of contraction on cooling from their molten state, and yet he observed that inlays cast with different metals all seemed to fit the cavity from which the pattern was taken. He thought that either the metals were prevented from undergoing their full contraction because of his technique of maintaining casting pressure for a few moments, or that the expansion of the mould was equalising metal contraction.

Various methods have been proposed to provide a proper amount of compensation for dental casting gold alloys. The method most extensively used for crown and inlay casting employs the thermal expansion of gypsum-bonded investments and is the type to be discussed in this study.

1.2 Dimensional Changes of Gold and Its Alloys

It is the general view in dental casting that contraction of liquid metal in the mould can be readily compensated by adding more liquid metal from the crucible, until the solidification temperature is reached (Price, 1908, 1911; Coleman, 1928; Earnshaw, 1958; Greener, Harcourt and Lautenschlager, 1972; Phillips, 1982). On the other hand, compensation of the contraction of the solidified metal, as it cools from the solidus to room temperature, has been one of the major interests in this discipline. The

latter has been studied by various measurements of either thermal expansion or contraction.

An experimentally simple and reliable means of measuring thermal expansion is the push-rod dilatometer method (Touloukian, et al., 1977), in which the expansion of a specimen is transferred out of the heated zone of a furnace to an extensometer, by means of a rod of some stable material. A value recommended for the linear expansion of gold from room temperature to 1027 °C is 1.76 per cent (Touloukian et al., 1977). The temperature range is not to melting temperature (1064 °C). This is because measurement becomes increasingly difficult as the melting temperature is approached. The thermal expansion value at the melting temperature can only be calculated by extrapolating the expansion values obtained at lower temperatures to that temperature. Recently, Finger and JØrgensen (1980) measured the thermal expansion of twelve dental gold alloys by the push-rod dilatometer method. Each specimen, 25 mm long and 6 mm in diameter, was annealed and heated to a temperature which was approximately 50 °C below its solidus temperature. The mean thermal expansions calculated by extrapolation, for the range room to solidus temperature, fell between 1.68 and 1.80 per cent.

Methods of measuring thermal expansion can be divided into two classes: (1) relative methods, in which the expansion of the material being investigated is measured relative to that of another material; and (2) absolute methods, in which the expansion is measured directly (Touloukian et al., 1977). The push-rod method becomes absolute when the expansion of a specimen is measured by two rods that penetrate the hot zone of a furnace in a direction perpendicular to the specimen axis, instead of in line with it. This is the Baudran or scissors dilatometer (Touloukian et al., 1977).

There have been only a few papers in which absolute methods were used in measuring thermal expansion of dental casting alloys. An absolute method, the twin-telemicroscope (comparator) method, was used by Coleman (1926, 1928). This method is most useful for measuring expansion of large specimens at high temperatures. The best results are obtained when the two microscopes are rigidly mounted to a bar of low expansion material and the length change is

measured with filar micrometer eyepieces (Touloukian et al., 1977). Coleman, using rods 30 cm long and 1 cm in diameter, measured the thermal expansion of gold and a gold alloy from 25 to 1014 and 860 °C, respectively. These were the highest temperatures at which the samples remained rigid. This particular alloy (90Au - 10Cu) melts over the range 940 to 926 °C. By extrapolation, Coleman gave thermal expansion values of 1.76 per cent for gold and 1.62 per cent for the gold alloy. It is interesting to note that the former value (extrapolated to 1064 °C) is the same as the reference value recommended (to 1027 °C) by Touloukian and as such is slightly low.

Long before Coleman's measurement, Price determined the linear expansion of gold first by the push-rod method (1908) and then by a single telemicroscope (end comparator) method (1911). The expansion values determined by the latter method agree, up to about 1000 °C, with Touloukian's reference. However, Price corrected the data for error caused by radiation from the specimen and then calculated the expansion value at melting point by extrapolation. A value of 2.20 per cent was finally obtained. This was very close to his value of 2.25 per cent obtained by the previous push-rod method.

The correction appears to be inadequate as the value is considerably higher than the reference value (1.76 per cent) to 1027 °C. Expansion values determined by extrapolation depend on the accuracy of the measurement near the sagging point. Similar difficulties were also probably encountered by Coleman, as evidenced by his slightly low value of 1.76 per cent by extrapolation to 1064 °C compared with the reference value 1.76 per cent to 1027 °C. It is questionable whether the extrapolation to melting point is essential, since the contraction of a gold alloy can be easily altered at such high temperatures where yielding of the alloy could occur (Kasahara, 1984).

Another absolute method of measuring thermal expansion is to utilise the fact that liquid surfaces have a tendency to assume a shape that minimizes their surface area. Hence, liquid droplets take on the shape of a sphere, although external forces commonly act to alter or flatten this ideal shape. A method for measuring surface tension, the Sessile drop method, involves the measurement of the maximum

diameter and the distance between this diameter and the summit of a drop of liquid resting on a surface (Bickerman, 1970). The Sessile drop method can also provide the density of a material, if an accurate method can be established for the calculation of droplet volume. Refinements such as multiple recordings of droplet shape by rotation and integral area summation of droplet shape by image analysis were attempted by Kawai, Hasegawa and Kato (1982).

The refinements gave a volumetric contraction of 5.2 per cent (linearly 1.73 per cent) of gold during the solidification (Kawai, 1982). Surprisingly, Price (1911) gave a similar value, for the linear contraction of gold upon solidification, of 1.64 per cent. Kawai also gave a value for volumetric contraction of 5.5 per cent (linearly 1.83 per cent) from melting to room temperature for gold. This value is comparable to the reference value, 1.76 per cent (1027 °C).

More commonly seen in the dental literature is a type of relative method of measuring the contraction of casting alloys. Since the measurement simulates the casting process, the contraction here is known as "casting shrinkage". Measurements of this type, where the size of a casting is compared with that of the mould of known dimensions in which the casting solidifies and cools have been called, in the dental literature, "direct measurements" of casting shrinkage (Hollenback and Skinner, 1946) or measurements of "actual casting shrinkage" as defined by Earnshaw (1958).

After determining the expansion of gold and a gold alloy (90Au - 10Cu) by the comparator method, Coleman (1926, 1928) carried out "casting shrinkage" measurements for gold and this alloy. Casting into an investment in a steel flask of known dimensions, he determined the shrinkage of the gold alloy (8.3 cm long) rod to be about 1.25 per cent.

Since this value differed from that he had obtained using the comparator method (1.62 per cent), Coleman (and Souder, 1927) suggested two possible explanations. Either the shrinkage was being restricted by frictional interlocking between the casting and the walls of the mould, "stretching" the casting as it cooled, or molten metal entered after the peripheral areas of the casting had

solidified. Coleman appears to indicate that the "casting shrinkage" value thus obtained is influenced by the factors entering into the casting process. As such it should be considered variable. His statement, that variations in casting pressure or mould temperature from 40 - 300 °C had very little effect on the value determined (1.25 per cent), obscures this crucial point.

It seems that there was a general acceptance of Coleman's figure, 1.25 per cent, as a fixed entity. It was used as the value to be compensated in making small dental castings (Souder, 1927, 1930). Since no single investment was available, at the time, to fully compensate for the contraction of gold alloys, various methods of partial compensation were put forward. Total of the partial compensations, implemented at different stages of the casting process, always needed to be 1.25 per cent. Van Horn (1930), while having much to say about the method of compensation, accepted the amount of gold contraction without question. A dental casting investment (75 per cent cristobalite and 25 per cent plaster of Paris) developed at the American National Bureau of Standards in 1930 was said, at the time of its introduction, to possess "sufficient thermal expansion to compensate completely for....the 1.25 per cent casting shrinkage of gold" (alloy) (Taylor, Paffenbarger and Sweeney, 1930). Two patents for dental casting investments lodged in 1933 on behalf of major American dental companies contain statements that the expansion of an investment should be around 1.25 per cent to offset the shrinkage of (gold alloy) castings during cooling (Moore, 1933; Van Allen, 1933). Neither Taylor nor the patent holders cited a reference for the 1.25 per cent shrinkage.

The fact seems to have been universally known and having been discovered, "it became a simple mathematical formula to develop a technique....to compensate for the shrinkage of gold" (Hollenback, 1943). It appears that the researchers at the time regarded Coleman's "casting shrinkage" value as a fixed entity.

Measurements of "casting shrinkage" continued. Hollenback and Skinner (1946) tried to measure it by using specimens more closely approximating the size of an inlay than the 8.3 cm long specimen cast by Coleman. Their

investment mould was kept at room temperature to avoid dimensional changes. Casting shrinkage was measured to be 1.67 ± 0.02 per cent for gold and 1.50 ± 0.01 per cent for a 22 carat dark gold alloy.

Earnshaw (1960) cast rods 6.35 cm long and 0.32 cm in diameter into a cool investment mould, and measured the shrinkage of gold to be 1.74 ± 0.03 per cent. He stated that this value agreed closely enough with the 1.67 per cent obtained by Hollenback and Skinner, and that differences might be due to differences in experimental methods. Earnshaw's result is close to Touloukian's reference value, 1.76 per cent (1027 °C).

1.3 Development of Gypsum-bonded Investment

Gypsum moulds were used initially for gold castings. Price (1908) listed plaster of Paris as an investment material, reporting that its maximum thermal expansion at 177 °C was between 0.30 and 0.45 per cent. Plaster of Paris is of course unsuitable for accurate casting, since cast gypsum undergoes rapid contraction after this initial small expansion (Price, 1908; 1911; Taylor, Paffenbarger and Sweeney, 1930; Volland and Paffenbarger, 1932; Phillips, 1982; Mori, 1986).

The investment Taggart preferred at the time of his paper (1907) was Peck's which, according to Price (1908), expanded about 0.8 per cent at 538 °C. By 1908 Taggart had marketed an investment under his own name. It was regarded as one of the best investments of the day, expanding 0.85 per cent at 538 °C (Price, 1908), or 0.77 per cent (Shell, 1960). It contained 37.5 per cent plaster of Paris, 57.5 per cent silica and 5 per cent graphite (Shell, 1960).

In 1930 Taylor, Paffenbarger and Sweeney measured physical properties of thirty eight commercially available investments. They consisted of a mixture of plaster of Paris (19 - 54 per cent), silica in the form of quartz (78 - 42 per cent) and other additives such as boric acid and graphite (up to 5 per cent), and they were divided into three classes based on plaster content (and thus thermal expansion).

The investments containing over 40 per cent plaster of Paris expanded about 0.1 - 0.2 per cent when heated to about 100 - 300 °C, but then underwent marked contraction. This may explain the fact that mould temperature 40 - 300 °C had little effect on the "casting shrinkage" determined by Coleman (Section 1.2). The second group containing about 30 - 40 per cent plaster of Paris expanded about 0.1 - 0.2 per cent initially, contracted and then showed a second expansion (about 0.2 - 0.8 per cent at 700 °C). The third group, "high silica investments", contained a high proportion of quartz and less than 30 per cent plaster. They expanded more or less continuously (up to about 0.9 per cent) to casting temperature but were weak at high temperatures.

Weinstein (1929) patented the use of boric acid to increase the thermal expansion of gypsum-bonded investment and to increase its high temperature strength. It was still used in some commercially available investments in 1954 (Glasson, Sweeney and Shoonover). Ten out of thirty-eight investments tested by Taylor, Paffenbarger and Sweeney (1930) contained 0.2 to 1.8 per cent boric acid. Later, Moore (1933) obtained a patent on the use of sodium, potassium and lithium chlorides to increase the thermal expansion of gypsum-bonded investment. Sodium chloride was found to be most effective of the three, and Moore suggested a concentration in the investment powder of 0.8 per cent.

The 1930 survey by Taylor, Paffenbarger and Sweeney, together with that made by Coleman two years previously (on eleven commercially available investments), and an investigation carried out by Volland and Paffenbarger (1932) show that, up to 1930, no investment possessed sufficient thermal expansion to compensate for the 1.25 per cent "casting shrinkage" determined by Coleman (Section 1.2). Setting expansion, although known, was not considered an important part of investment expansion, most probably because casting rings at the time were unlined. The only way to make an accurately fitting crown was to augment thermal expansion of an investment by utilising thermal expansion of the wax pattern, an idea initially proposed by Van Horn in 1910.

A breakthrough came when an investment containing 75 per cent cristobalite and 25 per cent plaster of Paris

was developed at the American National Bureau of Standards. Its W/P ratio was 0.40 and it was said at the time of its introduction to possess sufficient thermal expansion to compensate completely for the 1.25 per cent gold alloy "casting shrinkage". The first data on this material appeared in the 1930 survey by Taylor, Paffenbarger and Sweeney as an experimental investment; its setting expansion was 0.34 per cent and thermal expansion 1.27 per cent at 700 °C (W/P ratio 0.42). The thermal expansion exceeded by far those of the thirty eight investments available at the time.

The high thermal expansion of this investment necessitated provision of a cushioning layer in casting rings and Taylor, Paffenbarger and Sweeney (1930) described the application of a wet asbestos liner for use with this new investment containing cristobalite (cristobalite investment). Previously, thermal expansion of investment containing quartz (quartz investment) had been generally small enough to be accommodated without a liner by the thermal expansion of ring materials, while the setting expansion would have been almost completely restricted. The thermal expansion curve of the new investment was relatively flat in the range 538 to 871 °C and Volland and Paffenbarger (1932) drew attention to the excellent range of temperatures at which castings could be made. They showed that castings made at various temperatures over this range all fitted steel MOD dies. It appeared that the ideal investment had been found.

Another important development was taking place around this time; a wet-calcined (autoclaved) plaster marketed under the name Hydrocal was developed in 1933 by Randel and Dailey (1933). Wet-calcined plaster (more commonly known as dental stone) and dry-calcined plaster (plaster of Paris) are different in the amount of water required to give a workable mix. Typical W/P ratios are 0.25 - 0.30 for wet-calcined plasters and 0.50 for dry-calcined plasters, and the difference results in significant strength increases (two to three times) of the cast gypsum specimens prepared from the former (Earnshaw, 1978; Combe, 1981). It is thought that the traditional plaster of Paris in dental casting investments has been replaced by dental stone (Shell, 1960; Phillips, 1982). However, it is not generally

known which type of hemihydrate is used in a given commercial investment.

Differences between wet- and dry-calcined plasters, when they are heated, have been the subject of many papers and a considerable number have shown that the two types of hemihydrate can be distinguished by differential thermal analysis (Powell, 1958; Fleck et al., 1960; Kuntze, 1965; Holdridge, 1965; Miyazaki, 1966a, 1966b; Ball and Urie, 1970; Bushuev and Borisov, 1982). The method may reveal the type of hemihydrate incorporated in commercial gypsum-bonded investments.

The first commercial cristobalite investment (Kerr Cristobalite investment, W/P = 0.40) appeared in a paper by Van Horn (1934). It was said to possess a thermal expansion of 1.35 per cent at 649 °C. The type of hemihydrate, plaster of Paris or dental stone, was not known. Van Horn found that castings made from MOD wax patterns were 0.3 per cent undersized and he continued to recommend slower setting investments that allowed expansion of the wax pattern by means of a warm water bath. He also showed a thermal expansion curve of an experimental investment with even higher thermal expansion at very high temperatures. This investment was too weak for ordinary dental use. Van Horn expected the 25 - 30 per cent plaster content of Kerr Cristobalite investment to make it too weak. Despite this and the reports that "casting shrinkage" of gold alloys is in the range 1.67 to 1.74 per cent (Hollenback and Skinner, 1946; Earnshaw, 1960), this investment material has been widely used until today, with little change in basic properties such as thermal expansion and W/P ratio (Sybron/Kerr, 1985). This is probably because the concept of combining setting and thermal expansions has been widely accepted (Souder, 1927; Coleman, 1928; Van Horn, 1934; Greener, Harcourt and Lautenschlager, 1972; Phillips, 1982).

1.4 Investment Expansion and Casting Accuracy

Scheu (1932) was the first to discover the phenomenon of enhanced setting expansion of gypsum-bonded investment in the presence of water; in 1933 he named it "hygroscopic expansion". It was not until 1935 that attention was drawn to the fact that some form of enhanced expansion was

unintentionally occurring in casting rings lined with wet or dry asbestos (Scheu, 1935). Scheu demonstrated that the setting expansion of a cristobalite investment was least when cast against a glass slab, greater when cast against dry asbestos, and greatest against wet asbestos.

Hygroscopic techniques have been generally discredited as many investigators have found that they cause considerable distortion of invested wax patterns (JØrgensen, 1953; Suffert and Mahler, 1955; Fusayama, 1959a, 1959b; Mumford and Phillips, 1958a; Van Aken, 1961; Mahler and Ady, 1963). It is also generally considered that expansion and/or distortion of wax patterns invested in casting rings lined with wet asbestos liners, although much less than that caused by immersing investments in water, is significant (Fusayama, Sakurai and Suzuki, 1957; Fusayama, 1959a; van Aken, 1961; Shell, 1969).

For this reason, many authors have recommended reducing investment setting expansion (Skinner, 1933; Fusayama, Sakurai and Suzuki, 1957; Mumford and Phillips, 1958a; Fusayama, 1959a; van Aken, 1961; Earnshaw, 1969a; Finger and JØrgensen, 1980; Finger, 1980) or reducing its effect by using a waterproofed lining (Fusayama, 1959a, 1959b; van Aken, 1961; Hanari, 1967; Shell, 1969). For this to be possible, an investment is required with sufficient thermal expansion to fully compensate for the contraction of gold alloys.

Research work by Fusayama, Earnshaw, and Finger and JØrgensen may represent the efforts made to increase the thermal expansion of gypsum-bonded casting investment.

For Fusayama, providing for cement space and minimising investment setting expansion were an essential part of his thinking (Fusayama 1959a, 1959b, 1962; Fusayama et al., 1963, 1964). Using a figure of 2 per cent for the shrinkage of full gold alloy crowns, he concluded that this would also be the ideal amount of total expansion for an investment (1.95 per cent thermal expansion and 0.05 per cent setting expansion). This figure was completely unrealistic; such an investment was not available (Fusayama, 1959a; 1959b; 1962).

Fusayama stated that the best way to compensate for the lack of thermal expansion was to use a slightly increased

setting expansion. During his visit to the United States in 1956 and 1957, he used an experimental investment (Ransom and Randolph Company) of 0.22 per cent setting expansion and 1.80 per cent thermal expansion (Fusayama, 1959b). Crowns (William's Hard Inlay Gold) made with this investment showed a dimensional change from the wax pattern of -0.04 per cent. Fusayama put forward another method to compensate for the lack of high thermal expansion, an expanded stone die; he suggested that if a 0.5 per cent expanded stone die was used, then it would only be necessary to have an investment with 1.5 per cent total expansion for full crowns. The materials he recommended to achieve this expanded die were an alginate impression material and a high setting expansion stone (Fusayama, 1959b; 1962).

After his return to Japan, the best investment available to him at the time had a total expansion of 1.6 per cent (thermal 1.32 per cent, setting 0.28 per cent). From his calculations (Fusayama et al., 1963) it can be deduced that the crowns made with this investment would not have fitted back onto their stone dies. Nevertheless, they should have provided a 10 - 20 micron cement space on their tooth preparations, as the preparations should have been smaller than the stone dies. If the factor of the expanded stone die were to be removed, then the dimensional change of the cast crown from the wax pattern would have been in the order of -0.3 per cent, which is the same as that Van Horn obtained with Kerr Cristobalite investment (1.35 per cent thermal expansion) in 1934 (Section 1.3).

It is obvious that Fusayama was searching for a higher thermal expansion investment but never found it. The restriction imposed by minimising the amount of investment setting expansion had forced Fusayama to look elsewhere for ways to enlarge the casting. Even including his "expanded working die", prior to introducing die relief, he still only had 10 - 20 microns of space for cement which, as he later discovered (Fusayama, Ide and Hosoda, 1964), caused the crowns to incompletely seat during cementation. In 1964 Fusayama resorted to die relief to increase the cement space.

Earnshaw studied the effect of additives on the thermal expansion of gypsum-bonded casting investments (Earnshaw, 1961, 1975), the ultimate objective being the development of

an investment with a very low setting expansion and a high thermal expansion. In 1961, he increased the thermal expansion of a commercial cristobalite investment from 1.1 per cent to 1.5 per cent at 700 °C by incorporating a 10 per cent glycerol solution instead of water. In 1975, he studied the effect of NaCl which was patented by Moore in 1933 (Section 1.3). An experimental investment with 0.2 per cent NaCl added to the powder, combined with the 10 per cent glycerol solution, exhibited up to 1.7 per cent thermal expansion at 700 °C. He also studied the effects of boric acid which was patented by Weinstein in 1929 (Section 1.3); he found that it had a similar effect to that of glycerol.

Finger and JØrgensen (1980) developed an experimental high thermal expansion (1.7 per cent) investment. The high amount of cristobalite and quartz together with a combination of glycerol and boric acid produced the high thermal expansion, while the addition of sodium citrate and potassium citrate kept the setting expansion low (0.05 per cent). The investment was strong and was for use without a steel casting ring. It is not commercially available.

High thermal expansion investments have never materialised. Investments having a thermal expansion of about 1.25 per cent, typically Kerr Cristobalite Inlay investment, have generally been used until today. It appears that this investment, using one layer of wet Kerr asbestos, has been producing gold alloy crowns of good dimensional accuracy. Morey (1986) found that the castings thus produced were very close to the size of the original wax pattern, 0.01 ± 0.06 per cent. The result is relatively high compared with those obtained by Van Horn (-0.3 per cent for a 1.35 per cent thermal expansion) and by Fusayama (-0.3 per cent for a 1.32 per cent thermal expansion) as described previously. The total linear expansion of Kerr Cristobalite investment cast against wet asbestos lining material has been reported to be 2.3 per cent (setting 1.15 per cent, thermal 1.15 per cent) (Earnshaw, 1982).

It appears that a slightly higher thermal expansion has been achieved. Using GC Cristobalite investment (thermal expansion value, 1.45 per cent) with a waterproofed asbestos liner (0.8 mm thick), Nakanishi (1975) was able to produce crowns which were larger (on average 0.15 ± 0.17 per cent at the occlusal, and 0.5 ± 0.21 per cent at the shoulder) than

the metal dies. The thermal expansion value of this investment is 0.2 per cent higher than that of Kerr Cristobalite investment, when the values provided by the manufacturers are compared.

Many investigators have shown that a space of 30 - 50 microns is essential for optimal seating of crowns after cementation (Jlg, 1959; Haupfaul, 1960); crowns having the so called frictional fit (presumably fitting to within 5 - 10 microns) produce a thick cement layer at the shoulder (Fusayama, Ide and Hosoda, 1964; Nakanishi, 1975). On a 10 mm crown preparation, a space of 30 - 50 microns represents a 0.6 - 1.0 per cent dimensional change from the size of the tooth preparation. On this basis, and assuming minimal dimensional change in the size of the wax pattern, a goal of establishing a 0 per cent dimensional change from the metal die in the laboratory experiment is clinically valid, only if a method of providing the 0.6 - 1.0 per cent (10 mm preparation) cement space is also established.

In the laboratory, the 0 per cent dimensional change from the die is the minimum requirement for a cast gold crown, since the casting should be at least large enough to fit back onto the die on which the pattern is made. Although the method of obtaining the 0.6 - 1.0 per cent cement space has been little studied, it appears that some allowance for cement space is usually achieved because of the combined effect of impression material shrinkage and stone expansion. JØrgensen and Finger (1979) filled this discrepancy between laboratory and clinic by introducing the term, a corrected master die; their aim is to obtain a slide fit (close to the 0 per cent dimensional change) on a relieved die, to produce a loose fit on the tooth preparation.

The use of asbestos ring liners has been regarded as a health risk (Priest and Horner, 1980; Yli-Urpo, Øilo and Syverud, 1982) and they have generally been replaced by alternative materials. These are of two types, cellulose and ceramic. The former readily absorb water and like asbestos are pre-wetted, while the latter, at atmospheric pressure, do not absorb water and are normally used dry (Nasu and Noguchi, 1982; Morey and Earnshaw, 1987). Morey (1986) showed that the 0 per cent dimensional change achieved with Kerr Cristobalite Inlay investment and

asbestos (0.4 mm thick) was altered to -0.1 to -0.2 per cent with ceramic liners. Crowns were further undersized when investing was carried out under atmospheric pressure; the original W/P ratio of the investment mix was greatly reduced as the water in the mix was absorbed by ceramic liners during vacuum investing. It is required to achieve the 0 per cent dimensional change with an asbestos substitute.

1.5 Measurement of Investment Expansion

The hydration of plaster or stone to form gypsum, when a gypsum-bonded investment is mixed with water, is responsible for most of the setting expansion. The setting investment increases in volume from the time of the disappearance of the aqueous phase into the pores formed by growing gypsum crystals, which is observed as the time of loss of gloss on the surface of the mix (Earnshaw and Marks, 1964).

In the laboratory casting process, the setting of investment is complicated by a number of factors. Asbestos casting ring liners have traditionally been wetted to prevent absorption of water from the investment (Taylor, Paffenbarger and Sweeney, 1930; Earnshaw, 1978). Wet asbestos liners cause additional water to be made available to the setting investment mix, resulting in increased setting expansion (Scheu, 1935). Absorption of water from the mix by dry asbestos liners lowers the effective W/P ratio of the mix, altering the setting time (Ohno et al., 1970). Dry liners then function as wet liners; the absorbed water is available to the setting investment which results in increased setting expansion (Ohno et al., 1970; Earnshaw, 1978, 1988). Vacuum investing also changes the W/P ratio when used with ceramic liners, which then function like any other wet liner (Morey, 1986).

Water in the liner acts in the same way as if it had been added to the original mix, that is, it increases the W/P ratio (Macasaet and Dickson, 1962; Earnshaw, 1967; Ohno et al., 1970). This means that where wet liners are used, the subsequent thermal expansion of the set investment is correspondingly reduced (Earnshaw, 1988). Laboratory measurements of investment specimens prepared separately for thermal expansion measurement do not reflect this effect.

This shows the importance of conducting measurements of setting and thermal expansion in sequence on the same specimen.

The method used for measuring setting expansion, described in Australian Standard 2795 (The Standards Association of Australia, 1985) consists of a V-shaped trough apparatus (51 mm long) lined with ring lining material. One end of the trough apparatus is designed to allow free expansion of the setting investment and is connected to an instrument which measures the horizontal movement due to expansion. The amount of measuring force during the setting (and thermal expansion) tests is important (JØrgensen, 1953; Earnshaw, 1964, 1966; Jones and Wilson, 1968). The total measuring force exerted on the specimen during the setting expansion test is in the range Ø.4 - Ø.6 kPa in the Australian Standard. A free expansion is also possible through the top surface of the specimen. An alternative method has been to measure the expansion in investment placed in casting rings (Mumford and Phillips, 1958a, 1958b; Fusayama, 1959a; Ady and Mahler, 1961).

The Australian Standard does not set any particular requirement for the value of setting expansion; rather it demands that the minimum total (combined setting and thermal) linear expansion of gypsum-bonded investment is 1.5 per cent for the thermal expansion type for gold inlays and crowns. The American Dental Association Specification No. 2 for casting investment for dental gold alloy (American Dental Association, 1974a) requires that the setting expansion in air be between Ø.Ø and Ø.5 per cent at 2 hours; the total expansion should be between 1.3 and 2.Ø per cent.

The two Standards are quite different in relation to the method of measurement of setting expansion. The American Specification uses the traditional method first described by Coleman (1926, 1928) in which the movement of markers is measured with a comparator microscope. This ensures that no restrictive force is applied to the setting investment by the measuring device. The markers are placed approximately 30 cm apart on a large specimen in a V-shaped trough which is lined with rubber dam. Some restraint is, however, exerted on the setting expansion by the frictional resistance of lining material (Skinner and Degni, 1957). In contrast to the Australian Standard, the American

Specification does not require that the setting and thermal expansion tests be conducted in sequence on the same specimen.

The apparatus used for measuring the linear thermal expansion of gypsum-bonded investments, described in the Australian Standard, is a vertically disposed vitreous silica "push rod" dilatometer. Setting expansion having been measured, the 50 mm investment specimen is transferred to the dilatometer. Total measuring force during the thermal expansion test should be in the range 0.4 - 0.6 kPa. For investments containing cristobalite the heating rate is reduced to 1 °C/min from 5 °C/min between 200 and 300 °C to ensure that the large expansion due to the inversion of cristobalite does not induce cracking of the investment specimen. The American Specification uses a similar method. However, specimen length is 20 cm and heating rate is 5 °C/min over the range 200 - 500 °C. No requirement is made regarding measuring force.

It is evident that the Australian Standard, being a more stringent testing procedure, provides values which are more reliable and can be more closely related to the practical situation.

CHAPTER 2 – PURPOSE AND SCOPE OF THE INVESTIGATION

The first part of the investigation is to compare two commercial cristobalite investments. One is the oldest of this type, Kerr Cristobalite Inlay investment (Section 1.3); the other is of quite recent origin and appears to have an increased thermal expansion, GC Cristobalite investment (Section 1.4). The investment powders are studied by means of differential thermal analysis, as this may identify the type of calcium sulphate hemihydrate incorporated in the investments (Section 1.3).

In the light of the investigation made by Nakanishi (Section 1.4), GC Cristobalite, which according to the manufacturers has an increased thermal expansion of about 1.45 per cent, may fulfil the goal of achieving a 0 per cent dimensional change from the wax pattern, when used with a ceramic liner. Both Kerr and GC investments, being overseas products, are not likely to be comparable to one another in terms of the manufacturers' values for setting and thermal expansions. It is also likely that the values may not apply to the behaviour of the investments in the presence of liners under a particular mixing condition. Therefore, the total linear expansion of the two investments is measured with a ceramic liner (Kaoliner) under conditions which best relate to the practical situation, that is, in accordance with Australian Standard 2795 (Section 1.5). This forms the second part of the investigation. Since ceramic liners absorb little water from the investment mix (Section 1.4), measuring the setting expansion in the presence of the liner may not be of such practical significance as it is, for instance, when asbestos liners are used (Section 1.5). Consequently, control measurements made on specimens cast against Teflon sheet are included.

Finally, after ascertaining the amount of increased thermal expansion, its effect on the dimensional accuracy of gold full crown castings is studied using the two investments and the ceramic liner.

CHAPTER 3 - EXPERIMENTAL METHODS

3.1 Materials

Two gypsum-bonded investments were used throughout the study. They were Kerr Cristobalite Inlay investment* (hereafter KCI), and GC Cristobalite Micro investment** (hereafter GCM). Data provided by the manufacturers are listed below. One brand of casting ring liner, Dentsply Kaoliner***, 1 mm thick, was used throughout the study.

	KCI	GCM
Recommended W/P ratio	0.38 - 0.42	0.33
Setting Time (mins)	10 - 14*	15
Setting Expansion (%)	0.20 - 0.25*	0.40
Thermal Expansion (700 °C) (%)	1.25*	1.47

* W/P = 0.40

3.2 DTA-TG Experiment of Investment Powder

Differential thermal analysis (DTA) and thermogravimetry (TG) equipment† was used in this experiment.

A quantity of 200 ± 1 mg of the investment powder was weighed†† for each analysis. The same weight of ignited reagent-grade alpha-alumina was used as the reference material. The test sample and the reference material were placed in separate compartments (60 x 12 mm) of a platinum sample holder, each of which had a recess at the base to accommodate the hot junction of a thermocouple.

The powders were heated to 700 °C at a heating rate of 10 °C/min. The difference in temperature between the inert reference material and the sample was recorded as a DTA

---

* Sybron/Kerr Products, USA. Batch number 1137.
** GC Dental Industrial Corp., Japan. Batch number 11881161.
*** Dentsply Int. Inc., USA. Batch number 111578.
† Thermoflex, Rigaku Denki Ltd., Japan.
†† AE Balance, 163, Mettler, West Germany.

curve. Any inclination of the balance beam, caused by the mass change of the test sample, is detected by a photoelement and electrically amplified. The current in the control coil which is used to eliminate the inclination of the beam, was recorded as a TG curve. The accuracy of the DTA-TG equipment was 0.3 per cent of full scale (± 3 °C for a full scale of 1000 °C and 0.6 mg for a 200 mg full scale).

At least five analyses were made for each investment powder. Peak temperature was determined for each endothermic and exothermic reaction appearing on the DTA curves and mass decreases at various temperatures were calculated from the TG curve for each sample.

3.3 Measurement of Investment Expansion

Setting and thermal expansions of the two investments were measured in accordance with Australian Standard 2795 (The Standards Association of Australia, 1985).

The apparatus for the measurement of setting expansion consisted of a brass trough of V-section, with one end closed and the other fitted with a movable partition. With this in place, the length of the closed trough was 51 mm. Specimen expansion was transmitted via an austenitic stainless steel shaft, to a linear transducer*. Its output, connected to a Y-T recorder**, was calibrated with a micrometer to provide a continuous expansion curve against time. The measuring force was 0.5 N, which exerted a pressure of 1.8 kPa on the expanding specimen.

The ceramic liner was cut into rectangular pieces, 51 x 26 mm. Two were laid along the walls of the trough (rough side facing outwards) and the third was put aside for later use. A plate, 1 mm thick, made of heat resisting alloy (Inconel 600), in the shape of an equilateral triangle with sides of 25 mm, was placed in the trough against the movable partition. The plate formed one end of the set specimen and when in position, gave a specimen length of 50 mm.

---

* 050 DC-D, Schaevitz Engineering, USA.
** Type 3066, Yokogawa Electric Co., Japan.

A standardized mixing procedure was followed using the recommended W/P ratios (Section 3.1). A W/P ratio of 0.40 was employed for KCI investment. The investment powders, homogenised in a powder mixer*, were mixed with distilled water, always using 50 g powder. Water (20 ml for KCI and 16.5 ml for GCM) was dispensed to an accuracy of 0.01 ml** and the powders were weighed to 0.01 g***. Mixing of the investment was done mechanically under vacuum using a Degussa mixing bowl driven by a Whip-Mix Combination Unit with a rotational speed of 425 r/min. The investment powder was sifted into the water, the powder and the water then were mixed by hand at a rate of 3 turns/sec for 10 seconds. During the next 10 seconds the mixing bowl was assembled and mechanical mixing under vacuum (96 KPa = 720 mmHg) was performed for the following 20 seconds.

Investment material was poured into the trough to the top of the Inconel plate. The third piece of lining material was then placed carefully on top of the mix. The whole assembly was covered by a tightly fitting Perspex lid. The recorder had been calibrated to a fixed range of 500 microns/10cm and since the specimens were 50 mm in length, the Y-axis corresponded to 1 per cent/10cm. Expansion of the specimens was determined to the nearest 0.01 mm, over a two hour period, and was expressed as a percentage of the original length of the specimen. Zero time for these measurements was set at time of commencement of mixing. At least three measurements were made for each investment.

The time of loss of gloss of the investment mix was recorded as a measure for the start of setting expansion. The mixing bowl containing the remainder of the investment was placed under an illuminator which emitted a collimated beam of light from an incandescent lamp. The time for the loss of gloss was taken when the reflection of the lamp filament could no longer be seen on the surface of the unset mix.

After each setting expansion measurement, the specimen was freed from the trough, the liners were removed from its sides and it was dried under ambient conditions (20 ± 1 °C

---

* Rotomixer, Forster Equipment Co. Ltd., Great Britain.
** Bürette Digital, Rudolf Brand GMBH & Co., West Germany.
*** Balance, Type PC 4400, Mettler, West Germany.

and 50 ± 5 per cent relative humidity) for at least 24 hours. The dried specimen was transferred to a vertically disposed vitreous silica tube which was positioned in a vertical tube furnace. A fused silica push-rod was positioned on a small recess formed on the surface of the Inconel plate (mass about 2.3 g) against which the investment had been cast. The plate distributed the measuring force of the dilatometer (0.2 N) uniformly over the specimen cross-section, giving a pressure of 0.7 kPa.

As the specimen expanded, movement of the rod was measured by means of a linear transducer*, the core of which was fixed to the top of the rod. Specimen temperature was recorded by a type K (chromel/alumel) thermocouple sheathed with Inconel, which projected into a recess formed at the base of the specimen. The thermocouple and the transducer were connected to an X-Y recorder**, which produced the thermal expansion curves.

A second thermocouple, placed close to the furnace wall and level with the specimen, was connected to a temperature controller/programmer***. Since the investments contained cristobalite, heating was slowed in the range 200 - 300 °C, to 1 °C/min. A heating rate of 5 °C/min was used for the rest of the temperature range, room temperature to 200 °C, and 300 - 700 °C. Heat soaking at 700 °C was 15 minutes. Water vapour released from the specimens during the measurement was exhausted under a soft vacuum. Thermal expansion was determined to the nearest 0.01 mm and expressed as a percentage of the original specimen length.

Control measurements were made on specimens cast against a sheet (51 x 50 mm) of Teflon, folded lengthwise and laid in the trough. At least three measurements were taken for each investment.

---

* 050 DC-D, Schaevitz Engineering, USA.
** Type 3036, Yokogawa Electric Co., Japan.
*** Temperature Controller/Programmer Type 822, Eurotherm Co., Great Britain.

3.4 Casting Experiment

The methods described by Morey (1986) for wax pattern making and casting were followed as closely as possible.

3.4.1 Preparation of Wax Pattern

Wax patterns were made in an inlay wax* classified as a Type C Class 1 wax, suitable for indirect wax patterns (American Dental Association, 1974b). They were prepared in Invar die and stainless steel mould assemblies.

The die base (A, Figure 3.4A) accommodated a 2 mm thick spacer in the form of a removable washer (B), which seated on the shoulder of the die and formed the gingival margin of the wax patterns. With this in place, the height of the crown section was 6 mm and the diameters 9.2 mm at the top and 9.8 mm at the bottom, giving a taper of 1/10. The occlusal end (C) of the crown section, 2 mm thick, was also separate, spigotted and threaded into place. When the fit of castings was measured both the occlusal end and the gingival washer were first removed, to allow oversize as well as undersize castings to be completely seated on the taper of the die.

The various parts of the die and mould assemblies were sprayed with a silicone mould release agent**. Melted wax (about 0.85 g) was poured into the space formed by the die and mould assemblies to give a moderate excess. The upper inner sleeve (D) defined the height (8 mm) and outer wall of the wax patterns, making the pattern 2 mm thick occlusally and 0.75 mm gingivally. As soon as the gloss had disappeared from the surface of the wax, the piston (E) was inserted and forced home by means of a small vice. Excess wax was extruded through the vent (F) in the piston. The wax was allowed to solidify under pressure for three minutes.

After removal of the mould assembly from the vice and removal of the outer sleeve (G) and piston, excess wax was carved flush with the top of the upper inner sleeve with a

---

* Kerr Blue Inlay Casting Wax (Regular). Sybron/Kerr Laboratory Products Division, USA. Batch number 022884 1306.

** Rocol PR, Rocol Advanced Lubricants, Australia.

sharp rigid blade. The upper inner sleeve and the lower inner sleeve (H) were then removed and the wax pattern was immediately sprued. A sprue former, 2 mm outer diameter hard drawn stainless steel tubing, was attached axially to the centre of the occlusal surface of the pattern. Six wax patterns were made from six die assemblies. Each pattern was scribed with a code letter and an index line to mark the correct position of the wax patterns and the resultant castings on their respective dies.

The sprued patterns on their dies were annealed in a laboratory oven maintained at 40 ± 1 °C for 5 hours; the oven was then turned off, so that the temperature fell slowly to ambient. The dies were removed 12 hours after placement in the oven. Each wax pattern was gently rotated off its die assembly and the gingival washer removed. The wax pattern was then replaced in the correct alignment. It was seated under a load of approximately 20 g by inverting the die with the wax pattern and placing it on a block counterbored to accommodate the sprue former.

Measurements of the distance separating the gingival margin of the wax pattern and the shoulder of the die (x) were made at four equispaced points around the die with a travelling microscope* at a magnification of 30 times. The micrometer drum of the microscope was graduated to 2 μm so that it could be easily read to 1 μm by interpolation. The mean of three measurements, made at the four positions for both the shoulder of the die and the gingival margin of the wax pattern, was calculated. The differences between the averages for the shoulder of the die and those for the gingival margin of the wax pattern were calculated. This gave the average distance separating the gingival margin of the wax pattern and the shoulder of the die for each of the four positions. The mean of these four averages gave a measure of the distance separating the gingival margin of a wax pattern and the shoulder of the die. In each case this was close to the thickness of the removable washer (2 mm).

3.4.2 Investing and Casting

A piece of Kaoliner ceramic liner (32 mm in width, 95 mm in length) was positioned in a casting ring with the rougher side towards the ring wall, finishing short of each

---

* R. and J. Beck Ltd., Great Britain.

end by 3.0 mm. The sprued patterns were mounted on Whip-Mix rubber crucible formers (No. 4801) in such a way that the length of exposed sprue was 2 mm. The casting rings were Kerr Flasks* No. 1C (30 mm inside diameter and 38 mm high) which, being stainless steel, have a coefficient of thermal expansion of 16.5 x 10^{-6}/K and expand 1.12 per cent in the range 20 to 700 °C (Touloukian et al., 1977).

The investments were dispensed and mixed as described earlier for the setting expansion measurement (Section 3.3). In order to mechanically invest the wax patterns, a Vac-U-Spat** Investor was used. After mechanical mixing, the vacuum on the Combination Unit was disconnected to invest under atmospheric pressure and the Vac-U-Spat was inverted under vibration for 30 seconds. Timing of the procedure followed a standardised program and the whole procedure took 1 min 20 sec. All patterns were invested within one hour of their first removal from the die. The investment was allowed to set for 24 hours before removal of the sprue base and sprue formers.

Burn-out and heating of the moulds to the casting temperature was carried out in an electric furnace*** fitted with a cam type program controller†. The furnace heating rate was 5 °C/min from ambient to 200 °C, 1 °C/min from 200 - 300 °C and then 5 °C/min from 300 - 700 °C. Mould temperature was monitored during burn-out by a type K thermocouple whose hot junction was embedded in the centre of a casting ring filled with KCl investment, placed amongst the moulds in the furnace. Thermocouple output was read by means of a temperature indicator††.

Castings were made in a centrifugal casting machine†††. The alloy used‡, which complies with Australian Standard 1620 (The Standards Association of Australia, 1976), contains 80 per cent precious metal (Engelhard Dental Products, 1978). A blowtorch‡‡, burning a mixture of mains

---

* Sybron/Kerr, Laboratory Products Division, USA.
** Whip-Mix Corp., USA.
*** Model 7, Scientific Engineering Services, Australia.
† PC-211, Shinko Electric Instrument Co. Ltd., Japan.
†† Therma 1, Duff and Macintosh Pty Ltd., Australia.
††† Kerr Centrifico. Sybron/Kerr Products, USA.
‡ Type B G-5. Engelhard Industries Pty. Ltd., Australia.
‡‡ No.7. The S.S. White Company of Australia Pty Ltd., Australia.

gas and air, was used to melt the alloy. The casting machine was wound 2.5 turns and approximately 10 g of the alloy was used for each casting. Casting was carried out at a temperature between 650 and 700 °C. The castings were quenched in water after bench cooling for 3 minutes. They were scrubbed, pickled in 50 per cent sulphuric acid and ultrasonically cleaned in water for 20 minutes.

Because of the investing technique, every casting was found to have one small nodule at the axio-occlusal line angle. This was removed under magnification with a small round bur. Apart from this the castings were completely free of other irregularities. The sprue and button were removed with a separating disc.

After the gingival and occlusal sections had been removed from the die assembly, each casting was seated under an axial load of 2 kg. The same method as described for the wax patterns was used to measure the distance (y) separating the gingival margin of the casting and the shoulder of the die.

The mean axial discrepancy (x-y) was converted to a measure of diametral accuracy. A reduction in the measurement y compared with the original x gave a positive value for x-y, indicating that the casting was oversized. Conversely undersized castings gave a negative value for x-y. The measurement of the axial discrepancy is a ten times magnification of the diametral accuracy by virtue of the taper. This value was expressed as a percentage of the gingival diameter of the die (9.8 mm) and defined as casting accuracy.

$$\text{Casting accuracy} = \frac{x-y}{10} \times \frac{1}{9.8} \times 100 \text{ per cent.}$$

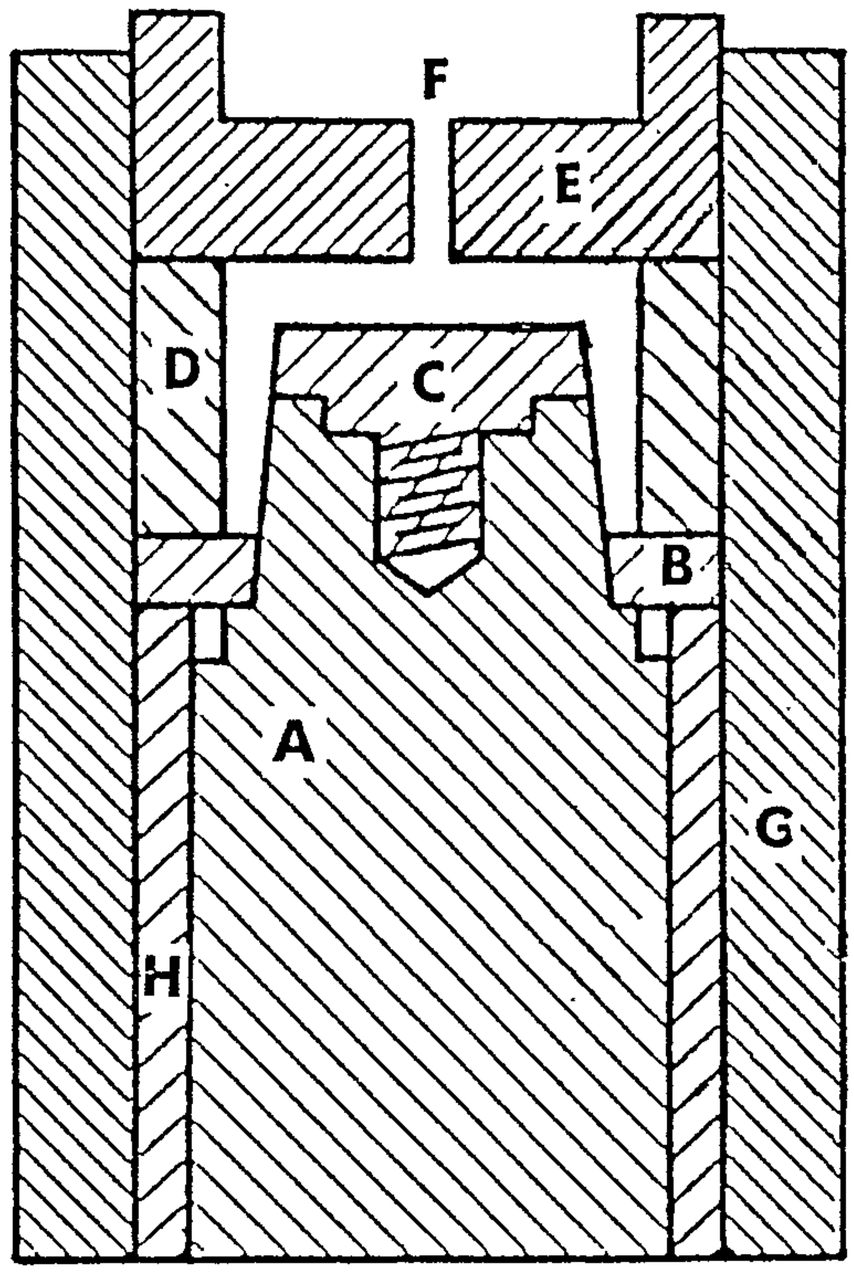

Figure 3.4A

The complete die and mould assemblies used for making wax patterns and for assessing casting accuracy (from Morey, 1986). A = die base, B = removable gingival washer, C = removable occlusal section, D = upper inner sleeve, E = piston, F = vent, G = outer sleeve and H = lower inner sleeve.

CHAPTER 4 - RESULTS

4.1 DTA-TG Experiment of Investment Powder

Representative DTA-TG curves obtained in this experiment are shown in Figure 4.1A and the results are summarized in Table 4.1A.

Upon heating to 700 °C, three endothermic and two exothermic reactions occurred. In the KCI powder, the first endotherm appeared as two consecutive small peaks at about 65 and 80 °C. A single endothermic peak occurred in the GCM powder at about 65 °C. Mean mass decreases of 0.26 (KCI) and 0.16 (GCM) per cent were recorded at 100 °C. A large endothermic peak appeared in the same temperature range for both materials, giving mean peak temperatures of 179 (KCI) and 176 (GCM) °C. Mean mass decreases at 200 °C were 2.08 (KCI) and 1.91 (GCM) per cent.

The first exotherm was quite different in magnitude for the two materials, appearing as a large sharp peak for GCM and a smaller peak for KCI. Mean peak temperatures were 194 (KCI) and 190 (GCM) °C. Little change in mass occurred during this reaction. The third endothermic reaction appeared in the same temperature range for both powders, giving mean peak temperatures of 246 (KCI) and 254 (GCM) °C. Little change in mass occurred during this reaction. The last reaction, marking a second well defined exotherm, appeared only in the KCI powder at a mean peak temperature of 444 °C. Again little change in mass was recorded as for the first exotherm.

After the large mass decrease accompanied by the second endotherm, only a small gradual decrease in mass of about 0.03 per cent occurred between 200 and 500 °C in both powders, giving mean decreases of 2.11 (KCI) and 1.94 (GCM) per cent at 500 °C. A slightly higher additional loss of 0.05 per cent followed between 500 and 700 °C in the KCI powder.

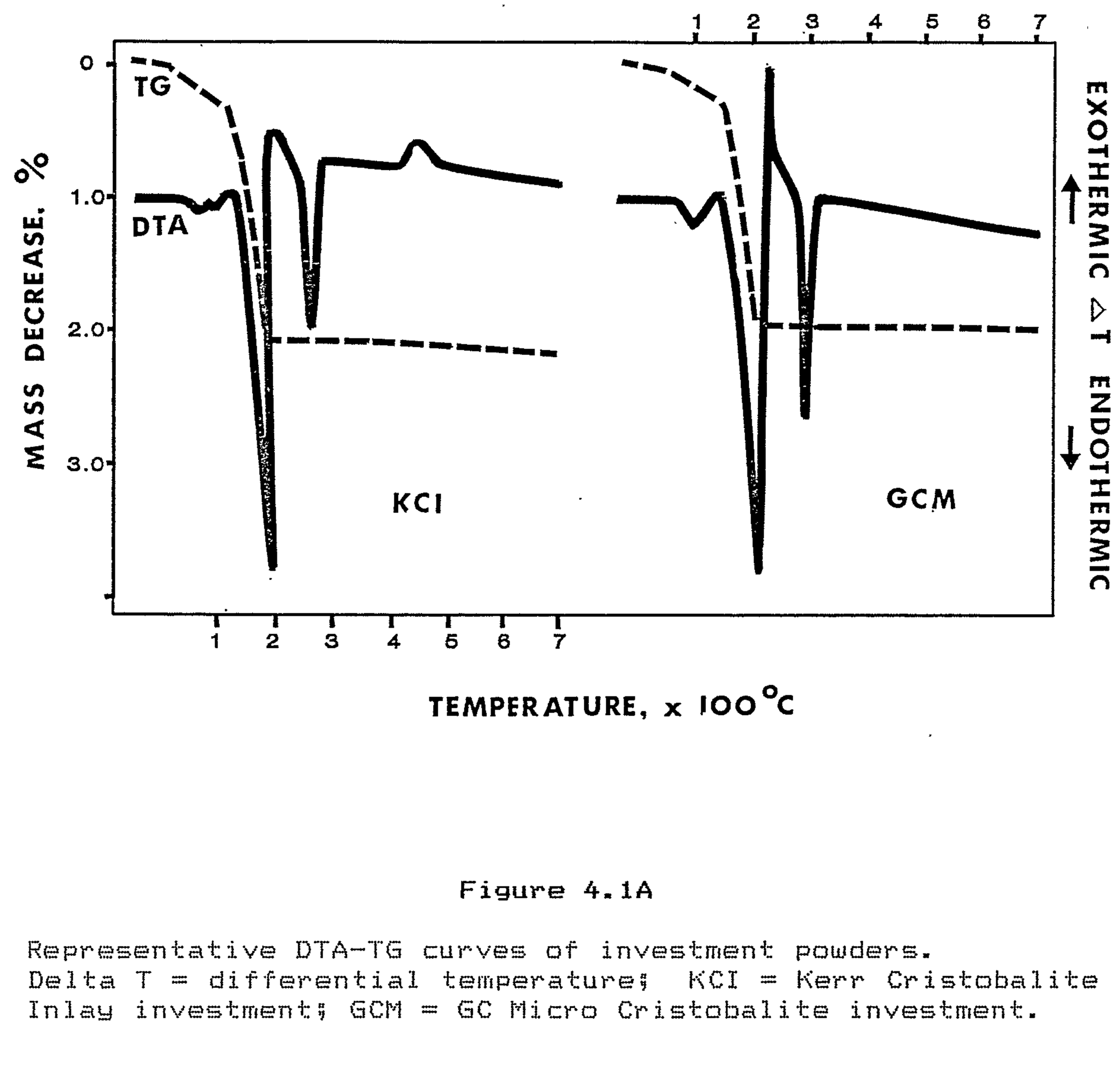

Figure 4.1A

Representative DTA-TG curves of investment powders.
Delta T = differential temperature; KCI = Kerr Cristobalite Inlay investment; GCM = GC Micro Cristobalite investment.

Table 4.1A

Results of DTA-TG experiment of investment powders. Mean values of at least five analyses are shown together with standard deviation in parentheses. KCI = Kerr Cristobalite Inlay investment; GCM = GC Micro Cristobalite investment.

	Peak Temperature (°C)					
	Endotherms				Exotherms	
	1st		2nd	3rd	1st	2nd
KCI	65 (1.6)	81 (1.0)	179 (1.3)	246 (0.0)	194 (1.5)	444 (0.5)
GCM	63 (3.6)	—— ——	176 (1.6)	254 (0.7)	190 (1.6)	—— ——

	Mass Decrease (%)						
	100 °C	200 °C	300 °C	400 °C	500 °C	600 °C	700 °C
KCI	0.26 (.01)	2.08 (.03)	2.10 (.03)	2.11 (.03)	2.11 (.03)	2.13 (.03)	2.16 (.03)
GCM	0.16 (.01)	1.91 (.02)	1.93 (.02)	1.94 (.02)	1.94 (.01)	1.95 (.01)	1.96 (.01)

4.2 Measurement of Investment Expansion

Representative setting expansion curves of the two investments are shown in Figure 4.2A. The times for loss of gloss determined with the residual mix are summarised in Table 4.2A. The results were the same for both KCI and GCM (about 12 mins). Despite this, all specimens cast against the ceramic ring lining material (K) began expanding earlier and showed a much greater setting expansion than did the control specimens (T). The start of expansion was read from each expansion recording and the results are included in Table 4.2A. Expansion started at about 6 (KCI) and 4 (GCM) minutes earlier with the ceramic liner.

Representative thermal expansion curves of the two investments are shown in Figure 4.2B. KCI investment showed an initial expansion of between 0.1 and 0.2 per cent. A small contraction at about 110 °C was followed by a plateau at 150 - 200 °C, and then an expansion to about 250 °C. A sudden massive expansion occurred at 250 °C, indicating the inversion of cristobalite. A further expansion took place to about 350 °C, at which point there was a second contraction to about 450 °C. The final part of the curves showed a gradual expansion to 700 °C.

In GCM investment, an initial expansion tapered off to a small plateau at about 120 °C. This was soon followed by a further expansion to 250 °C and then by a large isothermal expansion at 250 °C of cristobalite inversion. Expansion continued to about 350 °C when there was a small contraction to about 375 °C. The final part of the curve showed a gradual expansion to 700 °C.

KCI investment specimens, when cast against the ceramic ring liner (K), showed a lower final thermal expansion than did the control specimens (T). This is caused by the larger shrinkage at 350 - 450 °C (Figure 4.2B). Compared with this, the shrinkage of GCM specimens at this temperature range was similar for the control and ceramic lining.

The results of the setting and thermal expansion measurements are summarized in Table 4.2B and shown graphically in Figure 4.2C. Student t tests were performed using a confidence level of $p < 0.01$ to determine statistical significance.

The control KCI specimens cast against Teflon sheet gave a mean setting expansion value of 0.25 ± 0.02 per cent, while the control GCM specimens gave a much higher mean value of 0.79 ± 0.06 per cent. With Kaoliner ceramic ring liner, significantly higher setting expansion values were obtained in both investments, 0.48 ± 0.05 per cent (KCI) and 0.97 ± 0.04 per cent (GCM). This reduced the thermal expansion of KCI significantly, while there was no significant difference in the thermal expansion values of GCM cast against Teflon sheet and Kaoliner ring liner.

The results of particular interest in the casting experiments are those which apply to the investment specimens cast against the Kaoliner ceramic ring liner. The mean values for thermal expansion at 700 °C were 0.99 ± 0.06 per cent (KCI) and 1.50 ± 0.07 per cent (GCM). These values can be simplified as 1.0 and 1.5 per cent, respectively. Similarly, the setting expansion values are 0.5 (KCI) and 1.0 (GCM) per cent. These simplified values are used in the discussion on casting experiments (Section 5.3).

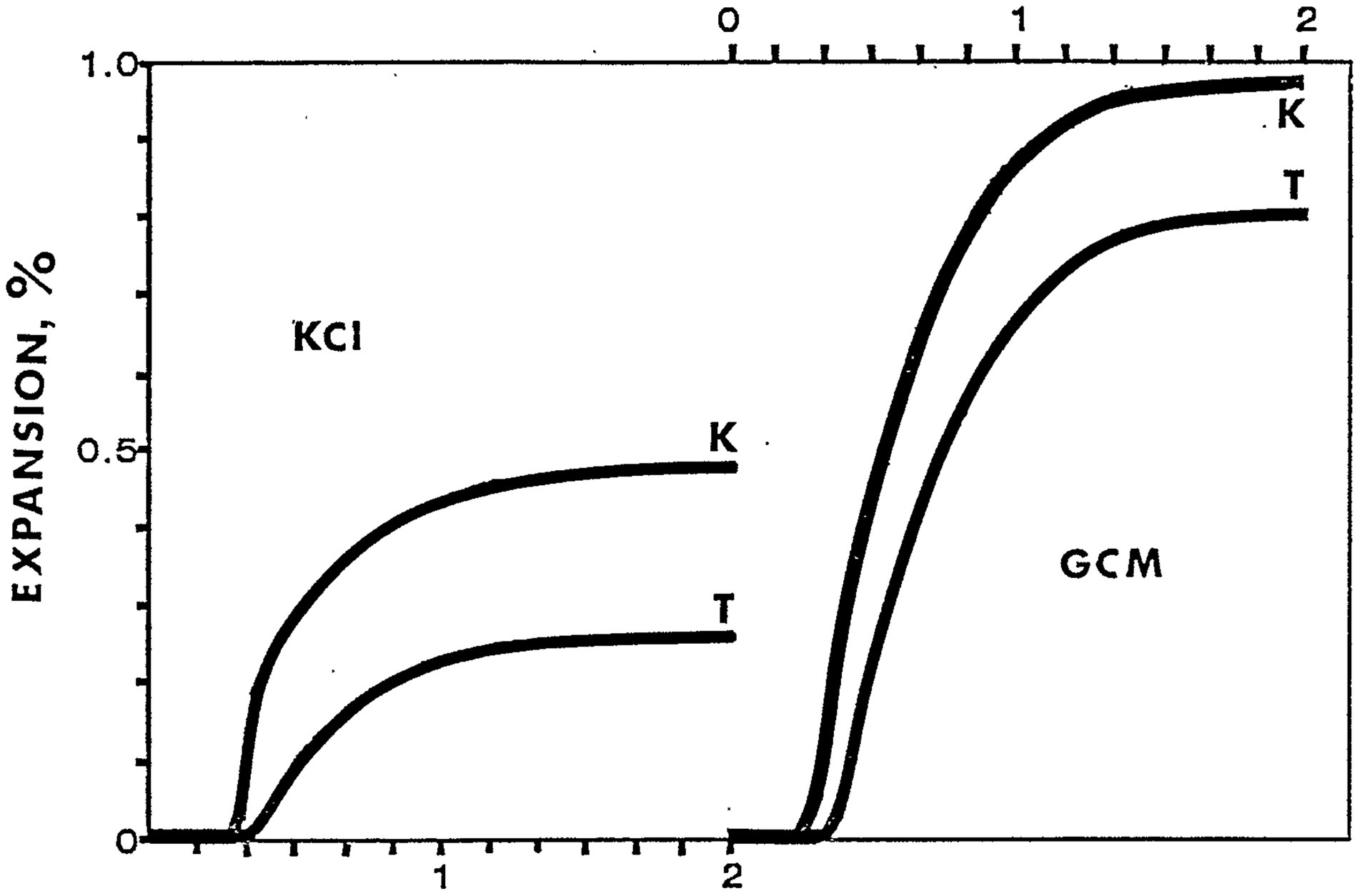

Figure 4.2A

Representative setting expansion curves. T = control specimens cast against a Teflon sheet, K = specimens cast against Kaoliner ceramic liner; KCI = Kerr Cristobalite Inlay investment, GCM = GC Micro Cristobalite investment.

Table 4.2A

Times for loss of gloss of residual investment mix and for the start of setting expansion. Mean values of at least three tests are shown together with standard deviation in parentheses. KCI = Kerr Cristobalite Inlay investment; GCM = GC Micro Cristobalite investment.

Investment	Code	Liner	Time (min) Loss of Gloss	Time (min) Start of Expansion
KCI	T	Teflon (control)	11.8 (.3)	18.7 (1.2)
W/P = 0.40	K	Kaoliner ceramic liner	11.8 (.3)	12.5 (1.3)
GCM	T	Teflon (control)	11.7 (.2)	17.0 (1.7)
W/P = 0.33	K	Kaoliner ceramic liner	11.7 (.2)	13.0 (.7)

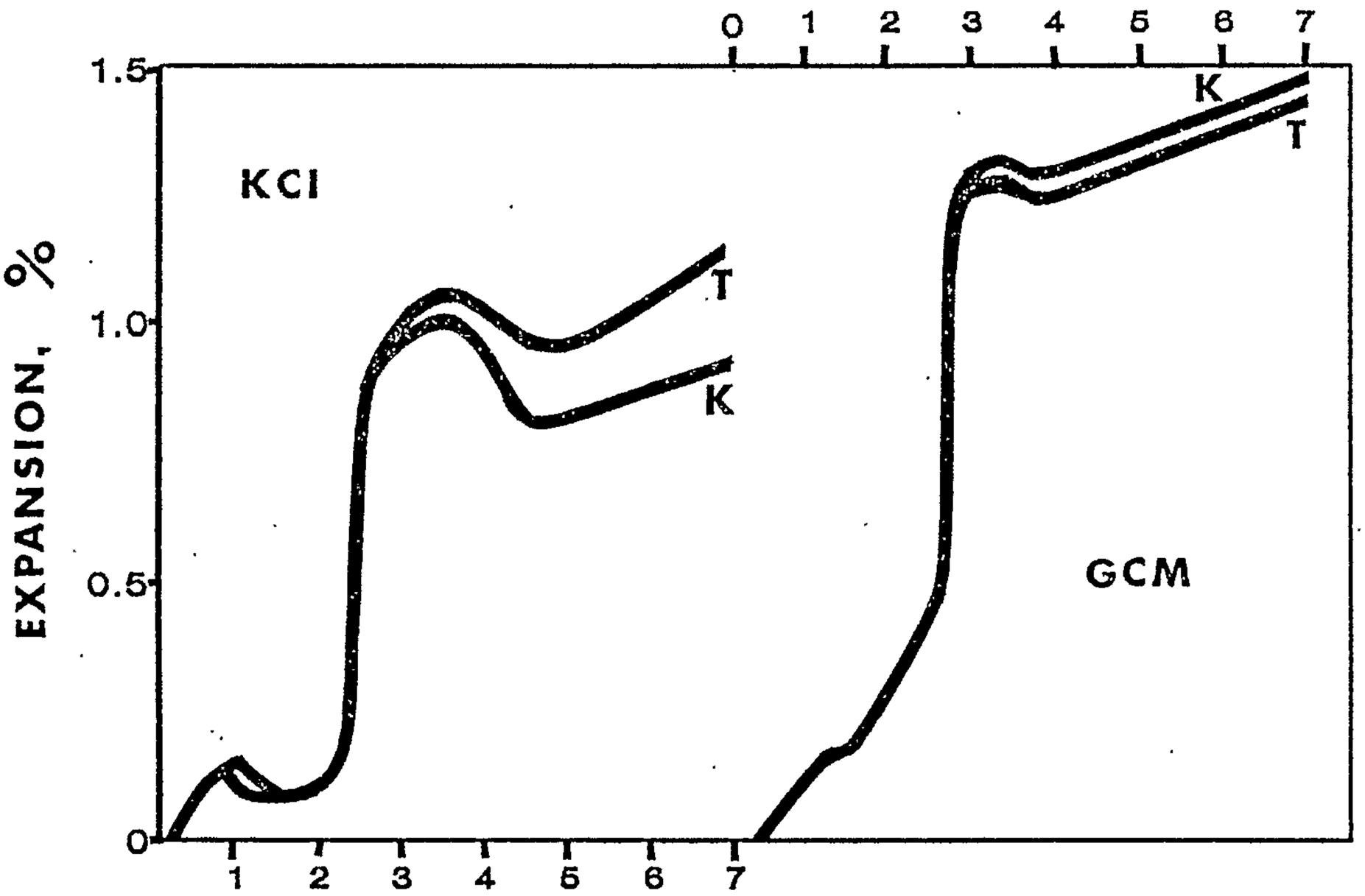

Figure 4.2B

Representative thermal expansion curves. T = control specimens cast against a Teflon sheet, K = specimens cast against Kaoliner ceramic liner; KCI = Kerr Cristobalite Inlay investment, GCM = GC Micro Cristobalite investment.

Table 4.2B

Results of setting and thermal expansion measurements. Mean values of at least three tests are shown, together with standard deviation in parentheses. KCI = Kerr Cristobalite Inlay investment and GCM = GC Micro Cristobalite investment.

Investment	Code	Liner	Expansion (%) Setting 2 hr	Thermal 700 oC	Total
KCI	T	Teflon (control)	0.25 (.02)	1.19 (.03)	1.44 (.04)
W/P = 0.40	K	Kaoliner ceramic liner	0.48 (.05)	0.99 (.06)	1.49 (.07)
GCM	T	Teflon (control)	0.79 (.06)	1.45 (.03)	2.28 (.09)
W/P = 0.33	K	Kaoliner ceramic liner	0.97 (.04)	1.50 (.07)	2.48 (.03)

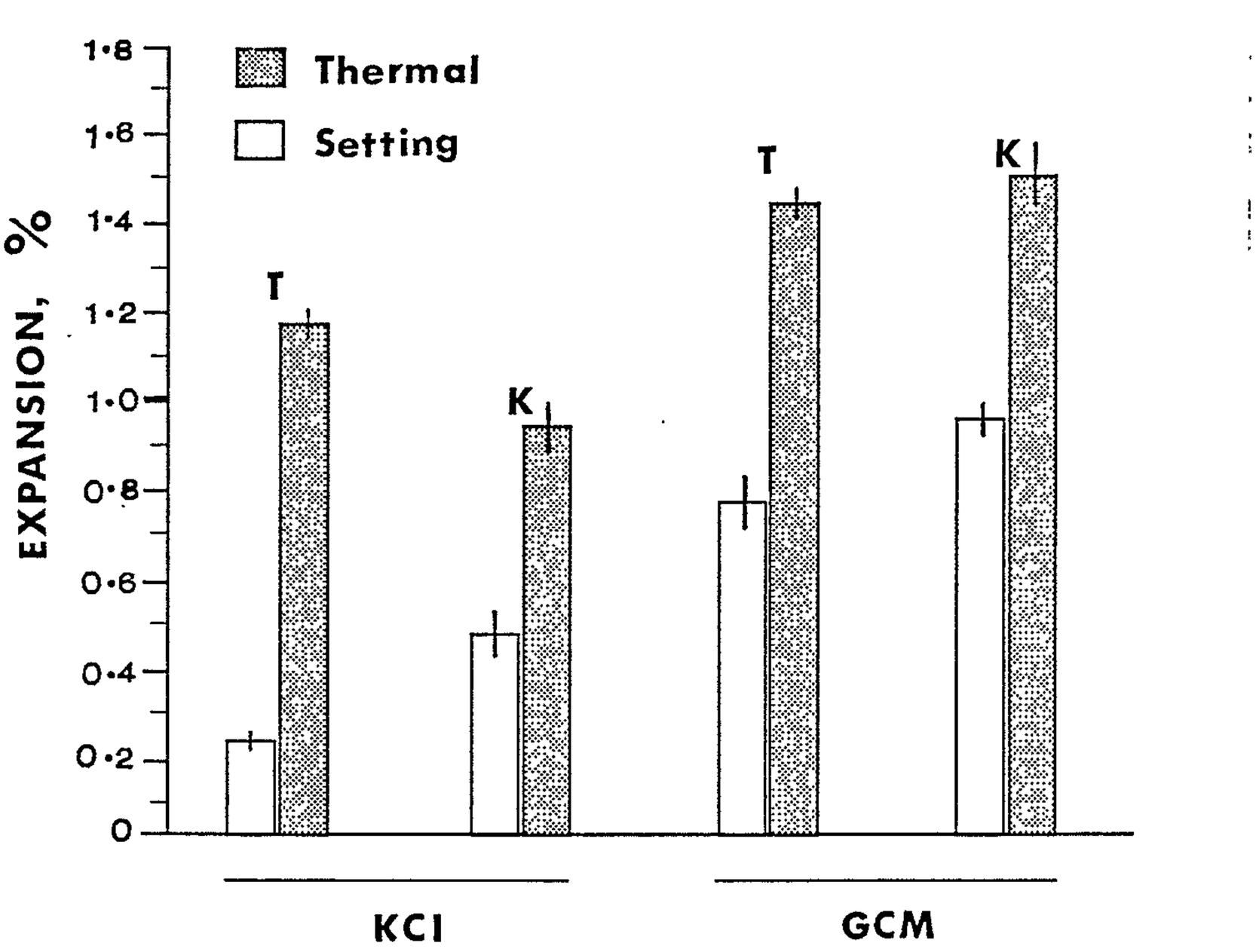

Figure 4.2C

Setting (2 hr) and thermal expansion (700 °C) of investments. The height of each bar represents the mean of at least three tests. The small superimposed bars show the standard deviations. T = control specimens cast against a Teflon sheet, K = specimens cast against Kaoliner ceramic liner; KCI = Kerr Cristobalite Inlay investment, GCM = GC Micro Cristobalite investment.

4.3 Casting Experiment

Table 4.3A shows the accuracy of full crown castings obtained with the two investments, KCI and GCM. The castings obtained with the former were undersized (-0.4 per cent), while those obtained with the latter achieved a 0 per cent dimensional change from the size of the wax pattern. Student t test was performed and the difference was highly significant ($p < 0.1$).

Table 4.3A

Accuracy of full crown castings. KCI = Kerr Cristobalite Inlay investment, GCM = GC Micro Cristobalite investment. A ceramic ring liner (Kaoliner) was used. Standard deviations are shown in parentheses.

	KCI	GCM
Accuracy (%)	-0.41 (.08)	+0.01 (.10)

CHAPTER 5 - DISCUSSION

5.1 DTA-TG Experiment of Investment Powder

Three endothermic reactions occurred in the same temperature ranges in both KCI and GCM powder. The first, at temperatures below 100 °C, was accompanied by small mean mass decreases, 0.26 (KCI) and 0.16 (GCM) per cent at 100 °C (Table 4.1A). It is possible to attribute this to the dehydration of gypsum, as surface rehydration of hemihydrate or unconverted dihydrate can account for the presence of a small amount of gypsum in some plaster and stone (Holdridge, 1965). Holdridge showed that even as little as 0.5 per cent dihydrate, added to wet- or dry-calcined hemihydrate powders produced a small endothermic peak prior to the dehydration of the hemihydrate itself. Although the dehydration of gypsum occurs in air slowly at about 70 °C or below (Weisser, Milligan and Ekholm, 1936), and rapidly at 90 °C and above (Fairhurst, 1960; Deer, Howie and Zussman, 1962), the endotherm associated with the dehydration of dihydrate to hemihydrate usually occurs at about 120 - 150 °C under dynamic heating conditions employed in DTA (Fleck et al., 1960; Kuntze, 1962, 1965; Holdridge, 1965; Tasaki, 1979; Mori, 1986; Hasratiningsih, 1987). Endothermic reactions at temperatures less than 100 °C, are unlikely then to be caused by the dehydration of gypsum and are probably caused by the removal of moisture adsorbed by the investment powders.

The second endothermic peak, 179 ± 1.3 °C (KCI) and 176 ± 1.6 °C (GCM), was accompanied by large mass decreases of about 2 per cent (Table 4.1A). This indicates the dehydration of hemihydrate in the investment powders to anhydrite. Again these temperatures are much higher than those (100 °C and above) reported for this change in static conditions (Weisser and Milligan, 1937). Taking the TG value reached at 500 °C as the final dehydration value, 98 per cent of the dehydration was complete at 200 °C in both KCI and GCM.

The theoretical mass decrease accompanying dehydration of hemihydrate to anhydrite is 6.2 per cent. Horibe, Kojima and Kikuchi (1971), in their DTA-TG study of dental gypsum-

bonded investment, estimated the amount of hemihydrate present in the investment samples. They assumed that all the weight loss resulted from the dehydration of hemihydrate to anhydrite. The amount of moisture adsorbed by the investment powders can be estimated by the mass decrease at 100 °C, as discussed previously. By subtracting this value, mass decreases of 1.85 (KCI) and 1.78 (GCM) per cent are obtained for the dehydration of hemihydrate to anhydrite at 500 °C. Comparing these figures with the theoretical dehydration value of 6.2 per cent, it can be deduced that the investment powders contain about 30 (KCI) and 29 (GCM) per cent hemihydrate. The amount is close to the limit below which the investments are too weak (Section 1.3).

The third endothermic reaction, 246 ± 0.0 (KCI) and 254 ± 0.7 (GCM) °C, indicates the inversion of cristobalite as it is accompanied by little mass change. Horibe, Kojima and Kikuchi (1971) showed that two types of gypsum-bonded dental casting investment, quartz and cristobalite, were able to be identified by the endothermic peak accompanied by the inversion of these refractories. The mean peak temperatures obtained in the present study agree with that (253 °C) of a commercial cristobalite investment reported by these investigators. They did not discuss the other endothermic reactions occurring in hemihydrate, as their main concern was to distinguish the investment of cristobalite type from that of quartz type by DTA.

The two investment powders investigated in the present study showed an important difference in the DTA; two exothermic reactions were recorded with KCI, while only one exothermic reaction was observed with GCM. Mean peak temperatures of the first exotherm were similar, 194 (KCI) and 190 (GCM) °C, although they were quite different in magnitude; GCM showed a large sharp peak whereas KCI showed a smaller peak (Figure 4.1A). The unique second exotherm in the KCI investment, at 444 ± 0.05 °C, was well defined.

Calcium sulphate anhydrite ($CaSO_4$) exists in three polymorphic forms. The terms I-$CaSO_4$, II-$CaSO_4$ and III-$CaSO_4$ are preferred to describe these forms, in order of descending temperature (Kruis and Späth, 1951; Arai and Yasue, 1974; Mori, 1986). Powell (1958) first reported that the transition III-$CaSO_4$ to II-$CaSO_4$ was shown by a sharp exotherm at 255 °C in several wet-calcined plasters, and by

a gradual exothermic reaction at a much higher temperature range of 300 - 500 °C in a dry-calcined plaster. Holdridge (1965) stated that this difference was sufficient to differentiate the two types of hemihydrate.

These early studies strongly suggest that a significant amount of dry-calcined hemihydrate is incorporated in KCI, although it also contains wet-calcined hemihydrate. This may explain why the first exothermic peak was so small in this investment. The two consecutive small endothermic peaks at 65 ± 1.6 °C and 81 ± 1.0 °C in this material could reflect the presence of wet- and dry-calcined hemihydrate.

Study on the two types of calcium sulphate hemihydrate originates from the classical work carried out by Kelly, Southard and Anderson (1941), who noted that the heats of hydration of wet- and dry-calcined hemihydrates were different. They used the designations "α" and "β" to distinguish such thermodynamic differences. The prefixes usually indicate crystallographic differences, but it has been shown that no crystallographic differences are found in the X-ray diffraction patterns of wet- and dry-calcined hemihydrates (Feitknecht, 1931; Weisser and Milligan, 1937; McAdie, 1964; Miyazaki, 1966a; Goto et al., 1966; Lehmann, 1967; Miyazaki and Takagi, 1970; Bensted and Varma, 1972). The thermodynamic method is not possible for the identification of the type of hemihydrate incorporated in gypsum-bonded investment, unless its amount is known and a reliable calorimetric method is available. The DTA method appears to be a viable alternative.

The W/P ratios recommended by the manufacturers are 0.38 - 0.40 (KCI) and 0.33 (GCM). Considering the similar amount of hemihydrate in both investments (about 30 per cent), this difference in W/P ratio is large; the amount of water necessary to convert 100 g plaster or stone to gypsum is 18.6 g (W/P = 0.19), and so only 5.6 g water is required for an investment containing 30 per cent plaster or stone.

There is always some excess water present in the set gypsum mass, more in the case of dry-calcined plasters. This is because the amount of water required to give a workable mix (water requirement) is considerably higher than the theoretical value, in particular with dry-calcined plasters. The difference in water requirement has been

explained by the structure of the compacted powders. Strong adhesive forces between the particles tend to stick at the point of first contact, giving a porous structure; weak adhesive forces allow the particles to slip over one another, packing closely to produce a dense structure. Thus the water required to give a workable mix is related to the amount of space formed between the compacted particles (Ridge, 1961; Ridge and Boell, 1962; Ridge and Beretka, 1969; Miyazaki and Takagi, 1970). Although it has been reported that water requirement is also related to the bulk porosity or particle size of the refractory (Takahashi et al., 1988), the significant difference in recommended W/P ratio of KCI and GCM strongly suggests that the former contains a considerable amount of dry-calcined hemihydrate.

The KCI samples showed a small (about 0.05 per cent) mass decrease between 500 and 700 °C. Holdridge (1965) and Walker (1965) noted the presence of a shallow depression and endotherms in the temperature range 550 - 800 °C, the result of decomposition of clay and carbonates originating from mineral gypsum. This small loss of mass observed in the KCI specimens in this temperature range is likely to be due to the decomposition of such impurities.

5.2 Measurement of Investment Expansion

5.2.1 Setting Expansion

The setting expansion values were considerably higher with GCM than with KCI (Table 4.2B). Under the scanning electron microscope, set investments show refractory particles embedded in an interlocking aggregate of gypsum crystals (Tasaki, Ohta and Yamane, 1978; Takahashi et al., 1988). Lower inherent porosity resulting from a lower W/P ratio produces more effective interaction of growing gypsum crystals (Earnshaw, 1975; Takahashi et al., 1988), and hence a higher setting expansion. The setting expansion values obtained in the present study were consistent with this traditional view.

The setting expansion value of control KCI specimens set against the Teflon sheet (T), (0.25 ± 0.02 per cent) was very close to the value given by the manufacturers (0.20 - 0.25 per cent). Earnshaw (1988) recently obtained a

higher setting expansion value for specimens set against modelling wax, 0.41 ± 0.01 per cent, for the same material and W/P ratio. He concluded that the manufacturer's value must have been obtained on specimens setting under a considerably higher restraint than the 1.0 kPa which he used. However, the same measuring load used in the present study produced the much lower value with the Teflon liner, and a comparable value (0.40 ± 0.05 per cent) with the Kaoliner ceramic liner (K).

Teflon was chosen as the control liner in this study because of its smooth surface and very low frictional resistance. Variation of setting time due to the difference in mixing conditions appears to be important in the interpretation of setting expansion results. This requires further investigation.

In the setting expansion measurement of control GCM specimens, the manufacturer's value (0.40) was considerably lower than that obtained in the present study (0.79 ± 0.06 per cent). The difference may be due to the method of measurement which uses a U-shaped trough lined with wax paper and records expansion at 30 minutes (Japan Industrial Standard, 1979). Similar expansion values as that obtained in the present control measurements have been reported (Nasu and Noguchi, 1982) for GC Cristobalite investment. This material, a predecessor of GCM used in the present study, has been claimed by the manufacturers to have a setting expansion identical with GCM.

The reason why the ceramic lining gave higher setting expansion values than the Teflon lining in both investment materials is obviously an example of hygroscopic setting expansion (Scheu, 1935). That is, the liner absorbed water from the mix and lowered its effective W/P ratio. The resulting increase in setting expansion was clearly shown in the setting expansion curves (Figure 4.2A). This was also accompanied by a significant difference in the time of start of setting expansion, on average about 6 (KCI) and 4 (GCM) minutes earlier with the ceramic liner (Table 4.2A). Obviously the time of loss of gloss, determined on the mix remaining in the mixing bowl, is not necessarily an indicator of setting time of the investment placed in the trough or casting ring.

The dry ceramic liner which absorbed water from the investment mix, returns the water and the investment is subject to a hygroscopic effect. This was typically seen in the setting expansion curve of KCl specimens which showed a rapid initial expansion at about 20 minutes (Figure 4.2A).

To ascertain whether the increase in setting expansion was not due to the cushion effect of the liner, but due to water uptake by the liner, additional measurements were made of GCM specimens. In this experiment, both sides of each piece of the ceramic liner were treated by spraying with a dry film* for 3 seconds. No statistically significant difference ($p < 0.01$) was found between the measurements of setting (and thermal) expansion, for the specimens cast against the waterproofed liner and the control Teflon liner (Table 5.2A). The waterproofed ceramic liner could have served as a control trough liner. The result proves that the ceramic liner used in this investigation absorbed water at atmospheric pressure, consistent with the results of Earnshaw (1988), and that it is this which was responsible for the increased setting expansion. It also confirms the results of Ohno et al. (1970), who found that the use of the dry film spray was a very effective method of preventing water uptake by the liner.

5.2.2 Thermal Expansion

When gypsum-bonded investment is heated, a number of dimensional changes take place. The changes occurring in the gypsum binder are mostly negative or contraction (Earnshaw, 1975, 1978; Phillips, 1982; Mori, 1986). This is because the density of gypsum (calcium sulphate dihydrate) is increased as it undergoes the phase changes to hemihydrate and anhydrites (Mori, 1982). The total linear contraction of cast gypsum prepared from dry-calcined hemihydrate (W/P = 0.50) and heated to 700 °C can be as high as 3 per cent (Earnshaw, 1978); the corresponding amount for cast gypsum specimens prepared from wet-calcined hemihydrate (W/P = 0.25) is about 1 per cent (Earnshaw, 1975; Mori, 1982; 1986).

The contraction occurring in the gypsum binder is masked by the thermal expansion of refractory. The refractory expands sufficiently to make the shrinkage of the

---

* Rocol, MRS Non-silicone Dry-film Mold Release Spray.

binder ineffective in relation to the investment mass as a whole (Earnshaw, 1961). Nevertheless, plateaux or small shrinkages may still appear in the thermal expansion curve due to the phase changes occurring in the gypsum binder.

The first such change is usually observed as a plateau in the range 100 - 200 °C (Taylor, Paffenbarger and Sweeney, 1930; Jones and Wilson, 1968; Sumii et al, 1975; Tasaki, Ohta and Yamane, 1978) and is related to the dehydration of gypsum (Tasaki, Ohta and Yamane, 1978; Tasaki, 1979; Mori, 1986). This shrinkage was marked in KCI specimens (Figure 4.2B), probably reflecting the porous investment mass due to the high W/P ratio.

At about 250 °C a massive expansion takes place due to the low-high inversion of cristobalite. This is because the high temperature phase is less dense (Sosman, 1965; Iler, 1979; Phillips, 1982). The expansion observed in both investments agreed with the third endothermic peak obtained in the DTA-TG result (Table 4.1A).

The contraction commencing at about 350 °C was much larger and prolonged in KCI specimens than in GCM. The large contraction in this temperature range is due to the transformation of III-$CaSO_4$ to II-$CaSO_4$ (Tasaki, Ohta and Yamane, 1978; Mori, 1982, 1986). Dehydration of the calcium sulphate hemihydrate in the investment powders was 98 per cent complete at 200 °C in the DTA-TG analysis. However, dehydration of cast gypsum to calcium sulphate anhydrite proceeds much more slowly in large dilatometry specimens, and is still taking place right up to the time of commencement of the transformation III-$CaSO_4$ to II-$CaSO_4$ at about 350 °C (Mori, 1986).

The contraction accompanied by the transition III-$CaSO_4$ to II-$CaSO_4$ is increased with increasing amounts of mixing water (Tasaki, 1979; Mori, 1982, 1986). The present results also show that the high W/P ratio of KCI investment is responsible for the much greater contraction between 350 and 450 °C.

The thermal expansion value of control GCM specimens (1.45 ± 0.03 per cent) was very close to the value given by the manufacturer (1.47 per cent). The thermal expansion value of control KCI specimens (1.19 ± 0.03 per cent) was

also close to the manufacturer's value (1.25 per cent). The thermal expansion curves of both investments cast against the ceramic liner were similar in shape to those of the control specimens. However, KCI specimens cast against the ceramic liner showed a significantly reduced final thermal expansion (0.99 ± 0.06 per cent), in agreement with the findings of Earnshaw (1988), who found a similar reduction for KCI specimens cast against various ceramic liners. The large hygroscopic nature of the setting expansion in this investment (Figure 4.2A) would make its already porous structure more porous, with larger distances between refractory particles and gypsum crystals. This has a similar effect as an increase in W/P ratio, and a greater densification occurs in the investment mass at temperatures 350 - 450 °C in particular (Figure 4.2B). The dense nature of GCM investment is apparent as there were no significant differences ($p < 0.01$) in thermal expansion between the specimens cast against the ceramic ring liner (1.50 ± 0.07 per cent) and control specimens (1.45 ± 0.03 per cent).

Investment contraction between 100 and 200 °C (Figure 4.2B) has been observed in a few instances, for example in a quartz investment (Tasaki, Ohta and Yamane, 1978), and in KCI specimens where high restrictive stresses were applied (Jones and Wilson, 1968). The latter was thought to be directly related to the collapse of the gypsum matrix preceding and during the inversion of cristobalite. However, the contraction in this range is generally seen as a plateau (Earnshaw, 1961; Sybron/Kerr, 1985). With such a difference, the final thermal expansion value can be easily increased by 0.1 to 0.2 per cent.

Increasing the vapour pressure around gypsum specimens increases the temperature at which dehydration occurs (Matsuya, Ohta and Yamane, 1979) and the same would be expected in gypsum-bonded investment specimens. The presence of moisture in investment specimens would have an important effect on the time of dehydration. When dehydration is delayed, the contraction is masked by the massive expansion of refractory.

Finger and Jørgensen (1980) showed that the thermal expansion of an experimental gypsum-bonded investment decreased with increasing storage time before heating (2 to 24 hours), and that immersion of the specimens in

water for 3 minutes before heating restored the amount of final expansion. Earnshaw (1961), on the other hand, found no correlation between thermal expansion and the period of ageing between 5 and 96 hours. He used investment specimens mixed with a 10 per cent glycerol solution and stored in sealed glass containers. Here, ageing did not cause drying.

Jones and Wilson (1968) found that KCl gave a higher thermal expansion when a faster heating rate of 20 °C/min was used for both 1 and 24 hour aged specimens, and suggested that the coincidence of loss of absorbed water and dehydration of gypsum to anhydrite, combined with the inversion of cristobalite, could result in extra expansion. While they discussed the importance of water at an early stage of heating, they used a furnace preheated to 100 °C, which is critical for the initial dehydration process.

In the present study, all specimens were stored in ambient conditions at least overnight before the thermal expansion measurements and were thus in a dried condition at the time of heating. This, combined with the constant heating from room temperature to 200 °C in 36 minutes (5 °C/min), provided a relatively dry dehydration condition and resulted in less overlapped thermal reactions of the investment components. This appears to be the cause for the prolonged contraction of KCl specimens at 100 to 200 °C (Figure 4.2B). The thermal expansion measurement may provide two different dehydration processes, typified by so-called wet and dry calcination. This has never been discussed and further study is required.

Because the ceramic liner absorbed water, it is still important to measure setting and thermal expansion in the presence of the ring liner and in sequence on the same specimens. Even though ceramic liners absorb only a small amount of water from the investment mix, the effect is great enough, particularly in some investments, to warrant measurement in this way. In addition, different types of ceramic liners might affect the behaviour of these investments in different ways. However, waterproofing such liners eliminates the effect of water in the setting expansion measurement and also on the subsequent thermal expansion measurement (Table 5.2A) and it is proposed that this would constitute better use of these liners in the casting ring.

Table 5.2A

Effect of waterproofed liner on the setting and thermal expansion of GCM specimens (W/P = 0.33). Mean values of at least three tests are shown together with standard deviation in parentheses. Results for the control specimens cast against the Teflon sheet are included for comparison.

Code	Liner	Expansion (%)		
		Setting	Thermal	Total
W	Waterproofed Kaoliner ceramic liner	0.82 (.03)	1.42 (.04)	2.24 (.02)
T	Teflon (control)	0.79 (.06)	1.45 (.03)	2.28 (.09)

5.3 Casting Experiment

The castings obtained with KCI were significantly undersized, -0.41 ± 0.08 per cent (Table 4.3A). This agrees with the prediction made by Morey (1986) that the castings will be undersized when ceramic liners are used and investing is carried out under atmospheric pressure (Section 1.4).

Thermal expansion of gold alloys from room to melting temperature is in the range 1.68 - 1.80 per cent (Finger and Jørgensen, 1980). There are, however, still many unknown factors such as size and shape of the specimen and permeability of the mould material, which may alter the contraction of these alloys. When casting crowns in particular, the effect of the investment core can be such that the thermal stress induced by the difference in the cooling rates of the mould and the alloy can be high enough to yield the alloy and alter the amount of contraction or even cause fracture (Kasahara, 1984). It can be assumed, however, that these unknown factors were constant throughout the present investigation and that a constant value can be taken as the contraction to be compensated. Taking 1.7 per cent as such a value, approximately 1.3 per cent mould expansion occurred in the KCI investment (1.3 - 1.7 = -0.4). Since the result of the thermal expansion measurement was 1.0 per cent (Section 4.2), it may be reasonable to assume that the actual setting expansion was 0.3 per cent; due to the restriction exerted by the wax pattern the full setting expansion of 0.5 per cent did not occur.

Castings having an average 0 per cent dimensional change (+0.01 ± 0.10 per cent) were produced with GCM. This value is slightly less than the result obtained by Nakanishi (1975), who produced crowns which were on average 0.15 ± 0.17 per cent larger at the occlusal section (Section 1.4).

Two reasons for this difference can be given; Nakanishi used a waterproofed thick asbestos liner and he compared the size of castings with that of the metal die. He also reported that these crowns were 0.50 ± 0.21 per cent larger at the shoulder. This discrepancy between occlusal and shoulder size has been attributed to the setting of the investment; while expansion at the occlusal section is restricted by the wax pattern, a less restricted (larger)

expansion can occur at the shoulder, especially when the setting expansion of the investment is high. This implies that the assessment of the fit of crowns is governed by the fit of crowns at the occlusal and not by the distorted shoulder section.

The method used for the assessment of accuracy in the present study has a distinct advantage in that removal of the occlusal section of the die eliminates the effect of small irregularities on the inner aspect of the occlusal end of the casting.

To examine the effect of this removable section, measurements were repeated with this occlusal section in position. This has been the common method of assessing the accuracy of undersized full crown castings (Volland and Paffenbarger, 1932; Van Horn, 1934; Fusayama, 1959a; Finger and Jørgensen, 1980). The results are shown in Table 5.3A. Where the castings are oversized the measurement is, of course, meaningless, because the castings seat on the occlusal section rather than slide down the taper. Table 5.3A shows that where the castings are undersized or close to 0 per cent, no difference was found between the two methods of measurement. Therefore, the method of removing the occlusal section proved to be an accurate and practical way of measuring the accuracy of undersized full crown castings as well as for the oversized.

The total expansion of GCM, 2.5 per cent (1.5 per cent thermal and 1.0 per cent setting), is 1 per cent greater than that of KCI (Section 4.2). Such a large difference was not obtained in the castings; the difference was only 0.4 per cent (Table 4.3A). Here again some restriction must be taken into consideration, this time, for the higher total expansion of GCM. Taking 1.7 per cent as the contraction to be compensated, and 0.3 per cent as the actual setting expansion, 1.4 per cent out of 1.5 per cent thermal expansion may have occurred. In this case, both setting and thermal expansion are assumed to be under restriction.

While laboratory setting and thermal expansion measurements are usually made under essentially unrestricted conditions, the present casting results indicate that the investment expansion in the mould is rather restricted under the conditions employed in the present experiment. This may

be because of restriction of setting expansion either by the wax pattern, a common phenomenon in MOD and full crown castings, or by the casting ring if there is insufficient cushion. It may also be due to restriction of thermal expansion by the casting ring if insufficient cushion remains after the investment sets.

Restriction of setting expansion by the wax pattern has been noted by many investigators (Jørgensen, 1953; Suffert and Mahler, 1955; Mumford and Phillips, 1958a; Fusayama, 1959a); it is sensitive to even small restrictive forces (Skinner, 1933; Docking, Chong and Donnison, 1948; Docking, Donnison and Chong, 1948; Docking and Chong, 1949; Landgren and Peyton, 1950; Skinner and Degni, 1957; Earnshaw, 1964, 1969a; Jones and Wilson, 1970). It appears reasonable, therefore, to assume that only 0.3 per cent out of the potential setting expansion occurred especially in the area critical for the assessment of casting accuracy in both KCI and GCM moulds.

While the assumed 0.3 per cent setting expansion is taking place in the investment surrounded by the wax pattern (core), the investment occupying the space between the pattern and the ceramic liner expands more freely, provided that the liner provides a proper cushion effect. This was illustrated by Kozono (1977) who measured pressure exerted on invested patterns by the setting investment. Pressure sensors were attached to the inner and outer proximal walls of MOD metal "patterns". Positive pressure, proportional to laboratory setting expansion, was registered on the inner wall. On the outer wall, however, positive pressure was registered only when the setting expansion was restricted by an improperly cushioned casting ring. Where sufficient cushion was provided, a negative or zero pressure was always registered. The outer portion and the core portion of a mould appeared to behave independently. The base of the core (gingival margin region), sandwiched between the two, is adversely affected.

The concept of total expansion is thus generally acceptable for the external diameter of crowns if the ring liner is able to allow the full setting expansion to occur. In addition, during heating, there should either be sufficient cushion still available or the casting ring should expand as much as the investment does. In short, the

external diameter of a crown is expected to be the same as that of the wax pattern, if the total expansion of the investment is equal to the metal contraction, in which case the compensation will be slightly insufficient for the internal diameter of the crown. This discrepancy is minimized if the setting expansion is kept low and a high thermal expansion is available.

Restriction of the thermal expansion by the casting ring is possible if insufficient cushion remains after the investment sets. The large 1 per cent setting expansion with GCM corresponds to a reduction in the thickness of the lining material of about 300 μ (150 μ on each side). Even though ceramic ring liners have been found to be much more compressible than wet or dry asbestos liners (Nagasawa et al., 1975; Nasu and Noguchi, 1982) it is doubtful whether the remaining cushion is sufficient to accommodate the thermal expansion of the investment, especially that attained during the inversion of cristobalite, as only a little expansion is expected in the ring at this low temperature (about 250 °C, Section 5.2.2). Nasu and Noguchi (1982) showed that a single layer of ceramic liner was insufficient for either the setting or thermal expansion of GC Cristobalite investment. The setting and thermal expansions of the newer GCM investment are similar to those of the older GC Cristobalite investment, and so the finding is relevant to the present situation.

To further investigate the possible restriction of investment expansion, additional castings were made using GCM investment. The casting rings were either unlined, or lined with two or three layers of Kaoliner. The internal layers were reduced in length to accommodate the reduced diameter, and the joints were staggered in the ring to provide a uniform cushion. The results are shown together with the result obtained with one layer of lining in Table 5.3B and Figure 5.3A. They were analysed by the Student t test.

Varying the amount of cushion up to three layers produced significant ($p < 0.01$) differences in the accuracy of full crown castings. Extreme restriction occurred in unlined casting rings where castings were greatly undersized and laboratory measurements for setting and thermal expansion were virtually unrelated to the amount of mould

expansion achieved. Here, setting expansion is probably completely restricted (Rice, 1931; Palmer, Roydhouse and Skinner, 1961). In addition, the thermal expansion appears to be much less than that of the casting ring (about 1.1 per cent at 700 °C for stainless steel) as only a 0.8 per cent (1.7 - 0.9) compensation appears to have occurred. This agrees with Nasu and Noguchi (1982) in that the high expansion during the inversion of cristobalite can induce an inward expansion.

It is interesting to compare the results of GCM (-0.88 ± 0.07 per cent) in unlined rings (Table 5.3B) with those of KCI by Morey (1986), -0.61 ± 0.05 per cent, in unlined cartridge brass rings. Working on the assumption that the alloy contraction to be compensated is 1.7 per cent, the accuracy of Morey's KCI castings, where thermal expansion was 1.2 per cent (control, Table 4.2B), might be expected to be about -0.5 per cent. Even though the expansion of the cartridge brass ring at 700 °C is in excess of 1.2 per cent, investment expansion during the inversion of cristobalite is greater than that of the casting ring (Van Horn, 1934; Fusayama, Sakurai and Suzuki, 1957). At these temperatures the expansion of the investment turns inwards, making the castings slightly more undersized than expected as shown in the result, -0.61 per cent. The additional thermal expansion of about 0.25 per cent in GCM (control, Table 4.2B), ascertained by the laboratory measurement, increased the inward mould expansion, making GCM castings smaller rather than larger, at -0.88 per cent.

The inward mould expansion has been demonstrated by Rice (1931) and Ohno et al. (1970). Ohno et al. measured the volume of a cavity invested in a casting ring immediately after the time of initial set. They filled the cavity with mercury which was connected to a manometer. Failure to provide any cushion resulted in a contraction of the mould cavity. Analogous comparison is prevented when a wax pattern exists. Their experiments, however, provide a good picture of what happens when mould expansion is restricted during heating.

In the present study, the size of castings increased dramatically with the provision of a ring liner and continued to do so with the addition of further layers. This proves the assumption that the mould expansion of GCM

is restricted with one layer of Kaoliner. As the number of layers of liner increases, the thickness of investment around the wax pattern decreases. It is known that when there is insufficient cushion, reducing the thickness of the investment increases the size of (U-form) castings (Fusayama, Sakurai and Suzuki, 1957). This is because the less investment between the cavity and the ring wall, the less inward thermal expansion, and the greater the resultant casting size.

Three layers produced little but statistically significant ($p < 0.01$) additional increase in accuracy over two layers (Table 5.3B). It is probable that three layers of liner are sufficient for full mould expansion with GCM. Working on the assumption that the alloy contraction to be compensated is 1.7 per cent, then about 2 per cent mould expansion occurred in the case of three layers (2.0 - 1.7 = +0.3). Also assuming that 0.3 per cent is still a reasonable estimation for the setting expansion of the occlusal section of the investment core, then in the largest castings, thermal expansion in that area must have been 1.7 per cent. The 1.5 per cent thermal expansion measured in the laboratory, using a force of 0.5 N, is not, then, a measure of full (unrestricted) thermal expansion. In fact, Kozono, Hayashi and Nishioka (1971) and Nasu and Noguchi (1982) showed that the thermal expansion of a mould cavity in unrestrained investment could be much larger than that measured by the conventional laboratory method. Further studies are required on this aspect of mould expansion.

For the castings made with KCl (-0.41 ± 0.08 per cent), if we again take 0.3 per cent as the contribution made by setting expansion, then the measured 1.0 per cent thermal expansion occurred, making the total mould expansion 1.3 per cent. One layer of ceramic liner appears to be sufficient for the thermal expansion of KCl investment. The increased size of castings produced with GCM and one layer of lining, is therefore due to the additional thermal expansion available in this material, some of which was directed inwards.

The 0.3 per cent taken to be the contribution made by setting expansion relates to the occlusal section of the investment core. A discrepancy between occlusal and

shoulder size is highly likely in the larger castings. With sufficient cushion, up to 1.0 (GCM) and 0.5 (KCI) per cent setting expansion could be occurring at the shoulders of these castings. How much distortion is occurring requires further investigation. Whether a constant 0.3 per cent setting expansion occurs also requires further investigation. An alternative explanation would have been that this contribution increases for increasing layers of lining. However, this increase seems most likely at the shoulder and the investment occupying the space between the wax pattern and the liners. This is supported by the fact that Stevens (1988) found setting expansion of phosphate-bonded investments to be of no value as a predictor of the accuracy of full crown castings.

The results obtained in the present study have demonstrated that the expansion of investment as a mould can be greatly different from that measured by the conventional laboratory methods. It has been very common in dentistry to compare the size of a casting with the size of the original wax pattern. Experiments of this type have been numerous (Lane, 1909; Shell, 1923; Scheu, 1932; 1933; 1935; Fusayama, 1959a; 1959b), and these measurements have been called "indirect measurements" of casting shrinkage (Hollenback and Skinner, 1946) and measurements of the "net casting shrinkage" as defined by Earnshaw (1958). Here three concepts, alloy contraction, mould expansion and casting accuracy, are combined in the single notion of "casting shrinkage". While "direct measurements of casting shrinkage" may be regarded as an alternative to the conventional dilatometry methods for determining the contraction of alloy (Section 1.3), "indirect measurements of casting shrinkage" all, more correctly, determine the accuracy of dental castings under various mould expansions and as such are simply casting experiments. It is proposed that the terms, alloy contraction, mould expansion and casting accuracy, should be used in preference to "casting shrinkage" for clearer understanding of dental precision casting.

Table 5.3A

Effect of method of assessing casting accuracy. Results for measurements obtained with the occlusal section of the die removed are included for comparison. KCI = Kerr Cristobalite Inlay investment, GCM = GC Micro Cristobalite investment.

	Accuracy (%)	
	KCI	GCM
Occlusal section in position	−0.43 (.09)	+0.00 (.07)
Occlusal section removed	−0.41 (.08)	+0.01 (.10)

Table 5.3B

Effect of lining on the accuracy of full crown castings made using GC Micro Cristobalite investment. Standard deviations are shown in parentheses. 0, 1, 2, and 3 = the number of layers of Kaoliner.

	Number of Linings			
	0	1	2	3
Accuracy (%)	-0.08 (.07)	+0.01 (.10)	+0.24 (.06)	+0.31 (.04)

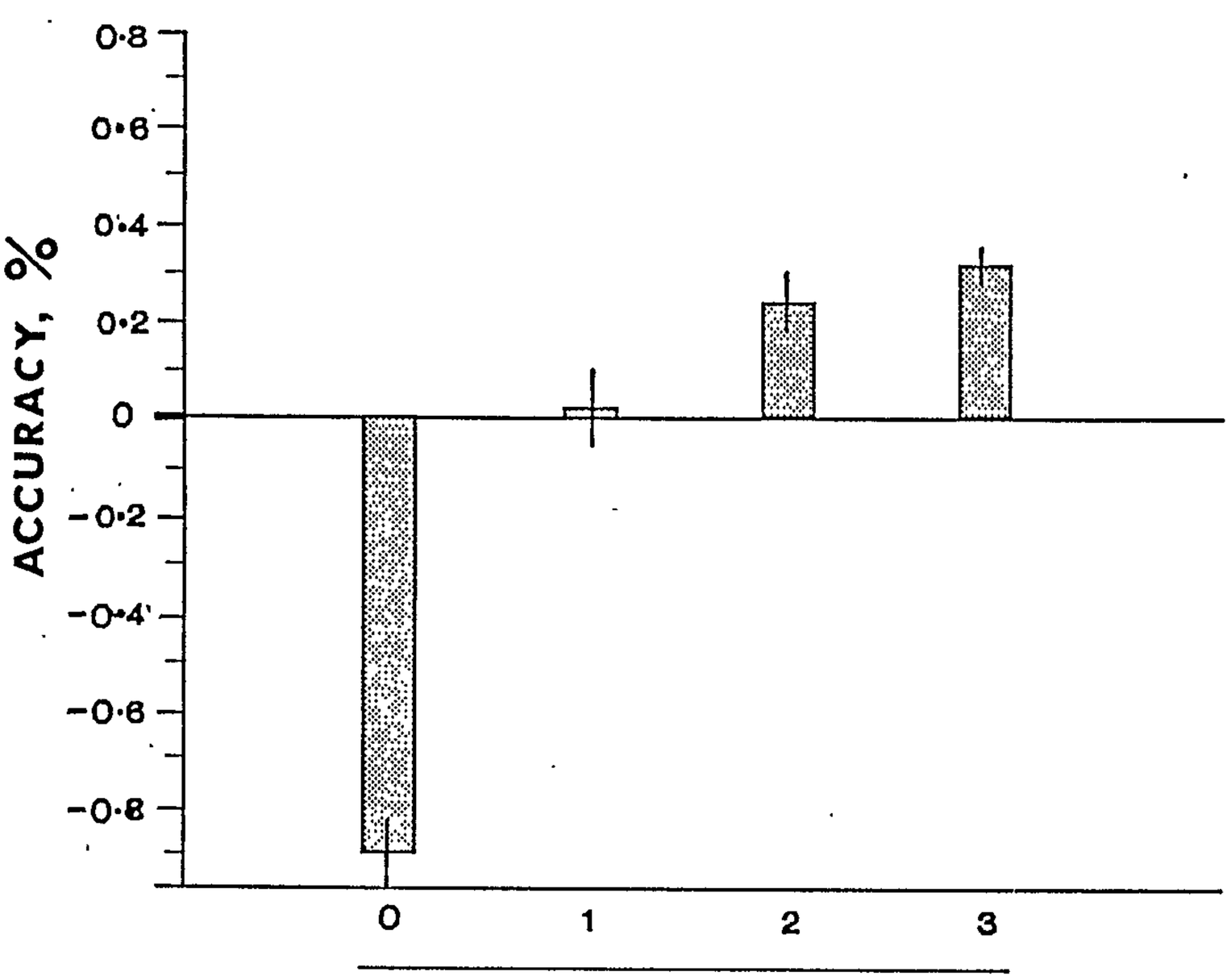

Figure 5.3A

Effect of lining on the accuracy of full crown castings made using GC Micro Cristobalite investment. The height of each bar represents the mean of at least ten castings. The small superimposed bars show the standard deviations. 0, 1, 2, and 3 = the number of layers of Kaoliner.

CHAPTER 6 – SUMMARY AND CONCLUSIONS

The aim of the present investigation was to study the effect of increased thermal expansion of gypsum-bonded investments to produce crowns which show a 0 per cent dimensional change from the size of the wax pattern with a ceramic ring liner (Kaoliner). For this, two gypsum-bonded casting investments, Kerr Cristobalite Inlay investment (KCI) and GC Micro Cristobalite investment (GCM), were compared by means of differential thermal analysis and thermogravimetry (DTA-TG), and setting and thermal expansions of the two investments were measured in accordance with Australian Standard 2795. The results of the laboratory expansion measurements were related to the dimensional accuracy of gold full crown castings.

The following conclusions were drawn:

1. The DTA-TG method provided a simple, reliable method to identify the type of calcium sulphate hemihydrate and refractory present in the investments, and to estimate the quantity of these components.

2. The amount of calcium sulphate hemihydrate was almost the same in the two investments (about 30 per cent). However, a significant amount of dry-calcined as well as wet-calcined hemihydrate was incorporated in KCI. The significant difference in recommended W/P ratio of KCI and GCM supported that the former contained a considerable amount of dry-calcined hemihydrate. The type of hemihydrate incorporated in gypsum-bonded investments has not been identified in the literature.

3. The setting expansion measurements made with the ceramic liner showed that the values were considerably higher (1.0 per cent) with GCM than with KCI (0.5 per cent).

4. Control expansion measurements made with Teflon sheet proved that the ceramic liner absorbed water at atmospheric pressure, and this gave the high setting expansion values (hygroscopic expansion) and changed the setting time of the investments. The increased setting expansion significantly decreased the thermal expansion in KCI.

5. Waterproofing the ceramic liner eliminated the effect of water absorption on the setting of the investments, and this would constitute better use of the liner in the casting ring.

6. Thermal contractions taking place in the binder of gypsum-bonded investments are generally masked by the expansion of refractory. Nevertheless, plateaux or small shrinkages may still appear due to the phase changes in the binder. These shrinkages were firstly in the range 100 - 200 °C, related to the dehydration of gypsum, and secondly in the range 350 - 450 °C, due to the transformation of III-$CaSO_4$ to II-$CaSO_4$. Both changes were much larger and more prolonged in the KCI specimens, reflecting the porous investment mass due to the high W/P ratio. The final thermal expansion values at 700 °C were 1.0 (KCI) and 1.5 per cent (GCM).

7. The castings obtained with KCI were undersized, -0.41 ± 0.08 per cent. This agreed with the prediction made by Morey (1986) that the castings would be significantly undersized when ceramic liners were used and investing was carried out under atmospheric pressure.

8. Assuming a constant value (1.7 per cent) as the contraction of the gold alloy to be compensated, only 0.3 per cent setting expansion appeared to be occuring in the core section of the investments due to restriction imposed by the wax pattern.

9. Castings showing an average 0 per cent dimensional change (+0.01 ± 0.10 per cent) were produced with GCM. However, the high thermal expansion of GCM (1.5 per cent) appeared to be under restriction. Increasing the linings proved this to be the case and indicated the necessity of considering the mould expansion separately from the expansion value obtained by the laboratory measurement. Three layers appeared to be sufficient for the full mould expansion of this investment. The 0 per cent accuracy applies only to one section of the crown, and the high setting expansion is likely to be producing a different accuracy at the shoulder and the outer sections of the crown.

10. In unlined casting rings, castings were greatly undersized and the results of laboratory measurements for thermal expansion were virtually unrelated to the amount of mould expansion. The increased thermal expansion of GCM (1.45 per cent) adversely affected the compensation of alloy contraction as a result of increased inward mould expansion.

11. It was indicated that the terms, alloy contraction, mould expansion and casting accuracy, should be used in preference to "casting shrinkage" for clearer understanding of dental precision casting.

BIBLIOGRAPHY

Ady B, Mahler DB. (1961)
Effective setting expansion of investment in casting rings. J Dent Res 39:760.

American Dental Association (1974a)
ADA specification No 2 for casting investment for dental gold alloy. In: Guide to dental materials and devices. 7th Ed. American Dental Association. 173.

American Dental Association (1974b)
ADA specification No 4 for dental inlay casting wax. In: Guide to dental materials and devices. 7th Ed. American Dental Association. 181.

Arai Y, Yasue T. (1974)
The crystal structure of I-$CaSO_4$. Sekko to Sekkai 132:28-32 (in Japanese).

Ball MC, Urie RG. (1970)
Studies in the system calcium sulphate - water. Part II. Kinetics of dehydration of B-CaSO4.½H2O.
J Chem Soc A:528-530.

Bensted J, Varma SP. (1972)
Investigation of the α- and β-forms of calcium sulphate hemihydrate. Cement Technol 3:67-70.

Bickerman JJ. (1970)
Physical surfaces. Academic Press. New York and London. 1-43.

Bushuev NN, Borisov VM. (1982)
X-ray differentiation of $CaSO_4 0.67H_2O$.
Russ J Inorg Chem 27:314-347.

Coleman RL. (1926)
Physical properties of dental materials.
Dental Cosmos 68:743-764.

Coleman RL. (1928)
Physical properties of dental materials (Gold alloys and accessory materials). Bur Stand J Res 1:867-938.

Combe EC. (1981)
Notes on dental materials, 4th Ed., Edinburgh Churchill Livingston. 259-262.

Deer WA, Howie RA, Zussman J. (1963)
Rock-forming minerals. Vol 5 Non-silicates. Longmans. London. 201-225.

Delgado VP, Peyton FA. (1953)
The hygroscopic setting expansion of a dental casting investment. J Prosthet Dent 3:423-433.

Docking AR, Chong MP. (1949)
The hygroscopic setting expansion of dental casting investments. Part 4. Aust J Dent 53:261-271.

Docking AR, Chong MP, Donnison JA. (1948)
The hygroscopic setting expansion of dental casting investments. Part 2. Aust J Dent 52:160-166.

Docking AR, Donnison JA, Chong MP. (1948)
The hygroscopic setting expansion of dental casting investments. Part 3. Aust J Dent 52:320-329.

Earnshaw R. (1958)
The casting shrinkage of cobalt-chromium alloys.
Aust Dent J 3:159-170.

Earnshaw R. (1960)
Investments for casting cobalt-chromium alloys.
Part 1. Brit Dent J 108:389-396.

Earnshaw R. (1961)
The effect of glycerol on the thermal expansion of gypsum-bonded investments. Brit Dent J 110:418-425.

Earnshaw R. (1964)
The effect of restrictive stress on the setting expansion of gypsum bonded investments. Aust Dent J 9:169-176.

Earnshaw R. (1966)
The effect of restrictive stress on the thermal expansion on gypsum-bonded investments. Part 1: Inlay casting investments, "thermal expansion" type.
Aust Dent J 11:345-356.

Earnshaw R. (1967)
The effect of restrictive stress on the thermal expansion of gypsum-bonded investments. Aust Dent J 12:123-126

Earnshaw R. (1969)
The effect of restrictive stress on the hygroscopic setting expansion of gypsum-bonded investments.
Aust Dent J 14:22-29

Earnshaw R. (1975)
The effects of additives on the thermal behaviour of gypsum-bonded casting investments.
Part 1. Aust Dent J 20:27-31.

Earnshaw R. (1979)
In: An outline of dental materials and their selection.
Edits O'Brien WJ, Ryge G. 59-72,259-271.

Earnshaw R. (1982)
The effect of casting ring liners on investment expansion.
J Dent Res 61.

Earnshaw R. (1988)
The effect of casting ring liners on the potential expansion of a gypsum-bonded investment.
J Dent Res 67:1366-70.

Earnshaw R, Marks BI. (1964)
The measurement of setting time of gypsum products.
Aust Dent J 9:17-26.

Engelhard Dental Products. (1978)
Dental products. Engelhard Industries Pty Ltd.
Melbourne. 1,6.

Fairhurst CW. (1960)
Compressive properties of dental gypsum.
J Dent Res 39:812-824.

Feitknecht W. (1931)
Zur Kinetic der Umwandlung der Verschiedenen Formen und Hydratstufen des Calciumsulfats. Acta Helv Chim 14:85-90 (in German).

Finger W. (1980)
Effect of thickness of peridental restorations on the casting precision. Scand J Dent Res 88:455-459.

Finger W, Jørgensen KD. (1980)
An improved dental casting investment.
Scand J Dent Res 88:278-284.

Fleck WEP, Jones MH, Kuntze RA, McAdie HG. (1960)
The differential thermal analysis of synthetic hydrates of calcium sulphate. Can J Chem 38:936-943.

Fusayama T. (1959a)
Factors and technique of precision casting.
Part 1. J Prosthet Dent 9:468-485.

Fusayama T. (1959b)
Factors and technique of precision casting.
Part 11. J Prosthet Dent 9:486-497.

Fusayama T. (1962)
Synthetic study on precision dental casting.
J Japan Res Soc Dent Mat Appl 7:34-55.

Fusayama T, Ide K, Hosoda H. (1964)
Relief of resistance of cement of full cast crowns.
J Prosthet Dent 14:95-106.

Fusayama T, Ide K, Kuroso A, Hosoda H. (1963)
Cement thickness between cast restorations and preparation walls. J Prosthet Dent 13:354-366.

Fusayama T, Sakurai S, Suzuki E. (1957)
Expansion of investment in casting rings.
Bull Tokyo Med Dent Univ 4:327-341.

Glasson GF, Sweeney WT, Shoonover IC. (1954)
The effect of preheating on thermal expansion of silica-gypsum investments. J Am Dent Assoc 48:433-440.

Goto M, Molony B, Ridge MJ, West GM. (1966)
The forms of calcium suphate hemihydrate.
Aust J Chem 19:313-316.

Greener EH, Harcourt JK, Lautenschlager EP. (1972)
Materials science in dentistry. The Williams & Wilkins Co. Baltimore. 204

Hanari M. (1967)
Mold distortion by four different investing techniques.
Bull Tokyo Med Dent Univ 14:435-445.

Hasratiningsih Z. (1987)
Phase and strength changes of gypsum in the dental lost wax method. MDS Thesis. University of Sydney.

Haupfaul, L. (1960)
Der Verschluss von Abzuglochern und die Vermeidung von Besserhohungen beim Einfugen gegossener Kronen.
DZZ 15:751-754 (in German).

Holdridge DA. (1965)
The characterization of plaster.
Br Ceram Soc Trans 64:211-231.

Hollenback GM. (1943)
Precision gold inlays made by a simple technic.
J Am Dent Assoc 30:99-109.

Hollenback GM, Skinner EW. (1946)
Shrinkage during casting of gold and gold alloys.
J Am Dent Assoc 33:1391-1399.

Horibe T, Kojima S, Kikuchi H. (1971)
Studies on instrumental analyses for dental materials (I)
Studies on thermal and infrared analyses for dental casting investments.
J Japan Res Soc Dent Mater & Appl 25:71-77.

Iler RK. (1979)
The chemistry of silica. New York, Wiley: 15-16

Japan Industrial Standard (1979)
Dental casting investment: No T6601.

Jlg, VK. (1959)
Untersuchungen zur "Indirecten technik".
DZZ 14:1035-1313 (in German).

Jones DW, Wilson HJ. (1968)
Variables affecting the thermal expansion of refractory investments. Brit Dent J 125:249-255.

Jones DW, Wilson HJ. (1970)
Setting and hygroscopic expansion of investments.
Brit Dent J 129:22-26.

Jørgensen KD. (1953)
Investigations of dental precision casting technic.
Goteborgs Tandlakare-Sallskaps 236:1-45.

Jørgensen KD, Finger W. (1979)
Die-spacing technique by diffusion precipitation.
Scand J Dent Res 87:73-78.

Kasahara S. (1984)
The effect of physical properties of alloys and dental casting investments at high temperature on the casting shrinkage. J Japan Dent Mat 3:122-139.

Kawai T. (1982)
Solidifying shrinkage measured by density (depending on the thermal) change in gold, silver, and copper. Shika Zairyo Kikai (J Jap Soc Dent Mat Dev) 1:286-298.

Kawai T, Hasegawa J, Kato M. (1982)
An apparatus for measuring the density of dental metals.
Shika Zairyo Kikai (J Jap Soc Dent Mat Dev) 1:89-98.

Kelly KK, Southard JC, Anderson CT. (1941)
Thermodynamic properties of gypsum and its dehydration products. Technical Paper 625. US Dept Interior, Bureau Mines. Washington. US Govt Printing Office.

Kozono Y. (1977)
Effect of the core on fitness of dental casting.
J Kyushu Dent Soc 31:154-169.

Kozono Y, Hayashi I, Nishioka F. (1971)
Studies on the dimensional change in dental casting cavity. (1st report). Correlation between thermal expansion of the cavity and investment mold dimension.
J Kyushu Dent Soc 25:130-135.

Kruis A, Späth H. (1951)
Forschungen und Fortschritte auf dem Gipsgebiet seit 1939 (Part I). Tonind Ztg Keram Rundsch 75:341-351 (in German).

Kuntze RA. (1962)
The determination of small amounts of gypsum in calcium sulfate hemihydrate by differential thermal analysis. Mater Res & Stand 2:640-642.

Kuntze RA. (1965)
Effect of water vapor on the formation of CaSO4.½H2O modifications. Can J Chem 43:2522-2529.

Landgren N, Peyton FA. (1950)
Hygroscopic expansion of some casting investments. J Dent Res 29:469-481.

Lane JG. (1909)
The casting process as applied to gold inlays and other dental uses. Dent Digest 15:497-502.

Lehmann H. (1967)
Die Phasenbezeihungen im System $CaSO_4$-H_2O. Tonind Ztg Keram Rundsch 91:6-12 (in German).

Macasaet AA, Dickson G. (1962)
Some factors affecting the dimensional changes of gold-alloy investments. Nat Bur Stand Report 7574.

Mahler DB, Ady B. (1963)
The influence of various factors on the effective setting expansion of casting investments. J Prosthet Dent 13:365-373.

Matsuya S, Ohta M, Yamane M. (1979)
Dehydration process of gypsum. Gypsum & Lime 158:10-16.

McAdie HG. (1964)
The effect of water vapor upon the Dehydration of $CaSO_4.2H_2O$. Can J Chem 42:792-801.

Miyazaki H. (1966a)
Thermal changes of calcium sulphate hemihydrate. Kogyo Kagaku Zasshi (J Jap Soc Chem Eng) 69:9-11 (in Japanese)

Miyazaki H. (1966b)
Effects of temperature and time on the formation of calcium sulphate hemihydrate in hydrothermal method. Kogyo Kagaku Zasshi (J Jap Soc Chem Eng) 69:1026-1029 (in Japanese)

Miyazaki H, Takagi N. (1970)
Differences between the α- and β-type of calcium sulphate hemihydrate. Kogyo Kagaku Zasshi (J Jap Soc Chem Eng) 73:1766-1769 (in Japanese).

Moore TE. (1933)
Method of making dental castings and composition employed in said method. US Patent No 1,924,874.

Morey EF. (1986)
The effect of casting ring liners on the dimensional accuracy of full crown castings.
MDS Thesis, University of Sydney.

Morey EF, Earnshaw R. (1987)
The fit of full crown gold alloy castings made with dry ceramic ring liners. J Dent Res Abst No 68.

Mori T. (1982)
The effect of boric acid on the thermal behaviour of cast gypsum. Dent Mater J 1:73-80.

Mori T. (1986)
Thermal behaviour of the gypsum binder in dental casting investments. J Dent Res 65:877-884.

Mumford GM, Phillips RW. (1958a)
Dimensional change in wax patterns during setting of gypsum investments. J Dent Res 37:351-358.

Mumford GM, Phillips RW. (1958b)
Measurement of thermal expansion of cristobalite type investments in the casting ring - preliminary report. J Prosthet Dent 8:860-864.

Nagasawa S, Nakamura K, Seki S, Kakuta K, Kawashima J. (1975)
Studies on the accuracy of the casts. Part III. On the influence of lining materials to the expanding stress, amounts of expansion and reacting temperature during setting of the investments. Shikwa Gakuho 75:286-292 (in Japanese).

Nakanishi A. (1975)
Study on reproducibility and cementing adaptation of the cast crown. J Tokyo Dent Coll Soc 75:1797-1817.

Nasu T, Noguchi H. (1982)
The cushion ability of lining materials for the setting and heating expansion of plaster bonded investment in casting ring. J Japan Soc Dent Apparat Mater 23:65-75.

Ohno H, Miyakawa O, Kondo S, Nakano S, Siokawa N. (1970)
Setting expansion of investment in the casting ring Part 1. A measuring method of volume change of the pattern space formed in the investment and some results obtained. J Japan Soc Dent Appl Mater 11:29-36 (in Japanese).

Palmer DW, Roydhouse RH, Skinner EW. (1961)
Asbestos liner and casting accuracy. Dent Prog 1:156-163.

Phillips RW. (1982)
Skinner's science of dental materials. W.B. Saunders, Philadelphia. 8th Ed. 367-381, 393-406

Powell DA. (1958)
Transformation of the α- and β-forms of calcium sulphate hemihydrate to insoluble anhydrite. Nature 182:792.

Price WA. (1908)
The laws determining casting or fusing results, their control and a new rational technique.
Items Interest 30:363-379.

Price WA. (1911)
The laws determining the behaviour of gold in fusing and casting. Dent Cosmos 53:265-294.

Priest G, Horner JA. (1980)
Fibrous ceramic aluminum silicate as an alternative to asbestos liners. J Prosthet Dent 44:51-56.

Randel WS, Dailey MC. (1933)
High strength calcined gypsum and process of manufacturing same. US Patent No 1901051

Rice WS. (1931)
Dimensional dental casting. J Am Dent Assoc 18:1280-1287.

Ridge MJ. (1961)
Factors determining the water requirement of gypsum plaster. J Appl Chem 11:287-293

Ridge MJ, Beretka J. (1969)
Calcium sulphate hemihydrate and its hydration.
Rev Pure and Appl Chem 19:17-44.

Ridge MJ, Boell GR. (1962)
Physical properties of calcined gypsum.
J Appl Chem 12:437-444.

Scheu CH. (1932)
A new precision casting technique.
J Am Dent Assoc 19:630-633.

Scheu CH. (1933)
Precision casting utilizing the hygroscopic action of plaster in investment in making expanded molds.
J Am Dent Assoc 20:1205-1215.

Scheu CH. (1935)
Controlled hygroscopic expansion of investment to compensate for shrinkage in inlay casting.
J Am Dent Assoc 22:452-455.

Shell JS. (1923)
Gold casting - with special reference to cast gold inlays.
J Am Dent Assoc 10:187-200.

Shell JS. (1960)
Milestones in the development of modern dental casting investment. Dent Survey 36:616-618,770-772.

Shell JS. (1969)
Setting and thermal expansion of investments: Part III. Effects of: no asbestos liner, coating asbestos with petroleum jelly, and double asbestos liner.
J Ala Dent Assoc 53:31-34.

Skinner EW. (1933)
The role of investment setting expansion in gold compensation casting techniques. Dent Cosmos 75:1009-1018.

Skinner EW, Degni F. (1957)
Hygroscopic expansion of dental investment.
J Am Dent Assoc 54:603-608.

Sosman RB. (1965)
The phases of silica. New Brunswick: Rutgers University Press. 38-42.

Souder W. (1927)
The selection of dental materials.
J Am Dent Assoc 14:189-199.

Souder W. (1930)
Problems in dental research. J Dent Res 10:547-560.

Stevens L. (1988)
Setting expansion of investment and accuracy of castings.
Dent Mater 4:367-370.

Suffert LW, Mahler DB. (1955)
Reproducibility of gold made by present day dental casting technics. J Am Dent Assoc 50:1-6.

Sumii T, Hirayama M, Arisaka H, Kashiwase M, Nakanishi T. (1975)
Testing of casting investments. DE (J Dent Eng) 32:20-29 (In Japanese).

Sybron/Kerr Products. (1985)
Cristobalite inlay investment directions.
Sybron/Kerr Products, Michigan, USA.

Taggart WH. (1907)
A new and accurate method of making gold inlays.
Dent Cosmos 49:1117-1121.

Takahashi J, Okazaki M, Kimura H, Haeuchi Y, Kubo F. (1988)
Effect of the porosity of the filler aggregates on the setting expansion of investment material.
J Dent Res 67:1278-1283.

Tasaki Y. (1979)
Thermal behaviour of gypsum-bonded investments (Part 1)
Thermal behaviour in heating process.
J Japan Soc Dent Appl & Mater 20:63-68.

Tasaki Y, Ohta M, Yamane M. (1978)
Dilatometry of gypsum-bonded investment
J Japan Soc Dent Apparat Mater 19:28-38.

Taylor NO, Paffenbarger GC, Sweeney WY. (1930)
Dental inlay casting investments: physical properties and a specification. J Am Dent Assoc 17:2266-2286.

The Standards Association of Australia (1985)
Australian Standard 2795-1985, Gypsum-bonded casting investments.

The Standards Association of Australia (1976)
Australian Standard 1620-1976, Dental casting golds.

Touloukian YS. (1977)
Thermophysical properties of matter. Vol 12. IFI/Plenum, N.Y. 3a-25a,125-133, 1216-1218.

van Aken J. (1961)
Distortion of wax patterns as influenced by setting and hygroscopic expansion of investment.
Tijdschr Tandheelk 68:583-610.

Van Allen GC. (1933)
Investment composition. US Patent No.83593.

Van Horn CS. (1930)
Expanded pattern casting technic.
J Am Dent Assoc 17:736-74.

Van Horn CS. (1934)
What constitutes efficiency in dental inlay casting?
Dent Cosmos 76:511-523.

Volland RH, Paffenbarger GC. (1932)
Cast gold inlay technic as worked out in the cooperative research at the National Bureau of Standards and applied by a group of practising dentists.
J Am Dent Assoc 19:185-205.

Walker EG, (1965)
The role of the mould in casting.
Br Ceram Soc Trans 64:233-249.

Weinstein LJ. (1929)
US Patent. No 1,708,436.

Weisser HB, Milligan WO. (1937)
The mechanism of the dehydration of calcium sulfate hemihydrate. II. Observations with large crystals. J Am Chem Soc 59:1456-1458.

Weisser HB, Milligan WO, Ekholm WC. (1936)
The mechanism of the dehydration of calcium sulfate hemihydrate. J Am Chem Soc 58:1261-1265.

Vli-urpo A, Oilo G, Syverud M. (1982)
The effect of asbest-alternatives on the accuracy of cast veneer crowns. Swed Dent J 6:127-131.

DENTISTRY LIBRARY
UNIVERSITY OF SYDNEY