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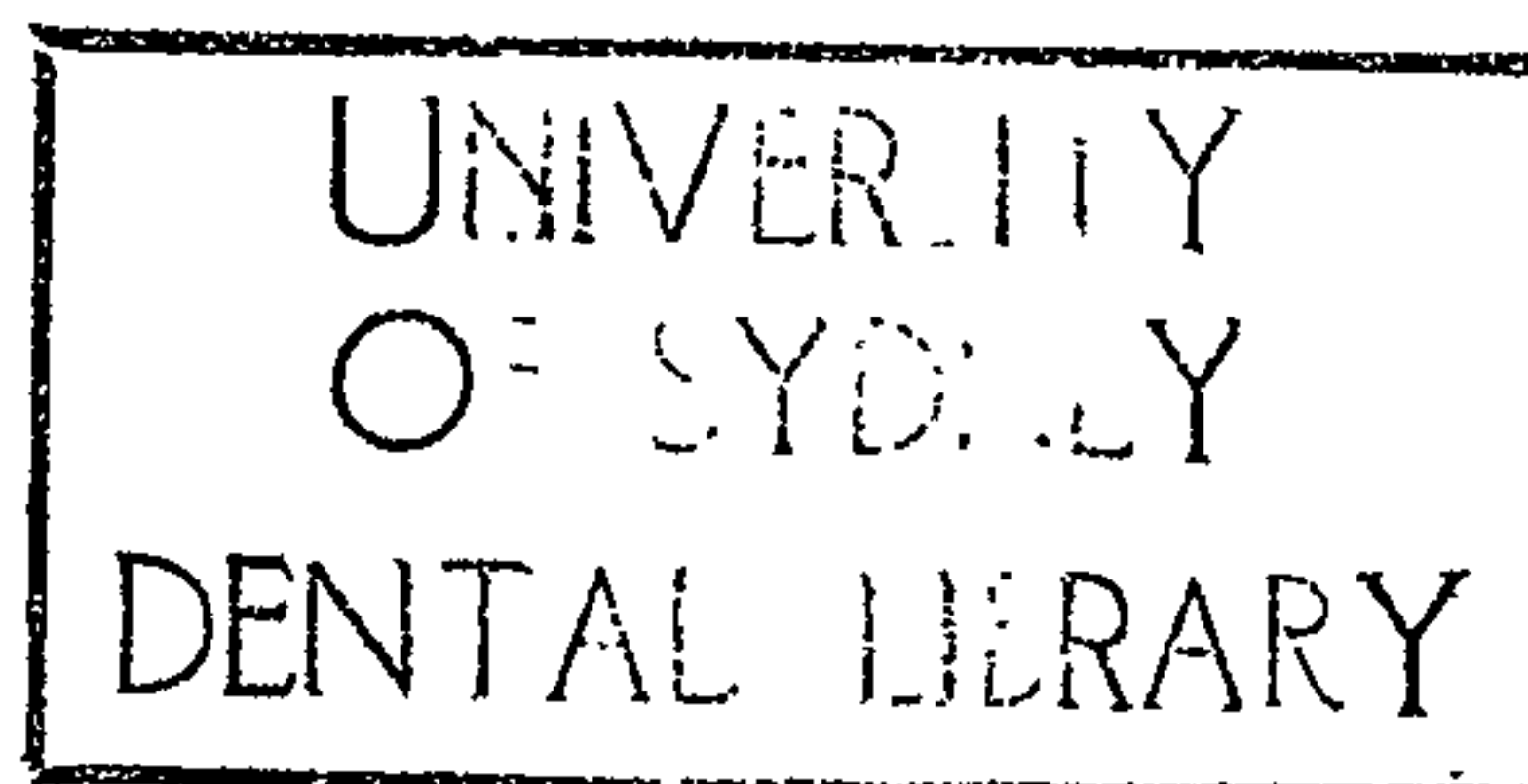
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THE EFFECT OF GOLD COATING AGENTS
ON RESIDUAL STRESS IN
ALLOY-CERAMIC SPECIMENS

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Candidate's Certificate

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

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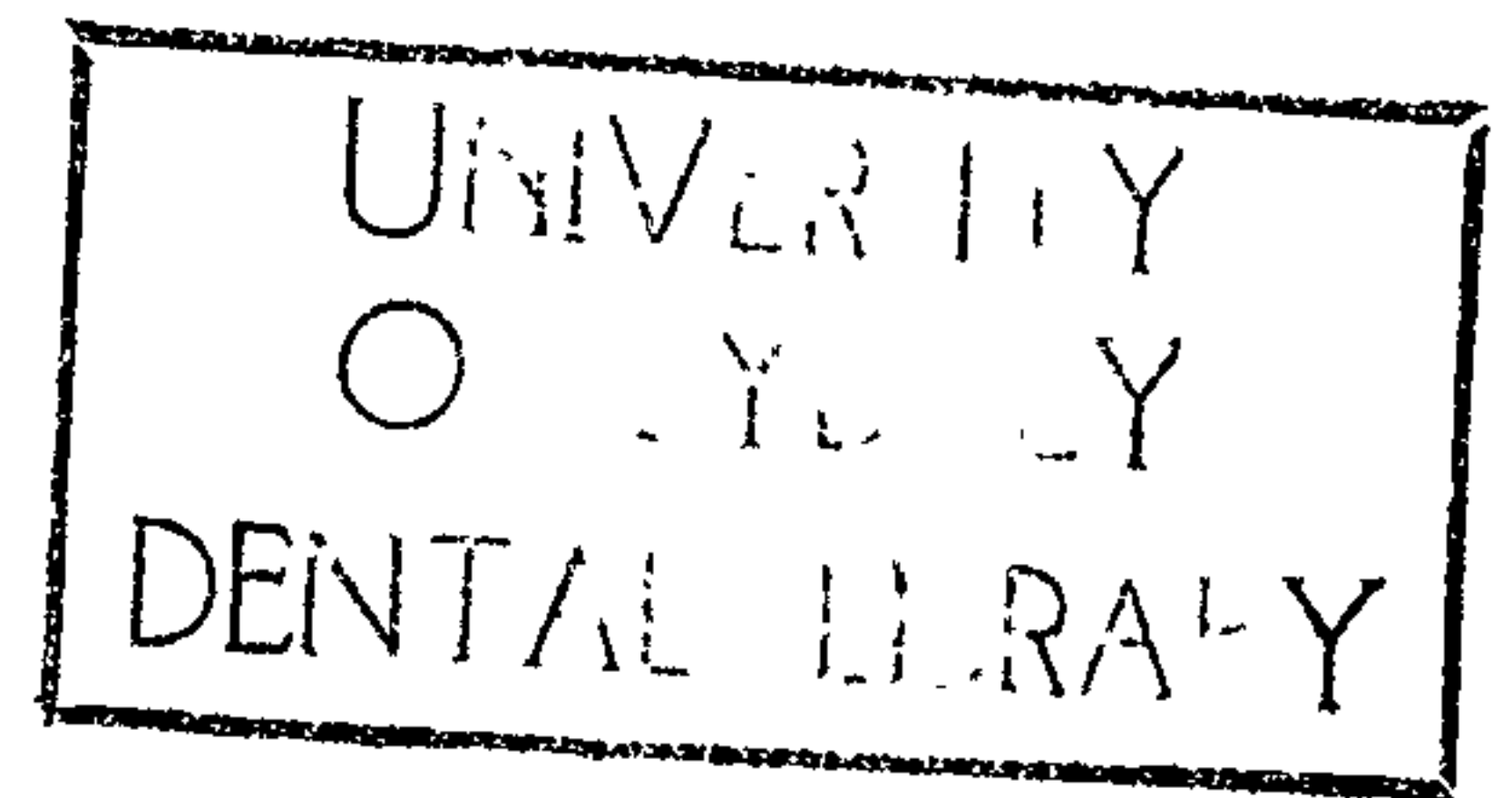
To My Family

CONTENTS

		Page
CHAPTER 1	LITERATURE REVIEW	1
1.1	INTRODUCTION	1
1.2	HISTORY OF ALLOY-CERAMIC RESTORATIONS	1
1.3	THE STRENGTH OF DENTAL PORCELAIN	2
1.4	STRENGTHENING OF DENTAL PORCELAIN	4
1.4.1	Removal Of Flaws	4
1.4.2	Dispersion Strengthening	5
1.4.3	Compressive Stressing	6
1.4.4	Bonding to Metallic Substrates	7
1.5	COMPOSITION OF THE BONDING PORCELAINS	8
1.6	DEVELOPMENT OF THE ALLOYS	12
1.7	THE ALLOY-CERAMIC BOND	20
1.7.1	Mechanical Interlocking	21
1.7.2	Chemical Bonding	23
1.7.3	Van der Waals Forces	26
1.7.4	Bonding by Residual Compressive Stresses in the Ceramic	27
1.8	THERMAL STRESS AND COMPATIBILITY IN ALLOY-CERAMIC SYSTEMS	28
1.8.1	Thermal Expansion Mismatch of Alloy and Ceramic	29
1.8.2	Porcelain Glass Transition Temperature Range	33

1.8.3	Porcelain Viscosity in the Glass Transition Temperature Range	36
1.8.4	Cooling Rates	37
1.8.4.1	Glass Transition Temperature Range	37
1.8.4.2	Annealing	38
1.8.4.3	Actual Thermal Expansion	40
1.8.5	Alloy Creep	41
1.8.6	Thermal Conductivity and Diffusivity	42
1.8.7	Specimen Geometry	43
1.8.7.1	Specimen Shape	44
1.8.7.2	Specimen Size	44
1.8.7.3	Porcelain Coverage	45
1.8.8	Porcelain/Alloy Thickness Ratio	45
1.8.9	Firing Effects	48
1.8.10	Porcelain Layers	50
1.8.11	Thermal History	52
1.8.12	Elastic Moduli	55
1.8.13	Composition of Porcelain and Alloy	57
1.9	TESTS FOR ALLOY-CERAMIC BOND STRENGTH	58
1.10	EVALUATING ALLOY-CERAMIC COMPATIBILITY	63
1.11	CALCULATION OF RESIDUAL STRESS IN ALLOY-CERAMIC SYSTEMS	67
1.12	EFFECT OF GOLD COATING AGENTS	72

CHAPTER 2	PURPOSE AND SCOPE OF THE INVESTIGATION	80
CHAPTER 3	MATERIALS USED	81
3.1	ALLOY	82
3.2	INVESTMENT	85
3.3	GOLD COATING AGENTS	87
3.4	PORCELAINS	89
CHAPTER 4	EXPERIMENTAL METHODS	92
4.1	PREPARING THE ALLOY SPECIMENS	92
4.2	PREPARING THE TEST PORCELAINS	98
4.3	MEASUREMENT OF THERMAL EXPANSION	98
4.4	THERMAL SHOCK TEST	109
CHAPTER 5	RESULTS	112
5.1	THERMAL EXPANSION	112
5.2	THERMAL SHOCK TEST	116
CHAPTER 6	DISCUSSION	120
6.1	THERMAL EXPANSION	120
6.2	THERMAL SHOCK TEST	121
CHAPTER 7	CONCLUSIONS	125
	BIBLIOGRAPHY	126

LITERATURE REVIEW1.1 INTRODUCTION

Ever since Dr. C. H. Land patented the first successful porcelain jacket crown in 1887 (Land, 1903), much research has been devoted to improving the mechanical strength of dental porcelain without sacrificing its aesthetic advantages.

The technique of constructing fixed restorations by bonding layers of ceramic to a cast alloy coping is one method which has achieved these ends. The impact strength and rigidity of the alloy in combination with the aesthetics and stain and abrasion resistance of the porcelain have resulted in widespread acceptance of the technique among the dental profession (Mumford, 1965).

1.2 HISTORY OF ALLOY-CERAMIC RESTORATIONS

As early as the 1880s Land experimented with fusing porcelain for facings, however opaque porcelains had not yet been developed and colour was a major problem (Wells, 1901). High-fusing porcelain was fused to iridio-platinum alloy castings for nearly half a century after the introduction of the lost wax casting process into dentistry in 1907 (Taggart, 1907). Again, colour control was inadequate and the alloy was difficult to cast (Sproull, 1977).

Credit for the first commercially successful alloy-ceramic composite is generally attributed to Dr. Abraham Weinstein in the late 1950s (Tuccillo, 1977). Since that time, the popularity of the porcelain-fused-to-alloy restoration has increased to the extent that 81% of fixed bridgework placed in the United States was of this type (Rand Research, 1981).

In this period there have also been enormous changes in the materials used for these restorations. The rise in the price of gold has stimulated the development of much of this new technology. Weinstein's alloy contained 84% gold (Weinstein, Katz and Weinstein, 1962), whereas now the most commonly used precious alloy in the United States is a palladium-silver type (Rand Research, 1981). In addition to the development of precious non-gold alloys there has also been an increasing emphasis on the use of nonprecious metal alloys such as nickel-chromium.

Changes in the formulation of the porcelains are more difficult to outline because, beginning in about 1960, commercial products were introduced and their compositions remain a closely guarded secret.

1.3 THE STRENGTH OF DENTAL PORCELAIN

The overriding aesthetic requirement has been a great limitation in the development of dental porcelains with greater strength (Jones, 1971). The noncrystalline (glassy) phase which forms the bulk of dental porcelain

has the greatest influence on its mechanical properties (Southan, 1970).

Theoretical calculations of tensile strength for glasses give values one hundred to one thousand times greater than the actual observed values (Griffith, 1920; Kingery, Bowen and Uhlmann, 1976; Eagan and Swearengen, 1978). This discrepancy can be explained by the presence of "Griffith flaws" in bulk glasses (Griffith, 1920). Stress concentrations around small cracks or flaws in ceramic materials remain high because, in contrast to metallic materials, ceramics lack the capacity for plastic deformation which would reduce sharp angles and relieve stress concentrations. Thus, the measured strength of dental porcelain is limited by the most highly stressed flaw in the area being loaded (McLean, 1979). Specially prepared flaw-free specimens have been found to have strength values close to those suggested by theory (Eagan and Swearengen, 1978).

Flaws may be internal or on the surface. In glasses that have been melted, stress raising flaws are usually only present on the surface. Abrasion, corrosion and surface devitrification are the main causes of these flaws. Dental porcelain, because of its predominantly glassy nature, is also most susceptible to surface rather than internal flaws (Southan, 1970; Kingery, Bowen and Uhlmann, 1976; Binns, 1983).

Ceramic materials are extremely brittle. Dental porcelain characteristically shows a critical strain

(strain at fracture) of about 0.1% (Jones, Jones and Wilson, 1972).

Another factor which in the long term reduces the strength of porcelain in the oral environment is the effect of moisture contamination (Baker and Preston, 1946; Wiederhorn, 1972; Southan and Jørgensen, 1974; Sherrill and O'Brien, 1974; Breustedt and Horn, 1979).

One explanation for the effects of moisture contamination is that replacement of alkali ions in the porcelain by hydroxyl ions decreases the apparent activation energy for crack growth (Hasselman, 1970; Wiederhorn, 1972). This phenomenon, which may eventually lead to fracture with relatively low stresses, is known in ceramics technology as static fatigue.

1.4 STRENGTHENING OF DENTAL PORCELAIN

Several different methods are effective in strengthening dental porcelain.

1.4.1 Removal Of Flaws

Internal and especially surface flaws act as stress raisers which lower the strength of glasses (Sugarman, 1967). The time and temperature of firing, whether firing is in air or under vacuum, and the size and distribution of the original porcelain frit particles all affect the size of both surface and internal flaws.

A significant reduction in surface flaws is found when the porcelain surface is glazed (Barghi, King and Draughn, 1975; McLean, 1979). Most dental porcelains are

self-glazing (McLean, 1979; Jones, 1983).

Internal porosity of the spherical type in feldspathic porcelain has little effect on strength (Jones and Wilson, 1975; Meyer, O'Brien and Yu, 1976; Binns, 1977). Weakening does result, however, from the irregularly shaped porosity found in aluminous porcelains (McLean and Hughes, 1965) and from any porosity at the interface with an alloy substrate (Southan, 1977; Jones, 1983).

1.4.2 Dispersion Strengthening*

The relatively high strength and high elastic modulus of crystalline alumina has prompted its use for dispersion strengthening of dental porcelain (McLean and Hughes, 1965; Sherrill and O'Brien, 1974).

It has been postulated that the alumina-glass composite acts as a constant strain system in which the alumina, because of its high elastic modulus, will take a higher proportion of any applied stress (Dinsdale, Camm and Wilkinson, 1967; Jones, 1983).

It has also been suggested that alumina crystals would limit the size of Griffith flaws thus inhibiting crack propagation (Hasselman and Fulrath, 1966).

These effects will be dependent on good bonding between the alumina and the glass matrix (Phillips, 1982;

* This is the term used by dental researchers although it is not strictly correct. Dispersion strengthening in the metallurgical sense refers to the dispersion of a submicroscopic second phase.

Jones, 1983) and on having a fairly close match of coefficients of thermal expansion between alumina crystal and glass matrix (Binns, 1962; Frey and Mackenzie, 1961; Phillips, 1982).

It has been found that strength of the glass is only enhanced when the alumina content is greater than 20% (Binns, 1962; Hasselman and Fulrath, 1966; Jones, 1983). Unfortunately the opacity of porcelain is increased by the inclusion of alumina particles (Phillips, 1973).

1.4.3 Compressive Stressing

Ion exchange techniques have been used in which large potassium ions are substituted for smaller alkali ions in the surface of the porcelain (Pendry and Bradshaw, 1971; Southan, 1975; Jones, 1977). Compressive stresses are produced by the distortion of the silicate network and these must be overcome before tensile failure can occur.

Another method of producing compressive stresses at the porcelain surface involves providing an outer layer with a lower coefficient of thermal expansion than the inner porcelain. This can be done in a number of ways.

Outer veneer porcelains are used with aluminous core porcelains possessing a higher coefficient of thermal expansion thus resulting in compression of the outer porcelain on cooling (Jones, 1983).

Overglazes of low thermal expansion have been used although McLean (1979) warns that this can result in cracking of the porcelain.

Jones (1977) has suggested that substituting potassium for sodium ions may also lower the thermal expansion of the surface porcelain.

1.4.4 Bonding To Metallic Substrates

Bonding the porcelain to an oxide-coated metallic substrate allows the production of a relatively flaw-free internal surface for a ceramic restoration (Sced, McLean and Hotz, 1977; Jones, 1983; Piddock, Marquis and Wilson, 1984). Thus, the potential for crack propagation from the fitting surface is reduced. This method also protects the fitting surface from moisture contamination from the cementing medium (Southan and Jørgensen, 1974).

Metallic substrates which have been used include platinum foil (Piddock, Marquis and Wilson, 1984), tin-plated platinum foil (McLean and Sced, 1976; Piddock, Marquis and Wilson, 1984), tin-plated electroformed gold (Rogers, 1979), and gold-coated platinum foil (Dorney, 1978; Hopkins, 1981).

The most commonly used metallic substrate is a cast alloy coping, and the use of this type of composite restoration is now the most popular method of increasing the fracture resistance of dental porcelain (McLean, 1979). It has been estimated that upwards of 95% of crown and bridge restorations in the United States are of

this type (Jones, 1982).

The cast alloy coping, whilst offering the same advantages as other metallic substrates, also protects the overlying porcelain from tensile stresses because of its high strength and high modulus of elasticity (McLean, 1979; Jones, 1983; Piddock, Marquis and Wilson, 1984).

1.5 COMPOSITION OF THE BONDING PORCELAINS

The modern low-fusing feldspathic porcelains used in porcelain jacket crown construction are composites of crystalline minerals in a glass matrix, their physical properties being a function mainly of the glassy phase (Southan, 1975). Binns (1983) gives the composition of a typical jacket crown porcelain as:

SiO ₂	67.3%
Al ₂ O ₃	10.8%
CaO	2.2%
Na ₂ O	4.6%
K ₂ O	7.9%
B ₂ O ₃	6.8%

The basic glass forming material, fused silica (SiO₂), when fluid, is a powerful solvent for other oxides (Lacy, 1977). The added oxides or fluxes improve such properties as resistance to pyroplastic flow, hardness, hydrolytic stability, and lower the fusing temperature, without causing susceptibility to devitrification. Most of these ingredients are found in

naturally occurring high potash feldspars which are mainly a mixture of monocline ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) and albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) (Southan, 1975).

Oxides of univalent metals (e.g. Na_2O , K_2O) lower the fusing temperature and increase thermal expansion. Oxides of divalent metals (e.g. MgO , CaO) act similarly but with less effect (Lacy, 1977). Alumina (Al_2O_3) increases fusing temperature, fracture resistance, and viscosity but lowers thermal expansion, thus tending to neutralize the effects of additions of oxides of univalent and bivalent metals.

Boron oxide (B_2O_3) is a glass forming oxide; when added in low percentages, it is highly effective in lowering the softening range whilst increasing viscosity and hardness (McLean, 1979).

The addition of the virtually insoluble zirconium oxide (ZrO_2) forms the opaque porcelains. This oxide increases viscosity, increases fusing temperature, and because it promotes crystallization, it has a marked opacifying effect in only small concentrations (Nally, 1968; Lacy, 1977).

Historically, the formulation of porcelains used for bonding to alloys has not been well documented because of the secrecy of manufacturers regarding their products. It has been established, however, that these porcelains are similar to the feldspathic jacket crown types, but with some important modifications. In addition to satisfying the requirements of jacket crown

porcelains, the bonding porcelains must meet the two requirements for a good glass-to-alloy seal (Hull and Berger, 1934; Pask, 1977):

1. The molten glass must wet the alloy.
2. Stresses arising from differences in thermal expansion of solidified glass and alloy must be controlled.

The first published analysis of bonding porcelains showed them to be more complex than their jacket crown counterparts (Nally, 1968). The opaque porcelains contained stannous and titanium oxides in addition to zirconium oxide, all of which acted as opacifiers. Indium was also demonstrated in one opaque porcelain. These constituents appeared to be involved in matching the thermal expansion of the porcelain and alloy. Binns (1983) gives the composition of a typical bonding porcelain as:

SiO ₂	63.2%
Al ₂ O ₃	17.5%
CaO	0.8%
Na ₂ O	5.7%
K ₂ O	11.7%
B ₂ O ₃	1.0%

Jacket crown porcelains have thermal expansion coefficients in the range $5.5-7.5 \times 10^{-6}/K$ (Binns, 1983). Ceramics suitable for bonding need to have thermal

expansion coefficients in the range $13.5-15.5 \times 10^{-6}/K$, so that an adequate match is obtained with the thermal contraction of the substrate alloys (Binns, 1983).

To achieve this high thermal expansion, the alkali content must be increased (McLean, 1979). Increasing the potash (K_2O) content was particularly effective in this regard. It was found that if glasses contained at least 11% K_2O , crystallization of leucite, with a coefficient of thermal expansion of $21.7 \times 10^{-6}/K$, occurred (Hoshikawa and Akagi, 1972). This increased K_2O content has, unfortunately, caused other problems. Manufacturers found that achieving an adequate thermal expansion in this way made the formation of a stable glassy phase extremely difficult.

Jacket crown porcelains have only a small amount of crystalline phase, the result of the presence of quartz found as an impurity in the original feldspar (Southan, 1975; McLean, 1979). In contrast, leucite formation is responsible for the presence of a significant amount of crystalline phase in the bonding porcelains (O'Brien and Ryge, 1964; Binns, 1983).

The leucite crystals have a refractive index close to the basic porcelain matrix, so have little effect on translucency (Binns, 1983). It is important, however, that crystal growth is not excessive as this will reduce strength and increase, to an undesirable extent, the thermal expansion (Binns, 1983).

Aside from the K_2O content, the amount of leucite

formation is determined by the time and temperature of heat treatment. Overfiring has little effect on jacket crown porcelains. The bonding porcelains are extremely sensitive to overfiring or multiple firing which can cause devitrification (i.e. crystalline precipitation from the glassy matrix), resulting in cloudiness in the porcelain (McLean, 1979). It has also been shown that this increased crystalline content results in an increase in the thermal expansion (Shoher, 1971).

An additional flux which has been used is lithium oxide (Li_2O); however this decreases viscosity and therefore increases the risk of devitrification (McLean, 1979).

1.6 DEVELOPMENT OF THE ALLOYS

The development of alloys suitable for alloy-ceramic systems has largely been determined by the need to satisfy these specific requirements (McLean, 1977b, 1979; Tuccillo and Cascone, 1983):

1. The alloy must possess adequate physical properties including high strength, hardness, modulus of elasticity, tarnish resistance and fatigue resistance.
2. Oxides should be formed on the surface of the alloy which are soluble in the porcelain but do not cause discoloration or interfere with glass formation.
3. The alloy must exhibit acceptable working characteristics such as ability to cast fine

margins, accuracy of fit, ease of soldering and burnishability.

4. The alloy or its oxides should not corrode or produce toxic effects in the surrounding tissues.
5. The alloy should exhibit thermal stability (i.e. no phase changes) and sag resistance at porcelain firing temperatures.
6. The alloy should not be susceptible to "hot tearing" when cast.
7. The alloy or its interaction products must not induce high residual stresses in the porcelain because of a large mismatch in the coefficients of thermal expansion.

The other important factor affecting alloy development was the deregulation of the gold price in 1968. The rapid increase in the cost of gold which followed gave great impetus to the development of alternative alloy systems (O'Brien, 1977b).

The first successful alloy for porcelain bonding was basically a gold-platinum-palladium alloy with 84% gold (Weinstein, Katz and Weinstein, 1962). Many similar alloys were soon introduced, followed by reports on their clinical use (Johnston, Dykema and Cunningham, 1956; Lyon et al., 1960; Johnston et al., 1962). The main problem with these alloys was their relatively poor strength properties. This was solved by the addition of less than one percent iron, hardening being the result of an FePt_3

precipitate (O'Brien, Kring and Ryge, 1964; Fuys, Fairhurst and O'Brien, 1973; Smith et al., 1979).

Another problem of the alloys was their high melting and casting temperature (over 1150°C) brought about by the addition of platinum and palladium (McLean, 1979). It was claimed that this high melting range was necessary to avoid metal distortion during porcelain firing (Hobo and Shillingburg, 1973). These high casting temperatures caused breakdown of the gypsum-bonded investments being used at the time (O'Brien and Nielsen, 1959).

The solution came in the form of phosphate-bonded investments which were originally developed for casting partial denture frameworks from cobalt-chromium alloys (O'Brien, 1977b). These investments have a high hot strength, and a thermal contraction much lower than that of solidified casting alloys, so that tensile stresses induced in the castings during cooling sometimes caused hot tearing, particularly in gold-based alloys.

According to Tuccillo and Cascone (1983) the coarse grain size of the original alloys caused this susceptibility to hot tearing, and they claimed that the problem was solved by the use of grain refiners. It had been shown earlier that in ordinary gold casting alloys, elements such as iridium and ruthenium were powerful grain refining agents when added in quite small concentrations (Nielsen and Tuccillo, 1966). Tuccillo

and Cascone (1983) claimed that grain refining in gold alloys designed for porcelain substrates gave improved strength properties, a more homogeneous microstructure, and also eliminated hot tearing. These fine grain alloys also demonstrated more consistent properties eliminating the problem of variations in hardness which had been encountered (Fairhurst and Leinfelder, 1966; Civjan, Huget and Marsden, 1972).

It seems feasible that fine grained alloys are less susceptible to hot tearing as a result of an increased potential for slip deformation in response to stresses at high temperatures.

Base metals such as indium, zinc and tin were also used in these alloys. They hardened the alloy and refined the grain structure (O'Brien, Kring and Ryge, 1964; Vickery and Badinelli, 1968; Tuccillo, 1977) and most importantly, formed surface oxides necessary for a chemical bond to the ceramic (Shell and Nielsen, 1962). Copper and nickel were unsuitable alloying elements because they discoloured the porcelain (O'Brien, Kring and Ryge, 1964).

The main hardening mechanism in these alloys involved precipitation of a second phase during cooling from above 900°C (O'Brien, Kring and Ryge, 1964; Tuccillo and Nielsen, 1967; Vickery and Badinelli, 1968). The size, shape, distribution and stability of the precipitated phase would determine the resultant strength and creep resistance (Tuccillo and Nielsen, 1967).

Further strengthening could be achieved by aging the alloy at a constant temperature (Fairhurst and Leinfelder, 1966; Leinfelder, Servais and O'Brien, 1969; Civjan, Huget and Marsden, 1972). However, this could increase the risk of porcelain devitrification (McLean, 1979).

The only remaining problems for the gold-platinum-palladium type alloys were a modulus of elasticity that was considered to be too low for long span bridges and an excessive susceptibility to creep (Tuccillo and Cascone, 1983).

Creep at porcelain firing temperatures caused distortion of alloy frameworks (Johnston, Dykema and Cunningham, 1956; Tuccillo and Nielsen, 1967).

The solution to both of these problems involved substituting palladium for gold (Tuccillo and Cascone, 1983). The argument against this procedure, that the resultant alloys would be white instead of yellow, was quickly overcome as the price of gold rose. Thus, the medium noble content alloys were introduced in 1972 (Tuccillo, 1977).

The next development was that of the gold-palladium-silver system (Williams and Ingersoll, 1977). Gold was reduced to around 50%, platinum eliminated, palladium held at around 30%, silver increased to 10-15%, and tin and indium increased (Katz, 1974; Tuccillo, 1976; Tuccillo and Cascone, 1983).

The increased tin and indium hardens these alloys

by solid solution strengthening (Tuccillo, 1977). The replacement of gold and platinum by palladium and silver lowered the density by over 20% and reduced cost significantly (Williams and Ingersoll, 1977).

This system displayed physical and working properties at least the equal of the traditional alloys (Civjan et al., 1974; Huget, Dvivedi and Cosner, 1976; Nitkin and Asgar, 1976). It was also claimed that superior mechanical properties made this system more suitable for long span bridgework (Williams and Ingersoll, 1977) and the higher melting range decreased the chances of distortion by creep (Tuccillo and Cascone, 1983).

The system had two problems. Palladium has a high affinity for hydrogen and this hydrogen gas may be evolved during firing of porcelain causing porosity in the opaque porcelain (McLean, 1979).

The other more serious disadvantage was "greening" of the porcelain caused by the silver content (Williams and Ingersoll, 1977).

Despite these problems, the effort to lower the intrinsic cost of the precious alloys saw the introduction of the gold-free palladium-silver alloys in 1974 (McLean, 1979; Tuccillo and Cascone, 1983). These alloys consisted of palladium (50-60%), silver (25-40%), and tin and indium (10-20%) (Huget, Dvivedi and Cosner, 1976; Tuccillo and Cascone, 1983).

Tin and indium were responsible for solid solution

hardening (Huget, Dvivedi and Cosner, 1976; Tuccillo and Cascone, 1983).

It was claimed that the fit of castings of these alloys was inferior (Nitkin and Asgar, 1976). Others suggested that their physical properties could be similar to other systems but their use required a more exacting technique (Tuccillo, 1977; Williams and Ingersoll, 1977).

The major problem with these alloys was that their high silver content introduced the risk of discoloration of the porcelain, which was difficult to predict and control (Tuccillo, 1977; Williams and Ingersoll, 1977). Methods used to control this effect include gold coating agents, ceramic metal conditioners and regular furnace decontamination (Tuccillo and Cascone, 1983).

The problems of silver discoloration led to the introduction of a silver-free gold-palladium system (Cascone, 1978a). This system was similar to the gold-palladium-silver system with palladium content increased and gallium replacing tin. The higher intrinsic cost of this system is offset by its superior working characteristics (Tuccillo and Cascone, 1983).

The escalating price of gold has, however, given great impetus to investigation of non-gold systems. One such system, recently introduced, but growing rapidly in the U.S. market, despite a lack of published information, is the palladium-copper-gallium type (Asgar and Dootz, 1984; Cascone, 1984). This system is composed mainly of palladium (70-80%), copper (5-15%) and gallium (5-10%).

A copper/gallium oxide which forms on the surface appears to be responsible for bonding. Unfortunately, copper may also cause porcelain discoloration (McLean, 1979).

The physical properties and handling characteristics appear to be satisfactory (Caputo and Matyas, 1983; Schaffer, 1984; Byrne et al., 1984; Compton, Lacefield and O'Neal, 1985) as does corrosion resistance (Sumithra et al., 1983; Paradiso, 1984; Lane et al., 1985).

Adherence to porcelain appeared to be adequate in the testing carried out by Caputo and Matyas (1983) although Cascone (1983) has claimed that porcelain adherence is poor.

Anusavice et al. (1984) concluded that the system may be susceptible to unacceptable levels of creep caused by transient but high incompatibility stresses during porcelain cooling.

The development of nonprecious alloys for porcelain bonding was also due in no small part to the rising cost of precious metals (McLean, 1979). These alloys are based on either nickel-chromium with or without beryllium or cobalt-chromium with or without ruthenium (Tuccillo and Cascone, 1983).

Although Moffa et al. (1973) concluded that these alloys had physical properties which were superior to gold-based alloys, other workers disagreed. The fit of castings was found to be inferior (Nitkin and Asgar, 1976;

Stevens, 1977; Goldestaneh, 1979; Duncan, 1980). The nonprecious alloys were technique-sensitive and difficult to handle (Vincent, Stevens and Basford, 1977; Lubovich and Goodkind, 1977).

In addition, bonding failures occurred because of the difficulties in controlling chromium or nickel oxide formation (McLean and Sced, 1976). This problem was exacerbated by a lowering of the thermal expansion of the porcelain due to the entry of chromium or nickel oxides, leading to a high residual stress at the bond (McLean, 1977b).

Another problem which still plagues the nonprecious alloys is the controversy over the potential dangers of nickel and beryllium (Bergman, Bergman and Söremark, 1980; Ingersoll, 1982; McLean, 1983).

Despite the many alternatives now becoming available, the gold-based alloys still remain the standard with which other alloys must be compared. In Europe, at least, the gold-based alloys are still the most popular for porcelain bonding (Tuccillo and Cascone, 1983).

1.7 THE ALLOY-CERAMIC BOND

Although the nature of bonding forces developed between alloy and ceramic in dental restorations has been studied quite intensively over the last 25 years, complete understanding of the phenomenon has yet to be reached.

Four factors have been cited as being responsible for alloy-ceramic bonding (Shell and Nielsen, 1962; McLean, 1979; Bertolotti, 1983); their relative importance is still controversial.

1. mechanical interlocking
2. true chemical bonding
3. retention by van der Waals forces
4. bonding by residual compressive stresses in the ceramic

1.7.1 Mechanical Interlocking

When porcelain fills small irregularities in the alloy surface, retention is achieved by mechanical interlocking (Silver, Klein and Howard, 1960). The importance of this factor in alloy-ceramic adherence has been disputed.

Shell and Nielsen (1962) found no significant contribution from mechanical bonding. Other workers proposed that its value could be up to one third of the total shear bond strength (Knapp and Ryge, 1966; Vickery and Badinelli, 1968).

It has been claimed that surface roughness produced by sandblasting provided mechanical bonding (McLean and Sced, 1973a; Lugassy, 1977). Ringle, Mackert and Fairhurst (1983) concluded that adherence values for alloy-porcelain composites were extremely sensitive to the state of surface roughness. Investigations of non-dental enamel-metal systems have suggested that

mechanical interlocking induced by a roughened metal surface increased bond strength only when bonding was weak because of poor chemical adherence (Patrick, Porst and Spencer-Strong, 1953; Richmond et al., 1953; King, Tripp and Duckworth, 1959; Pask, 1977a).

One disadvantage of increasing surface roughness of the casting in order to provide mechanical retention of the porcelain is that it will result in increased stress concentrations in the ceramic coating and these can cause failure of the bond under relatively low applied stresses (King, Tripp and Duckworth, 1959; Kelly, Asgar and O'Brien, 1969; Katz and Bergen, 1977).

Another problem which may arise with excessive surface roughness is that the high viscosity of opaque porcelains at fusing temperatures may allow them to bridge across the peaks of a rough surface (Brooks, 1977).

Yet another problem is that coarsely abraded metallic surfaces may have deformed metal tags which can trap air which is then released into the porcelain during firing procedures (Brooks, 1977; Bertolotti, 1983).

McLean (1979) has claimed excellent results by pressure blasting the alloy surface with 30 μm aluminium oxide particles. The major benefit of surface roughness may be the resultant increase in interfacial area available for chemical reaction rather than mechanical interlocking (King, Tripp and Duckworth, 1959; Pask and Fulrath, 1962; McLean and Sced, 1976; Lugassy, 1977).

It has been demonstrated that as chemical reactions occur during porcelain bonding, the interface is roughened (Pask and Fulrath, 1962; von Radnoth and Lautenschlager, 1969). This may result in some mechanical interlocking (Pask, 1977a) and so may explain why shear bond strength values for roughened or polished alloys have been found to be about the same (Shell and Nielsen, 1962).

1.7.2 Chemical Bonding

A strong chemical bond at the interface is the fundamental requirement for good adherence between a glass and a metallic substrate (Pask and Fulrath, 1962). This proposal is generally accepted as being true for alloy-ceramic systems for dental applications.

Chemical bonding is characterised by the existence of continuous primary interatomic bonding across the interface (Pask, 1977a). It has been claimed that this occurs when oxides of the metal in its lowest valency state are present in equilibrium at the interface (King, Tripp and Duckworth, 1959; Pask and Fulrath, 1962; Bhat and Manning, 1973; Pask, 1977a).

Strong chemical adherence requires that the interface be saturated by the metal oxide. Thus the rate of oxide formation and solution in the ceramic at the interface must be greater than the diffusion of dissolved oxide away from the interface (Pask and Fulrath, 1962; Cascone, 1977; Bertolotti, 1983). Ideal conditions for

adherence were thought to occur when there existed a monomolecular oxide layer at the interface (Pask and Fulrath, 1962; Claus, 1983; Bertolotti, 1983). Experiments with iron and a sodium disilicate glass by Jach, Joshi and Sengupta (1980) have shown that although the reaction zone decreases with increased time and temperature of heating, it does not vary greatly. In fact, the iron and glass never came into contact without an intermediate oxide layer and this layer was never very thin.

It has been noted that if a definite oxide layer exists, it must strongly adhere to the metal and must have adequate strength itself (Hull and Berger, 1934; Pask and Fulrath, 1962; Mackert et al., 1984a).

Shell and Nielsen (1962) found that the presence of oxidizable base metals in noble alloys increased adherence of porcelain. Other workers have proposed the effectiveness of oxidation of tin to provide a chemical bond (Marboe and Weyl, 1949; McLean and Sced, 1976). It was also shown that preoxidation of noble alloys improved bonding (McLean and Sced, 1973).

The importance of oxidizable trace metals was further demonstrated by the high concentration of such elements as iron, tin and indium found near the interface in both the alloy and the porcelain in microprobe analyses by various workers (Nally, Monnier and Meyer, 1968; Lautenschlager, Greener and Elkington, 1969; von Radnoth and Lautenschlager, 1969; Fairhurst, 1977;

Lugassy, 1977; Laub et al., 1978; Claus, 1983). High indium concentrations were also reported near the interface in both alloy and porcelain by Goeller, Meyer and Nally (1972).

Atmospheres which promoted oxidation of metals were also found to promote ceramic-alloy adherence (Knapp and Ryge, 1966; Leone and Fairhurst, 1967).

Research into non-dental applications has demonstrated the efficacy of alkali oxides present in the glass in promoting chemical adherence (Borom and Pask, 1966; Borom, Longwell and Pask, 1967; Brennan and Pask, 1973).

The importance of the presence of metal oxides in porcelain for dental systems has been supported by Anusavice, Horner and Fairhurst (1977). They concluded that tin oxide (SnO_2) was responsible for the chemical adherence in a noble alloy-ceramic system and that tin atoms found in high concentration in the alloy near the interface had diffused through from the opaque porcelain.

Chemical bonding mechanisms have been examined in non-noble metal ceramic systems and have been found to be similar (McLean and Sced, 1973a; Anusavice, Ringle and Fairhurst, 1977).

The problem with the base metal alloys was one of excessive oxidation. Chromium in nickel-chromium and cobalt-chromium alloys formed a thick, weak, oxide layer at the interface. This can be most effectively controlled by the addition of beryllium to the alloy; however

beryllium is toxic (Bertolotti, 1983). In addition there is a high diffusion rate of nickel and chromium oxides into the porcelain (Anusavice, Ringle and Fairhurst, 1977; McLean and Sced, 1973a; Lugassy, 1977; Claus, 1983). Chromium reduced constituents of the porcelain, producing chromium oxide and resulting in discoloration (McLean and Sced, 1973a).

The nature of chemical adherence in dental alloy-ceramic systems is dependent on a multiplicity of factors including diffusion of trace elements to the alloy surface; oxidation of these elements which will be affected by firing atmosphere and vacuum level; dissolution of the metal oxides by the molten porcelain; oxidation-reduction reactions at the interface; and diffusion of trace elements in the porcelain (Cascone, 1977; Cascone and Tuccillo, 1977; Anusavice, Horner and Fairhurst, 1977).

1.7.3 Van der Waals Forces

Van der Waals forces refer to the adhesion which results from wetting without the formation of an equilibrium transition zone at the interface which occurs in true chemical bonding.

Shell and Nielsen (1962) considered that van der Waals forces were responsible for up to one third of shear bond strength. O'Brien and Ryge (1964, 1965) concluded that these forces could account totally for ceramic-alloy adherence and that surface oxides merely

increased wetting. Other workers have doubted the contribution of van der Waals forces to bonding (Vickery and Badinelli, 1968; Anthony et al., 1970).

Pask and Fulrath (1962) stated that van der Waals bonding occurred when conditions were unsatisfactory for chemical bonding and resulted in weak adherence. Inconsistency between contact angle measurements and adherence values for alloy-ceramic specimens suggests also that van der Waals forces do not play a large role in bonding (Mackert et al., 1984).

Van der Waals forces may be partially responsible, however, for the increased adherence resulting from sandblasting the alloy surface (McLean and Sced, 1976; Lugassy, 1977; Lubovich and Goodkind, 1977; Jochen, Caputo and Matyas, 1984) as wetting (resulting from a low contact angle) is facilitated by increasing surface roughness (Wenzel, 1936; Glantz, 1969).

1.7.4 Bonding by Residual Compressive Stresses in the Ceramic

If the substrate alloy has a higher thermal expansion than the porcelain, the porcelain will be placed in compression on cooling and higher applied stresses will be necessary before tensile failure of the bond will occur.

This is claimed to be an important factor in bond strength by numerous authors (Vickery and Badinelli, 1968; Moffa et al., 1973; Lugassy, 1977; Weiss, 1977;

McLean, 1979). The proviso is that thermal expansion mismatch must not be too great or the resultant residual stresses will contribute to bond failure (McLean, 1977b).

It has been stated that this type of compressive bonding would only be applicable in the situation where the porcelain completely encompasses the alloy (Binns, 1983). It would also seem that symmetrical specimen geometry would be required, hardly likely in dental applications.

In fact, DeHoff and Anusavice (1984a) have reported how misleading this condition is when assessing the bond strength of alloy to porcelain with a symmetrical test specimen design.

1.8 THERMAL STRESS AND COMPATIBILITY IN ALLOY-CERAMIC SYSTEMS

Anusavice et al. (1983) have given a good definition of the term "thermal compatibility". It "refers to the ability of a metal and contiguous porcelain to undergo a series of thermal expansion and contraction cycles without the generation of sufficient transient or residual stress to cause immediate laboratory failure such as porcelain chipping and metal distortion or subsequent clinical failure of the porcelain structure".

A multitude of factors has been implicated in studies of alloy-ceramic compatibility. The most important of these is the mismatch in coefficients of

thermal expansion of the components of an alloy-ceramic system. The result of this mismatch is the development of residual thermal stress (Nielsen and Tuccillo, 1972a), provided bonding has occurred (Ingersoll, 1977; Fairhurst et al., 1981). The level of residual stress which arises from thermal incompatibility is dependent upon the glass transition range of the porcelain, its viscosity in the glass transition range, cooling rates, alloy creep, thermal conductivity and diffusivity, specimen geometry (framework design), porcelain-alloy thickness ratio, firing effects, porcelain layers, thermal history, elastic moduli, and composition of porcelain and alloy. The significance of these factors, though highly interdependent, will be considered separately.

1.8.1 Thermal Expansion Mismatch of Alloy and Ceramic

If two adherent bodies have exactly identical coefficients of thermal expansion, no interfacial stresses develop as a result of temperature changes (Kingery, Bowen and Uhlmann, 1976). As the coefficients of thermal expansion of the two bodies become increasingly different, internal stress increases correspondingly. If the strength of one of the bodies or the strength of the interface is exceeded, cracking will occur (Hunter and Brownell, 1967).

The importance of controlling the thermal expansion of the alloy and the porcelain in dental systems has been pointed out (Shell and Nielsen, 1962; Moffa, 1977;

McLean, 1977b).

Shell and Nielsen (1962) maintained that coefficients of thermal expansion of alloy and ceramic should be exactly matched. In practice, this aim is almost impossible to achieve (Nielsen and Tuccillo, 1972a; Ringle et al., 1978; McLean, 1979; Dorsch, 1981). Other workers have claimed that the alloy should have a slightly higher thermal expansion than the porcelain (a positive thermal expansion mismatch) (Vickery and Badinelli, 1968; Moffa et al., 1973; Cascone, 1978, 1979). Still others have been in favour of matching coefficients of thermal expansion as closely as possible (Nielsen and Tuccillo, 1972a; Doremus, 1973; O'Brien, 1977b; Craig, O'Brien and Powers, 1983; Bertolotti, 1983).

Observations of commercial dental systems have shown that most are designed to have a positive thermal expansion mismatch (Ringle et al., 1978; Asgar and Giday, 1979; Whitlock et al., 1980; Fukui et al., 1980) although a few porcelain-alloy combinations have exhibited a negative mismatch (Fukui et al., 1980; Al-Azzawi, Sorensen and Argawal, 1980; Fairhurst et al., 1980; Whitlock et al., 1981).

It is fairly well established that alloy-ceramic combinations can withstand, at most, only a very small negative mismatch and that any such mismatch is probably undesirable (Tuccillo and Nielsen, 1972; Cascone, 1979; Al-Azzawi, Sorensen and Argawal, 1980; Anusavice et al.,

1982; Cascone and Nabatian, 1982). In contrast, however, Walton and O'Brien (1985) have reported that a negative thermal expansion mismatch did not cause higher residual stress than a positive mismatch. It has also been determined that too large a positive thermal expansion mismatch will result in failure (Nielsen and Tuccillo, 1972a; Walton, 1981). There is, however, no general agreement as to whether coefficients of thermal expansion should be matched as closely as possible or whether a small positive mismatch is more beneficial.

The argument in favour of a positive mismatch is based on the fact that porcelain is stronger in compression than in tension (Southan, 1975). Once cooling commences after porcelain sintering, the alloy will contract more than the porcelain resulting in a residual compressive stress in the porcelain (Vickery and Badinelli, 1968; Cascone, 1979). This residual compressive stress must be overcome before tensile failure of the porcelain will occur. The compressive forces will also act to prevent crack propagation.

It has been argued that this compression can help the porcelain to withstand forces whose main component is perpendicular to the interface; on the other hand, shear stresses set up at the interface will weaken the resistance of the porcelain to an applied shear loading; especially at restoration margins (i.e. the ends of the interface) (Binns, 1983; Shoher, 1984).

It has also been claimed that so-called

"compressive bonding" will occur (Vickery and Badinelli, 1968; McLean, 1979). This last contention would seem to be somewhat oversimplified.

In one study, Rowe and Asgar (1976) found no correlation between bond strengths and differences in positive mismatch. In another investigation, it was concluded that a positive mismatch gave higher porcelain-alloy adherence values than a negative mismatch but the "ideal" difference in coefficients of thermal expansion between alloy and ceramic was found to extend over a large range (Al-Azzawi, Sorensen and Agarwal, 1980).

Käse, Case and Tesk (1983) have used sonic resonance to study two porcelains used for fusing to alloy substrates. They concluded that both porcelains, like all glassy ceramics, showed evidence of having a slightly microcracked structure. This finding may lend weight to the argument that introducing compressive stresses into the porcelain may be important in preventing crack propagation.

The argument for attempting to match coefficients of thermal expansion of porcelain and alloy is based on the reasoning that large residual stresses, compressive or tensile, in the porcelain or at the interface, must be avoided (Nielsen and Tuccillo, 1972a; O'Brien, 1977b; Bertolotti, 1983).

This fairly logical approach would seem to be easy to co-ordinate with the thoughts of those who consider that a small positive thermal mismatch is preferable. It

has been generally agreed that a negative thermal mismatch is detrimental to the ceramic-alloy composite. Also, perfectly matched coefficients of thermal expansion are not possible. It will be shown that the actual thermal expansions of a porcelain and its substrate alloy in a porcelain-alloy composite may be markedly different from the coefficients of thermal expansion obtained from dilatometer measurements of separate porcelain and alloy specimens. A small positive thermal expansion mismatch (according to dilatometer measurements) would reduce the possibility that an alloy-ceramic restoration would have negative thermal expansion mismatch which is known to be much less well tolerated. Thus a (dilatometer measured) positive thermal expansion mismatch may, when the many variables are taken into account, be the most acceptable way of approaching the minimal stress state considered to be so important by those who believe that matching coefficients of thermal expansion is the ideal.

1.8.2 Porcelain Glass Transition Temperature Range

The porcelain glass transition temperature range is the temperature range over which the porcelain changes from glassy state to liquid state behaviour. This region is characterised by a marked increase in coefficient of thermal expansion of the porcelain at around 550°C (Bertolotti, 1983). For convenience, a glass transition temperature (T_g) found by extrapolation is often quoted

in this range (Figure 1.1).

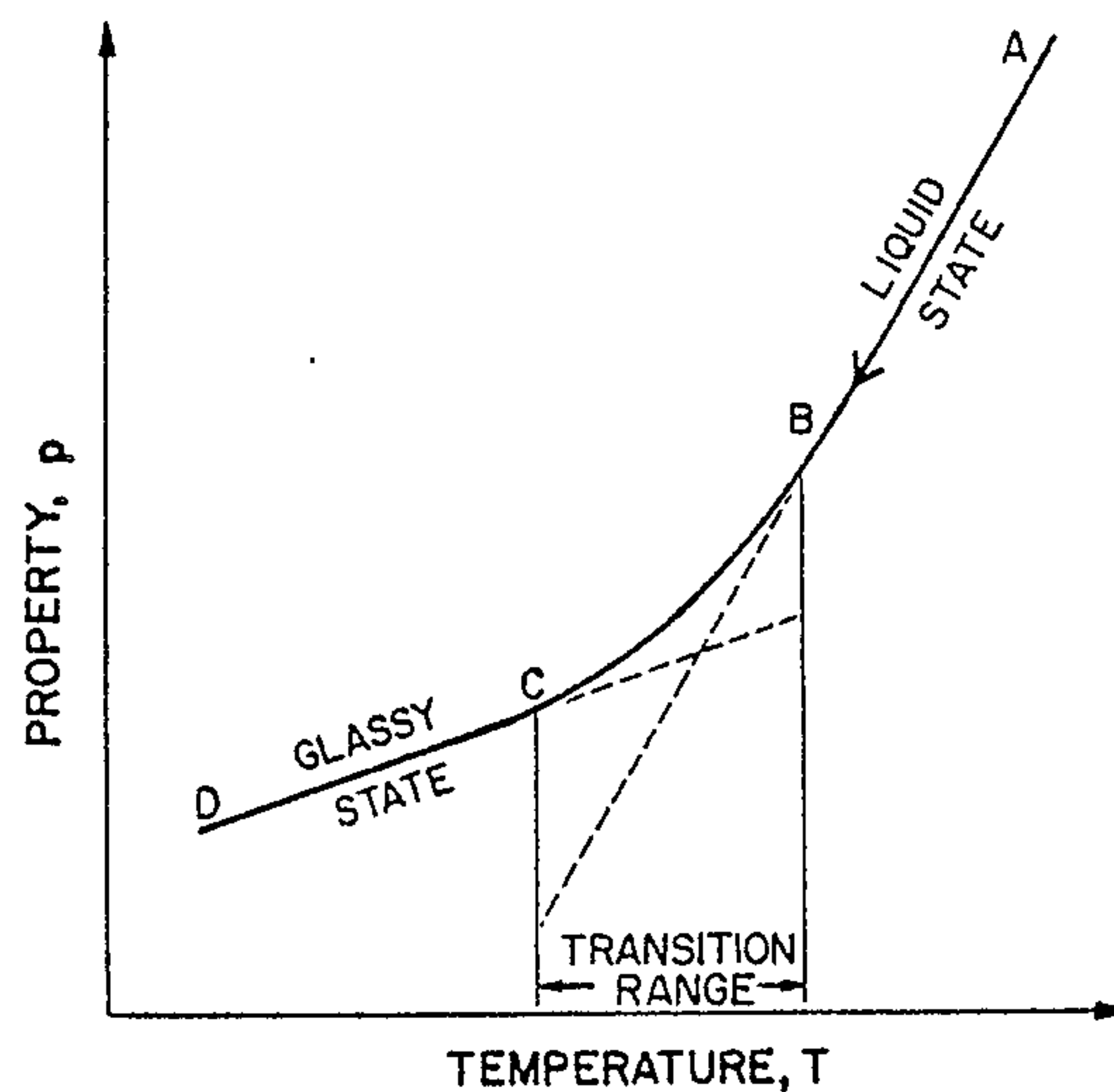


Figure 1.1 Determination of glass transition temperature by extrapolation (from Narayanaswamy, 1971)

Stresses which are induced by thermal expansion mismatch will remain after cooling only if they arose at temperatures lower than those at which rapid plastic flow can take place. Thus the magnitude of residual stresses at any temperature vary according to the glass transition temperature range of the porcelain.

Some workers, by various methods, have derived a single temperature for the glass transition of dental porcelain (an "assumed" glass transition temperature), and have emphasized the large influence that small changes in this "assumed" temperature have on residual stress (Anusavice, DeHoff and Casteel, 1981; Fairhurst et

al., 1981; Cascone and Nabatian, 1982; DeHoff and Anusavice, 1983, 1984a).

Though not doubting the importance of the glass transition temperature range, others have rejected the idea of a specific transition temperature (T_g) to describe this large temperature interval (Rekhson, 1979; Bertolotti and Shelby, 1979; Fairhurst, Hashinger and Twiggs, 1981a; Bertolotti, 1982; Scherer, 1983).

Fairhurst, Hashinger and Twiggs (1981a) found that the glass transition range could not be adequately described by a single glass transition temperature. Bertolotti and Shelby (1979) claim that dental porcelains exhibit a slower change of viscosity than do typical glasses because of the large amount of crystalline material which interferes with glass flow.

It has been shown that the transition region for glasses may extend over a range of about 200°C (Hagy and Ritland, 1957).

On cooling from the liquid state, stresses begin to arise at temperatures well above the assumed glass transition temperature (Bertolotti and Shelby, 1979; Rekhson, 1979; Scherer, 1983). In addition, stress relief occurs at temperatures well below the glass transition temperature (Rekhson, 1979; Cascone, 1979; Bertolotti, 1980; Tesk et al., 1981a). Thus the effects of the glass transition are manifested over an extended temperature range.

1.8.3 Porcelain Viscosity in the Glass Transition Temperature Range

Viscosity is the property, usually of a fluid, whereby it tends to resist relative motion within itself, as a result of shear stress.

The behaviour of porcelain in the glass transition range is unusual in that its viscosity is both temperature and time dependent (Narayanaswamy, 1971; Kingery, Bowen and Uhlmann, 1976; Rekhson and Mazurin, 1977; Rekhson, 1979; Hlaváč, 1983). The nature and importance of the time dependence of this viscosity will be discussed in section 1.8.4.2.

Reducing the temperature produces a rapid increase in the viscosity of dental porcelain (Bertolotti and Shelby, 1979; Bertolotti and Fukui, 1982; Tesk et al., 1981).

During cooling of a porcelain-alloy composite after porcelain sintering, stresses build up at the interface and within the porcelain.

Stress relaxation is the result of a rearrangement of atoms within the porcelain (viscous flow) (Kingery, Bowen and Uhlmann, 1976). Thus the rate of decrease of stress is inversely proportional to the viscosity of the porcelain (Preston, 1925; Bertolotti and Shelby, 1979). Viscosity is also, of course, dependent on the composition of the porcelain.

The viscosity of the porcelain also affects its ability to flow into surface irregularities in the alloy

surface. Thus a lower viscosity will tend to result in less porosity at the alloy-ceramic interface (Southan, 1977; Jones, 1983).

1.8.4 Cooling Rates

The complex effects of the cooling rate on alloy-ceramic specimens and the associated lack of understanding of these effects have resulted in a plethora of suggestions for the ideal cooling rate. These suggestions include cooling under a glass cover (Johnston, Phillips and Dykema, 1971; Tylman and Malone, 1978), cooling in ambient air (The Ceramco Technical Manual, 1976), slow oven cooling (Malhotra and Maickel, 1980; Guinn, Griswold and Vermilyea, 1982), rapid cooling in an ice chest (Guinn, Griswold and Vermilyea, 1982), isothermal soaking (Bertolotti, 1980b; Walton and O'Brien, 1983), and slow cooling at the muffle entrance of the dental furnace (McLean, 1979).

The rate at which a ceramic-alloy specimen is cooled after the ceramic has been sintered will affect the glass transition temperature range of the ceramic, reduction of stress by annealing, and the actual thermal expansion.

1.8.4.1 Glass Transition Temperature Range

It has been shown that observed glass transition temperatures for glasses are dependent upon the heating and cooling rates (Moynihan et al., 1974). These

researchers showed that higher heating and cooling rates resulted in higher measured glass transition temperatures.

This is also valid for dental porcelain (Tuccillo and Nielsen, 1968; Bertolotti and Shelby, 1979; Whitlock et al., 1981; Fairhurst, Hashinger and Twiggs, 1981; Bertolotti and Fukui, 1982; Bertolotti, 1981).

The result of this higher glass transition temperature range is an increase in porcelain viscosity when compared with slowly cooled porcelain at the same temperature: thus there is an increase in residual stress after cooling (Rekhson, 1979; Bertolotti, 1982).

Rekhson (1979) has shown that the stress, in a glass-to-ceramic seal after cooling to room temperature, could vary by up to 50% with a 5°C variation in the "setting temperature" (i.e. the upper limit of the glass transition temperature range).

1.8.4.2 Annealing

Stresses which arise as the result of rapid cooling of dental porcelain can be largely eliminated by holding the ceramic in the annealing temperature range for a sufficiently long period and then cooling it slowly to room temperature (Jastrzebski, 1976).

Annealing of porcelain in a porcelain-alloy composite is dependent upon viscous flow resulting in stress relaxation; however, the behaviour of the porcelain during such a treatment is interesting in that

the volume and the viscosity of the porcelain change with time according to the thermal history of the ceramic (Narayanaswamy, 1971; Kingery, Bowen and Uhlmann, 1976; Rekhson and Mazurin, 1977; Rekhson, 1979; Scherer and Rekhson, 1982; Scherer, 1983; Hlaváček, 1983).

Both the volume and viscosity change with time, tending toward an equilibrium structure (Kingery, Bowen and Uhlmann, 1976; Hlaváček, 1983).

If the ceramic enters the annealing range from a previously higher temperature, there is a rapid decrease in volume towards an equilibrium and a much slower decrease in viscosity (Kingery, Bowen and Uhlmann, 1976). The rapid decrease in volume, which proceeds faster than stress relaxation, will initially result in an increase in tensile stress in the ceramic (Rekhson, 1979). As this decrease in volume concludes, stress relaxation will decrease these tensile stresses; however, the rise in tensile stress may cause fracture of the ceramic before the stresses are dissipated (Rekhson, 1979).

Conversely, if the ceramic enters the annealing range from a lower temperature, there is a rapid increase in viscosity and a much slower increase in volume (Kingery, Bowen and Uhlmann, 1976).

Thus the rate of stress relaxation of porcelain in the annealing range is not linear.

Annealing cycles have been suggested for ceramic-alloy specimens and, in the research laboratory, appear to be successful (Bertolotti, 1980b; Walton and O'Brien,

1983). Whitlock et al. (1981) have also suggested that isothermal annealing above T_g may be beneficial in reducing stress in the porcelain.

1.8.4.3 Actual Thermal Expansion

As described above, isothermal heat treatment will result in a change in porcelain volume and viscosity. If cooling is now continued, thermal contraction from the hold temperature to room temperature will differ from that of constant cooling without a hold (Rekhson, 1979, 1979a).

Fast cooling will also affect the thermal contraction of the porcelain, resulting in a lower thermal contraction than that measured by the dilatometer at slow rates (Burnett and Smith, 1972; Cascone, 1977; Whitlock et al., 1981; Fairhurst, Hashinger and Twiggs, 1981).

Either of these effects will result in a thermal expansion mismatch which differs from that calculated according to dilatometer data.

Another important property of glasses which is observed on cooling is that of thermal hysteresis (Rekhson, 1979). The contraction curve does not follow the expansion curve. This factor has led to the suggestion from many authors that it is of more relevance to compare contraction rather than expansion curves of porcelain (Bertolotti and Shelby, 1979; Rekhson, 1979; Fairhurst et al., 1980; Whitlock et al., 1981; Scherer,

1983; Bertolotti, 1983).

It should be noted, however, that maximum reported heating and cooling rates used in dilatometer measurements have been $30^{\circ}\text{C}/\text{min}$. (Fairhurst, Hashinger and Twiggs, 1981a; Bertolotti, 1981), whilst initial cooling rates for porcelain-alloy samples in dental laboratories are reportedly as high as $1500^{\circ}\text{C}/\text{min}$. (Fairhurst, Hashinger and Twiggs, 1981). Thus any comparison of expansion or contraction curves of alloy and porcelain should probably remain qualitative rather than quantitative. This problem has also been acknowledged in the literature (Cascone, 1977; Anusavice et al., 1983a; Preston, 1984).

1.8.5 Alloy Creep

Creep is the progressive permanent deformation of a material under a constantly applied load, usually at elevated temperatures (Tuccillo and Nielsen, 1967). Creep is a thermally activated process which occurs at temperatures above half the solidus temperature of the alloy measured in kelvin (Bertolotti and Moffa, 1980).

Creep of substrate alloys has been examined by a number of researchers (Tuccillo and Nielsen, 1967; Moffa et al., 1973; Lugassy and Kumamoto, 1974; Anusavice, Ringle and Weber, 1979; Bryant and Nicholls, 1979; Bertolotti and Moffa, 1980; Bridger and Nicholls, 1981; Bertolotti, 1981; Anusavice et al., 1984; DeHoff and Anusavice, 1984). The loads which the alloy undergoes

during fusing of porcelain are the result of gravity and of the thermal expansion mismatch between porcelain and alloy (Anusavice, 1983).

Alloy creep, then, is a function of the temperature and applied stress. In addition, creep is influenced by the melting range, microstructure, density, and framework geometry of the alloy in an alloy-ceramic specimen (Tuccillo and Nielsen, 1967; McLean, 1979; Anusavice et al., 1984).

Creep due to gravitational forces has a detrimental effect on the fit, particularly of long span bridges (Bryant and Nicholls, 1979; Bridger and Nicholls, 1981).

Creep caused by thermal expansion mismatch has been cited as the cause of margin "opening" during porcelain firing when alloy-ceramic restorations have very thin alloy margins (Shillingburg, Hobo and Fisher, 1973; Bertolotti and Moffa, 1980).

Bertolotti (1981) has pointed out that creep in the alloy coping may also have a beneficial effect. Plastic deformation of the alloy could be effective in reducing stresses arising because of a thermal expansion mismatch.

1.8.6 Thermal Conductivity and Diffusivity

Thermal conductivity is the rate of heat transfer along a body by conduction. It has been shown that for transient temperature changes, thermal diffusivity (thermal conductivity/specific heat x density) is probably the more relevant property (Braden, 1964).

A high thermal conductivity and diffusivity will reduce thermal gradients and their attendant stresses caused by thermal expansion which arise during heating and cooling of a body (Kingery, 1955; Crandall and Ging, 1955).

In fact, dental porcelain conducts heat very poorly. Alloys for ceramic bonding conduct heat 500 to 1000 times faster than does porcelain (Cascone, 1979).

Cascone (1979) has proposed that thermal gradients which arise during cooling of a porcelain-alloy composite after porcelain sintering could result in temporary stresses high enough to cause failure. It has also been claimed that the low thermal conductivity of porcelain, with rapid cooling after firing, is the main cause of "in-porcelain" stresses in alloy-porcelain composites (Shoher, 1984).

In addition, thermal gradients arising during cooling after sintering will affect the actual thermal expansions of the porcelain layers (Cascone, 1979; Shoher, 1984).

DeHoff, Anusavice and Boyce (1983) employed a thermal shock test which attempted to partially simulate intraoral conditions, and concluded that high tensile stresses which developed in the specimen were the result of temperature gradients in body porcelain.

1.8.7 Specimen Geometry

Under this heading, consideration must be given to

the size and shape of the composite restoration, and the extent of porcelain coverage employed.

1.8.7.1 Specimen Shape

Timoshenko (1925) proposed a method of determining stress development in a bimaterial strip on heating or cooling. This has been used as a basis for determining stress in a compound cylinder and a compound sphere.

Nielsen and Tuccillo (1972a) reported that the magnitude of stress increased proportionately from a bimaterial strip to a compound cylinder to a compound sphere. Stress development for these three shapes is not proportional (Love, 1944; Widera et al., 1981; Scherer, 1983). However, it has been shown that a compound sphere does develop the greatest residual stress (Love, 1944; Kingery, 1955; Walton and O'Brien, 1985).

Nielsen and Tuccillo (1972) have likened porcelain veneers to bimaterial strips while full coverage pontics or crowns lie between compound cylinders and compound spheres in geometry. They have suggested that residual stress may be increased by as much as 70% from veneer to complete coverage restoration.

1.8.7.2 Specimen Size

Walton (1981) concluded that residual stress in compound spheres was increased if the radius of the spherical alloy substrate was increased. This may in part be explained by the increased thermal gradients

brought about by increasing specimen size (Kingery, 1955; Walton and O'Brien, 1985).

1.8.7.3 Porcelain Coverage

The increased residual stress which may accompany the change from porcelain veneer to full porcelain coverage was mentioned previously.

In the case of a bimaterial strip or porcelain veneer, the alloy with its much higher thermal diffusivity will cool at a higher rate than the porcelain after fusing (Cascone, 1979). Cascone and Nabatian (1982) claimed that this would cause the porcelain at the porcelain-alloy interface to solidify first, resulting in compressive stresses occurring at the outer surface of the porcelain. This would increase the tolerance to thermal expansion mismatch of an alloy-ceramic composite. Shoher (1984) found this relation to be dependent on porcelain thickness and this will be discussed later.

In contrast, the porcelain at the interface will solidify last in a compound sphere or full coverage pontic (Cascone, 1979). It has been observed that thermal stress failure of porcelains is seen more often in pontics than copings (Tuccillo and Cascone, 1983).

The actual thermal contraction should thus increase progressively from outer porcelain to inner porcelain.

1.8.8 Porcelain/Alloy Thickness Ratio

It has been shown that a change in thickness of

either the porcelain or the alloy will result in a change in stiffness of the structure, and this will cause a change in the rate of stress relaxation in the porcelain (Rekhson and Mazurin, 1977; Scherer, 1983).

Lowering the ratio of porcelain to alloy thickness by, for example, increasing the thickness of the alloy will result in a decrease in the "setting temperature" of the porcelain (Rekhson and Mazurin, 1977; Scherer, 1983; Bertolotti, Napolitano and Harley, 1983). Conversely, increasing the porcelain thickness will increase the "setting temperature", which can have a potent effect on residual stress as explained in section 1.8.2 (p. 33). This lower "setting temperature" changes the thermal expansion mismatch between the materials; thus differential contraction cannot be considered solely as a function of the physical properties of the individual materials (Rekhson, 1979). Changes in the porcelain/alloy thickness ratio may even change the sign of the mismatch (Rekhson, 1979; Dorsch, 1982; Scherer, 1983).

The effect of thickness ratio changes explains the finding that glasses of higher thermal expansion are required when sealing larger metal parts (Rawson, 1966; Bertolotti, 1983).

The "setting temperature" appears to be insensitive to the shape of the composite, whether it be planar, cylindrical or spherical (Scherer and Rekhson, 1982; Rekhson and Scherer, 1982; Scherer, 1983a).

The effect of extreme thinning of the alloy has already been discussed in section 1.8.5 (p. 41).

Nielsen and Tuccillo (1972) claimed that increasing porcelain thickness relative to alloy thickness had little effect on stress development. In the light of the foregoing discussion, this would appear to be incorrect.

Shell and Nielsen (1962) calculated that for thin porcelain coatings compressive stresses in the porcelain at the porcelain-alloy interface gradually reduced to zero at the porcelain surface. Experimental evidence has supported this theory (Tsutsumi et al., 1976; Dorsch, 1981; Shoher, 1984).

It was also claimed by Shell and Nielsen (1962) and Miller (1983) that for thick porcelain layers, stresses changed from compressive at the interface to zero in the porcelain body to tensile, increasing in magnitude toward the porcelain surface. Support for this claim can be found in the experiments of Dorsch (1981) and Dérand (1981).

Shoher (1984), however, found that stresses went from compressive at the interface to tensile in the body of the porcelain to compressive in the outer porcelain. This was claimed by the author to be a result of thermal gradients during cooling after sintering. The porcelain in the middle, having the highest temperature, would have the greatest actual contraction and thus would be in tension.

Walton and O'Brien (1985) also found that thicker

porcelain resulted in an increased incidence of cracking of the porcelain and acknowledged the possibility that this might be the result of thermal gradients.

1.8.9 Firing Effects

The most obvious effects of firing the porcelain on the alloy are manifested in changes which occur at the alloy-ceramic interface.

Susz, Meyer and Orosz (1979) claimed that increased indium concentration at the surface of noble alloys, caused by the migration of indium ions along grain boundaries during degassing* procedures, resulted in an increased coefficient of thermal expansion. Similar findings with respect to tin have also been reported (Stewart, Maroso and Schmidt, 1979).

In another study, tin was added to some dental gold alloys to simulate the increased tin concentration which had been found to occur at the alloy ceramic interface (Weertman and Lautenschlager, 1979). They found that the coefficient of thermal expansion was increased markedly over that for the original alloys.

It was concluded that this could result in a larger thermal expansion mismatch at the interface than that presumed from measurements of thermal expansion of the

* Degassing is the term commonly used to describe the heat treatment recommended for most bonding alloys, both to remove trapped gases and to oxidise the alloy surface.

bulk alloys and porcelain (Weertman and Lautenschlager, 1979). It has been previously mentioned, however, that increased concentrations of tin and indium are also found in the porcelain at the interface. The problem, then, may be the stress induced by differential thermal expansion occurring between porcelain at and near the interface and the bulk porcelain (Carter, 1976).

McLean and Sced (1973a) demonstrated that diffusion of chromium and nickel oxides from base metal alloys into dental porcelain reduced the coefficient of thermal expansion of the porcelain and might induce a high residual stress at the bond. This effect was thought to be beneficial by Moffa et al. (1973).

Tesk et al. (1983a) found that the effect of changing coefficients of thermal expansion of the alloy and porcelain at the interface from those representative of the bulk materials was dependent upon porcelain/alloy thickness ratio. Their complicated and confusing paper concluded basically that as porcelain thickness increases, interfacial effects quickly become negligible.

It has also been claimed that a narrower diffusion zone (as exists with noble alloys as opposed to chromium-based alloys) will result in greater stress because of the large difference in thermal expansion between material in the diffusion zone and the bulk material (Nielsen, 1977a; Pask, 1977; Tesk et al., 1983a).

Civjan et al. (1974) reported a significant

increase in apparent bond strength with multiple firings. A possible explanation may lie in the establishment of a wider diffusion zone.

Another phenomenon of the firing of porcelain on an alloy is the restrictive effect that the two members of the composite have on each other's thermal expansion and contraction (Vickery and Badinelli, 1968). Burnett and Smith (1972) found that deviations from equilibrium thermal expansion of an alloy resulted from changes in the mass of porcelain, relative to the mass of alloy substrate.

Residual stresses which arise as a result of casting of the alloy may be released during firing of the porcelain or degassing procedures (Anusavice, 1983). It would appear that these stresses are small and are mostly released during degassing procedures (Goldestaneh, 1979; DeHoff and Anusavice, 1983; Anusavice et al., 1983; Bagby, Marshall and Marshall, 1984). Although relief of these stresses will cause a distortion of the casting which may affect the fit of the restoration (Tsutsumi et al., 1975; Faucher and Nicholls, 1980), it is unlikely that there will be any effect on residual stress in the alloy-ceramic composite.

1.8.10 Porcelain Layers

McLean (1979) claims that there is a gradation of increasing thermal expansion from enamel porcelain to dentine or body porcelain to opaque porcelain. Thus each

layer of porcelain is put under compression by the layer beneath it. This, McLean says, will strengthen the entire ceramic body.

Results of dilatometer measurements on opaque and body porcelains do not support McLean's theory of increasing thermal expansion (Ringle et al., 1979; Fairhurst et al., 1980). Neither do considerations of the chemical compositions of the different porcelains (Lacy, 1977).

As previously mentioned, Shohar (1984) observed that stresses in porcelain change from compressive in the outer layers to tensile in the middle to compressive near the interface. He suggested that the explanation for this lies in thermal gradients set up during cooling and considered that the effects of different porcelain layers were unimportant.

In contrast, Fairhurst et al. (1981) concluded that residual stresses could develop between opaque and body porcelain, and that these stresses were equal to or greater than those between alloy and porcelain.

A thermal shock test has been conducted on opaque-body porcelain discs but it was found that results on these discs did not correlate with those obtained on composite specimens which included a cast alloy substrate (Anusavice, DeHoff and Casteel, 1981; Anusavice et al., 1983a).

In an attempt to measure alloy-ceramic distortion, Anusavice et al. (1983) found that increasing the

thickness of opaque porcelain increased alloy distortion. However, adding a second layer of body porcelain reduced alloy distortion. A number of possible explanations were advanced for this behaviour, including structural changes of the body porcelain, porcelain stress relaxation during the second firing, chemical interaction between opaque and body porcelain, increased porcelain/alloy thickness ratio, and the effect of thermal gradients. Not unexpectedly, it was concluded that further study of this behaviour was necessary.

In discussing results of a study on the effect of alloy-ceramic interfacial diffusion zones, Tesk et al. (1983a) concluded that stresses may be induced by reactions at the interfaces between different layers of porcelain, especially where these layers are thin.

Others have cautioned that when multilayered systems are considered complex patterns of stresses are developed which cannot be easily calculated using simple two layer systems for analysis (Widera et al., 1981; Tesk et al., 1981a).

1.8.11 Thermal History

The thermal history of an alloy-ceramic composite involves consideration of the rate of temperature rise in the firing cycle, the maximum temperature used, the time of hold at maximum temperature, the rate of cooling, and the number of firings which take place (Preston, 1984).

The effect of cooling rates has already been

discussed.

The maximum temperature reached must, of course, be high enough to promote porcelain sintering. Temperatures that are too high may result in an increase in the thermal expansion of the porcelain because of increased leucite formation (Lacy, 1977; McLean, 1979; Binns, 1983).

Similarly, leucite concentration and hence thermal expansion of the porcelain would be expected to increase if the composite is held at the firing temperature for an excessive time (McLean, 1979; Binns, 1983).

Repeated firing of the porcelain, such as may occur in the construction of an alloy-ceramic restoration, will also cause changes in the leucite content and thus change the thermal expansion (Dorsch, 1982; Binns, 1983).

Dorsch (1982) has suggested that repeated firing will cause an increase in thermal expansion of some body porcelains. Measurements by other workers have established that repeated firing of opaque or body porcelains does result in significant changes in their coefficients of thermal expansion; however, there is no specific trend towards increased or decreased thermal expansion (Ringle et al., 1978; Fairhurst et al., 1980; Binns, 1983).

It has been suggested that this effect may be important in determining the level of residual stresses in an alloy-ceramic specimen (Bertolotti, 1980a; Fairhurst et al., 1981; Scherer, 1983).

Nielsen and Tuccillo (1972) have suggested that refiring may cause an increase in the glass transition temperature which might result in higher interfacial shear stress. No evidence was found in the literature to support this theory.

Another effect of repeated firing of the porcelain may be to increase diffusion between alloy and porcelain and between different layers of porcelain. While this would tend to reduce differences between the diffusion zone and bulk material (see section 1.8.9, p. 48), porcelain colour problems may arise.

Excessive firing (time and temperature) of the porcelain can also lead to devitrification (Lacy, 1977; McLean, 1979).

Repeated firing also affects the substrate alloys. Chromium-based alloys have a tendency to develop an excessively thick oxidised layer which is weak and can lead to adhesive failure of the alloy-ceramic restoration (McLean and Sced, 1973a; Williams and Ingersoll, 1977; Tuccillo and Cascone, 1983).

It has also been found that some alloys show a shrinkage when subjected to thermal cycling as in repeated firing of porcelain (Rowe and Asgar, 1976). This effect was not explained. This and creep deformation, which may be increased after each firing (Moffa et al., 1973), would be expected to affect the fit of restorations but not the level of residual stress.

1.8.12 Elastic Moduli

The elastic modulus is defined as the theoretical stress required to produce an elastic strain of unity (i.e. 100%). The strain may be a change in length (Young's modulus); a twist or shear (modulus of rigidity); or a change in volume (bulk modulus).

The importance of high elastic modulus values for the bonding alloys is that this property is necessary in order to resist deformation of the alloy-ceramic restoration which will result in porcelain fracture (Riley, 1977; Meiners, 1980).

McLean (1977, 1977a, 1983a) and Preston (1984) have claimed that the higher the modulus of rigidity, the less thermal expansion mismatch is allowable because the alloy will not deform plastically and so relieve interfacial stresses. This contention is incorrect. The capacity for plastic deformation is not related to elastic moduli. In fact, it is a higher yield stress that will lower the expected plastic deformation.

Calculations of stresses in alloy-ceramic specimens have indicated that even if the modulus of elasticity is doubled, the stress values would only change by about three per cent (Timoshenko, 1925; Nielsen and Tuccillo, 1972). Tesk and co-workers (1983) tested the effect of increasing the elastic modulus of the alloy and showed that a higher value reduces stress levels in alloy-ceramic specimens. This finding was not explained.

Others have claimed that a higher modulus of

elasticity will allow the use of thinner alloy copings (Moffa et al., 1973; Williams and Ingersoll, 1977; Weiss, 1977). However, it has been shown that thickness is much more important and an increased modulus will only have a small effect (Riley, 1977; Jones, 1983).

McLean (1979) has implied that a high modulus of elasticity at low temperatures can be related to a high resistance to plastic deformation at porcelain sintering temperatures, and thus less stress relief would be possible during cooling after porcelain fusing. There is no evidence to support this supposition.

In fact, Moffa et al. (1977) and Bertolotti (1981) have demonstrated that stress relief by alloy deformation during porcelain cooling is a function of alloy solidus temperatures. Lower solidus temperatures result in more plastic deformation.

In a study which involved the effect of changing the modulus of elasticity of the porcelain, Widera et al. (1981) came to the interesting conclusion that, in theory, residual stress was sensitive to changes in elastic moduli, despite the fact that they could not demonstrate this experimentally.

Carter (1976) has suggested that a change in the modulus of elasticity in the porcelain-alloy diffusion zone may have a significant effect on residual stress. Tesk et al. (1983a) have calculated that changes in the elastic modulus of the materials at the interface produce a negligible effect.

Some authors have also mentioned the importance of a high yield strength for the alloys (Williams and Ingersoll, 1977; McLean, 1979, 1983a; Preston, 1984). Yield strengths are most often reported as proof stresses determined at 0.1% or 0.2% offset. It should be noted that the alloys generally have a modulus of elasticity equal to or higher than that of the porcelain. Therefore, when the alloy has been strained by 0.1% the porcelain has undergone at least 0.1% strain as well, and as has been noted this is the critical strain for porcelain.

Therefore, the important property for the alloy is the amount of stress necessary to produce a total strain of 0.1% (i.e. elastic and plastic deformation combined). Thus the 0.1% or 0.2% proof stress is unimportant as far as porcelain compatibility is concerned; because even 0.1% offset (i.e. a permanent deformation of 0.1%) represents a far greater total deformation. The yield strength, then, will only be of importance when plastic deformation occurs at less than 0.1% total strain of the alloy, otherwise the modulus of elasticity is the most important property. Certainly, the assertion that a higher yield strength may allow thinner metallic copings cannot be supported (Ingersoll, 1977; McLean, 1979).

1.8.13 Composition of Porcelain and Alloy

Clearly, all of the factors which have been discussed are highly dependent on the composition and

properties of the many different alloys and porcelains on the market.

It is unlikely that alloy properties could be classified by placing alloys in categories according to their main constituents.

As Moffa (1977) has pointed out, the construction of successful alloy-ceramic restorations rests not only on the composition of different alloys and porcelains, but also on the quality control and consistency of the ingredients used in their manufacture.

1.9 TESTS FOR ALLOY-CERAMIC BOND STRENGTH

The requirements for an ideal test for the bond strength of porcelain to alloy have been stated by Binns (1983) as:

- "1. The porcelain should be applied to cast metal specimens by a method compatible with those used in building up restorations, and the porcelain component should have dimensions comparable with those of restorations.
- "2. The porcelain-metal interface should be stressed in a way compatible with the stressing of a restoration in service, and the loading should be such as to encourage fracture propagation along the interface.
- "3. The test should give an unequivocal answer, preferably quantitative."

No test has yet been devised which satisfies all of

these criteria (McLean, 1979; Binns, 1983; Anusavice, 1983; Preston, 1984). Preston (1984) has made the important observation that studies of bond strength cannot be extrapolated as they are probably only valid within the particular study.

Shell and Nielsen (1962) used a test in which a block of porcelain was fused around an alloy rod and the load required to pull the rod out was measured. This has been called a pull-shear test and modifications of this test, in which alloy rods were either pushed or pulled from a ring of porcelain, have been devised by others (Leone and Fairhurst, 1967; Anthony et al., 1970; Lubovich and Goodkind, 1977; Asgar and Giday, 1978; Malhotra and Maickel, 1980).

The main problem with this type of test is the symmetrical geometry. Residual hoop stress occurring as a result of the thermal expansion mismatch between alloy and porcelain may account for a large proportion of measured bond strength (O'Brien, 1977b; McLean, 1979; Binns, 1983; DeHoff and Anusavice, 1984a). Another problem is the dependence of measured strengths on the moduli of elasticity of the materials (Asgar and Arfaei, 1976).

Another approach was the use of transverse bend tests involving three-point (Lavine and Custer, 1966; Heró, Waarll and Syverud, 1984) and four-point loading (Caputo, Dunn and Reisbick, 1977; Caputo, 1978; de Rijk et al., 1983) in which porcelain fused to a flat alloy

strip is placed in tension.

Fairhurst (1977) has described a test in which semicircular alloy-ceramic strip is flexed with the porcelain in compression, thus reducing the problem of porcelain tensile failure seen with other bend tests.

Direct tension has been used to pull alloy rods away from porcelain fused only at the end (Nally, 1968; Kelly, Asgar and O'Brien, 1969). This type of test may be liable to alignment problems (Anusavice, 1983).

McLean and Sced (1973) have proposed a test in which porcelain fused to an alloy cone is stressed along the axis of the cone, which has an included angle of 45° , in an attempt to put the interface into maximum shear.

A torsion test has been used in which an alloy strip has porcelain fused to both sides (Carter, Al-Mudafar and Sorensen, 1979).

A tension-shear test making use of two overlapping alloy strips fused together by porcelain has been advocated by Wight, Bauman and Pelleu (1977).

Planar shear tests have been devised in which porcelain is fused to a flat alloy surface and loaded sideways (Civjan et al., 1974; Chong and Beech, 1980; Drummond et al., 1984). One objection to this test is its rather unrealistic geometry (Binns, 1983).

Anusavice, DeHoff and Fairhurst (1980) reported the results of finite element stress analysis of eleven different bond tests. It was found that stress concentration effects were significant in all tests

except the planar shear test using rectangular porcelain shape with loading distributed across the full thickness of the porcelain, not just at the interface (Anusavice, DeHoff and Fairhurst, 1980; DeHoff and Anusavice, 1984a).

Anusavice (1983) has reported that an oblique shear test developed by himself and Fairhurst produces negligible stress concentration. However, he concedes that plastic deformation of the alloy surface leads to incorrect bond strength values.

O'Brien (1977a) classified failure of an alloy-ceramic composite according to the interface formed at fracture. Porcelain was considered to be the limiting material, so that the ideal, a cohesive failure through the porcelain, represented a bond strength which exceeded the strength of the porcelain. The idea of maximum bond strength approaching the cohesive strength of the porcelain was termed the "cohesive plateau theory of porcelain-alloy bonding" (O'Brien, 1977).

Johnston and O'Brien (1980) claimed that tests on the shear strength of dental porcelain showed that the shear bond tests of Shell and Nielsen (1962), Anthony et al. (1970), and Hamerink, Arfaei and Asgar (1975) were actually only measuring the shear strength of the porcelain, thus supporting the cohesive plateau theory.

Others have considered that cohesive failure of the porcelain does not necessarily indicate that the bond is stronger than the porcelain but rather may indicate that there is a problem with the test design (Rasmussen, 1978;

Anusavice, 1983).

However, a large number of workers seem to agree that cohesive failure of the porcelain does, in fact, indicate that the alloy-ceramic interface is stronger than the porcelain and that bond strength tests are only measuring the tensile or shear strength of the porcelain (Nally, 1968; Custer and Coyle, 1969; Nally, Farah and Craig, 1971; Ingersoll, 1977; Katz and Bergen, 1977; Nielsen, 1977; Pask, 1977; Rasmussen, 1978; McLean, 1979; Johnston and O'Brien, 1980; Walton, 1981; Hausselet and Clasing, 1982; Widera et al., 1983; Craig, O'Brien and Powers, 1983; Herø, Waarll and Syverud, 1984). In addition, alloy porcelain combinations which seem to be acceptable in bond tests have failed clinically (Fairhurst, 1977; Binns, 1983).

Hodges (1977) has stated in regard to bond tests that "the numbers themselves are less important than the relation between the bond strength and the cohesive strength of the porcelain, prepared under the same conditions."

In addition, Mackert et al. (1984a) have stated that "characterization of bonds between dental alloys and porcelain as either good or poor is probably all that is warranted by the current status of PFM bond testing".

Another approach to the evaluation of alloy-ceramic bond strength is that of impact testing.

Silver, Klein and Howard (1960) described a falling steel ball test used also by Nally (1968) to determine

the resistance of alloy-ceramic crowns to impact fracture. It was found in both of these studies that porcelain fracture was cohesive and bond failure did not occur. It was concluded that the bond was stronger than the porcelain itself.

Walton (1981) used an impact test and also found that failure was cohesive in the porcelain even when there was a very large thermal expansion mismatch. This author also concluded that bond strength was higher than the strength of the porcelain.

1.10 EVALUATING ALLOY-CERAMIC COMPATIBILITY

The doubt which has surrounded the value of bond testing has led to a change in research emphasis over the last few years. An increasing effort has been directed towards evaluating the compatibility of different alloy-porcelain combinations and measuring the magnitude of residual stress arising with various combinations. Rather than producing an alloy-ceramic restoration with the strongest bond, the aim is a composite with the best physical properties (Ingersoll, 1977).

In evaluating the compatibility of an alloy and a porcelain, the first factor examined was the relationship between the thermal expansion curves of alloy and ceramic. It was realised that since the contraction curve of porcelain differed from its expansion curve, it might be better to compare contraction curves (Cascone, 1977; Whitlock et al., 1981; Scherer, 1983; Binns, 1983;

Bertolotti, 1983).

One method suggested to assess compatibility was to place the thermal expansion/contraction curves of alloy and ceramic on one graph such that they intersected at the "setting temperature" of the porcelain (Cascone, 1977; Rekhson, 1979; Bertolotti and Fukui, 1982). The vertical distance between the curves at any lower temperature would give an idea of the stress which has developed because of thermal expansion mismatch. A great difficulty, as has been discussed previously, is in determining what is the "setting temperature" of the porcelain. Another problem is the effect of thermal history on the thermal expansion/contraction of the porcelain (Tuccillo and Nielsen, 1968; Bertolotti and Shelby, 1979; Fairhurst et al., 1981; Whitlock et al., 1981; Scherer, 1983). In addition, this approach did not take account of the effect of geometry, thermal diffusivities of the materials, porcelain layers, elastic moduli, and porcelain tensile strengths.

Comparison of thermal expansion/contraction data has proven not to be a reliable indicator of compatibility and clinical success of alloy-ceramic combinations (Anusavice, 1983; Bertolotti, 1983).

In an attempt to better correlate the many variables involved in porcelain-alloy compatibility, a compatibility index was proposed by Ringle et al. (1978, 1979) and slightly modified by Fairhurst, Hashinger and Twiggs (1981) and Fairhurst et al. (1981).

Others claimed that the compatibility index did not adequately provide for the effect of cooling rates (Whitlock et al., 1981; Bertolotti, 1982) or the different layers of porcelain (Tesk et al., 1981).

A thermal shock test was reported by Anusavice et al. (1981). A simulated alloy-ceramic crown was heat soaked at 90°C, then quenched in ice water (0°C), reheated to 90°C and examined for cracks. The process was repeated at 100°C and repeated at 10°C increments until cracking was observed. The temperature differential that caused failure was used to describe the system's resistance to thermal shock.

In another study, good correlation was found between the compatibility index and thermal shock resistance of porcelain-alloy systems (Anusavice et al., 1982). However, it was conceded in this paper that the effects of stress relaxation, thermal diffusivity, thermal history, elastic modulus, porcelain tensile strength and geometry needed further consideration.

The thermal shock resistance of discs composed of opaque porcelain fused to body porcelain was also evaluated although it was acknowledged that significant changes might result from the influence of the alloy substrate (Anusavice et al., 1983a).

DeHoff, Anusavice and Boyce (1983) claimed that failures occurring during the thermal shock test were the result of thermal gradients in the porcelain and not thermal expansion mismatch of the materials. They

further concluded that the strong correlation between thermal shock resistance and dilatometry-derived compatibility indices was mainly dependent on the tensile strength of the porcelain and not on the thermal expansion mismatch. This may be partly explained by the fact that thermal expansion mismatch between alloy and porcelain will result in additional stress in the porcelain; thus lowering its apparent tensile strength and increasing its susceptibility to fracture under the influence of thermal gradients.

It has also been reported that results derived from thermal shock tests of this type cannot be extrapolated to other geometries (Kingery, 1955). Also, results cannot generally be related to the effects of lower thermal stresses which might actually be encountered in service (Kingery, 1955).

A better approach might be to relate thermal shock resistance to porcelain tensile strength rather than thermal expansion mismatch (Cheng, 1951; Hasselman, 1969).

Walton (1981) proposed a thermal shock test in which alloy spheres of a size similar to that encountered with a large full coverage pontic are coated with porcelain. The porcelain is fired and then removed from the furnace and allowed to bench cool.

As has been noted previously, the spherical geometry results in the greatest stress. In addition, it was claimed that bench cooling was the severest thermal

treatment that restorations commonly undergo in use (Walton, 1981).

Specimens which exhibited no evidence of checking, cracking or rupture of the porcelain after six weeks were considered to represent a thermally compatible combination.

1.11 CALCULATION OF RESIDUAL STRESS IN ALLOY-CERAMIC SYSTEMS

Timoshenko (1925) presented a general theory of bending of a bi-metal strip as a result of heating. A general formula for the calculation of thermally induced stresses can be represented thus:

$$\sigma = K \cdot \Delta\alpha \cdot \Delta T$$

where σ is the bending stress, $\Delta\alpha$ is the difference in coefficients of thermal expansion of the two component metals, ΔT is the temperature range, and K is a constant dependent upon the moduli of elasticity of the two components and specimen geometry. It was assumed that the difference in coefficients of thermal expansion between the two metals was independent of the temperature.

Timoshenko (1925) also concluded that even if modulus of elasticity values varied greatly, there was little effect on stress.

Love (1944) claimed that Poisson's ratios must also be considered when calculating stress in compound cylinders and compound spheres. However, investigations

involving dental alloy-ceramic specimens have shown that variations in Poisson's ratio have negligible effect on stress levels (Anusavice, DeHoff and Fairhurst, 1980; Widera et al., 1981).

Nielsen and Tuccillo (1972, 1972a) modified Timoshenko's equation to take into account cylindrical and spherical shapes in an attempt to make calculations of stress which might be more applicable to alloy-ceramic restorations.

In a later paper, Tuccillo and Nielsen (1972) acknowledged that these calculations involved a high systematic error, this being the result of changes in porcelain thermal expansion dependent upon cooling rate and number of firings; variations in the glass transition temperature for porcelain; changes in thermal expansion differences between porcelain and alloy depending on temperature; the effect of viscous flow of the materials; and changing elastic moduli with temperature. They attempted to increase the accuracy of their measurements by relating stress to the radius of curvature of the bimaterial strip according to a formula proposed by Laucher, Cook and Andrews (1956).

A modification of Timoshenko's equation was proposed by Ringle et al. (1979) and similarly by Rekhson (1979) to take into account the changing differences in thermal expansion of alloy and porcelain according to temperature.

In an investigation utilising bimaterial strips

similar to those used by Tuccillo and Nielsen (1972), Bertolotti (1980) attempted to include the effect of cooling rate on measured stress. He determined that maximum interfacial stress during cooling occurs at a temperature about 100°C below the glass transition temperature; the stress then decreases slightly with further cooling to room temperature. Both the magnitude of this stress and the glass transition temperature itself were found to be dependent on the cooling rate.

Dorsch (1979, 1981) also made use of bimaterial strips in stress calculations. This author found that maximum deflection of the strip coincided with maximum compressive stress in the ceramic but that there was no proportional relation between stress in the ceramic and the amount of deflection.

Like Tsutsumi et al. (1976) and Tuccillo and Nielsen (1972), Dorsch (1981) found that even when stresses at the alloy-ceramic interface of a bimaterial strip are compressive, stresses at the porcelain surface may be tensile.

In industrial porcelain enamelling of metallic substrates, composite split rings have been used for many years in attempts to measure residual stresses and compatibility (Rosenberg and Langermann, 1936, 1937; Walton and Sweo, 1953). Using this method, measurements of dimensional changes across the split can be used to determine stress development (i.e. the greater the change in the gap, the greater the stress) (Whitlock et al.,

1980a; Tesk et al., 1981a).

Shoher (1971, 1984) has used this method to determine stress in dental alloy-ceramic systems. Whitlock et al. (1980a) also presented a split ring method which has since been used in a number of investigations (Widera et al., 1981; Whitlock et al., 1981; Tesk et al., 1981a, 1983a; Bertolotti and Fukui, 1982; Scherer, 1983).

Two advantages of this method have been cited (Whitlock et al., 1980a; Scherer, 1983):

1. The split ring has similar geometry to a crown (pontic geometry has been ignored).
2. The split ring can be fabricated using procedures similar to those used in dental laboratories for construction of alloy-ceramic crowns.

Unfortunately, a quantitative stress analysis derived from deflection of bimaterial rings is extremely complex and cannot be described by the simple bimaterial strip equation (Tesk et al., 1981a; Bertolotti and Fukui, 1982; Scherer, 1983).

The following factors have been claimed to be significant in the interpretation of split ring method data:

1. Porcelain firing procedures must duplicate those used in the dental laboratory for crown construction (Whitlock et al., 1981; Scherer, 1983).
2. Stress analysis based on two layer systems (i.e.

opaque porcelain and alloy) are inadequate when examining multilayered systems (i.e. alloy, opaque porcelain, body porcelain, enamel porcelain) (Widera et al., 1981; Tesk et al., 1981a).

3. Gap changes are insensitive to elastic moduli of the materials, yet stress is sensitive to these effects (Widera et al., 1981; Tesk et al., 1983).
4. The ring must be made with an appropriate alloy and ceramic thickness if it is to be analogous with dental crowns (Scherer, 1983; Shohar, 1984).
5. Stress analysis of the split ring method is complicated by end effects when the porcelain extends to the specimen endpoints (Tesk et al., 1981a; Scherer, 1983; DeHoff and Anusavice, 1983; Anusavice et al., 1983).

In an attempt to overcome end effects, Anusavice et al. (1983) use a D-shaped specimen. The straight section of the D comprised two flat strips extending inwards from the ends of the semicircular section, with a small gap in the centre. Porcelain was fused on to the outer surface of the semicircular section, and its resulting deformation was assessed by measuring the change in gap width in the straight section of the specimen.

Despite the use of complex mathematical modelling in conjunction with physical property data, quantitative stress calculation methods appear to have limited applicability because of the multiple materials and

complicated geometries involved in alloy-ceramic restorations (Bertolotti, 1983; Walton and O'Brien, 1983).

1.12 EFFECT OF GOLD COATING AGENTS

Gold coating agents for the alloy frameworks of alloy-ceramic restorations were originally introduced, primarily, to enhance the aesthetics of these restorations by masking the dark colour of the oxidized alloy surface and provide a more lifelike underlying hue for porcelain coverage (Vickery and Badinelli, 1968; Herzberg et al., 1972; Schwickerath, 1982a; Craig, O'Brien and Powers, 1983).

An analysis of two gold coating agents, Britecote and Culver-Guard, showed that they were basically colloidal dispersions of pure gold in an organic base (Nally, 1968).

Another agent, Inzoma P, designed for application to precious metal alloys, consists of gold (95%), silver (3%) and copper chloride (2%) (Eggenberger, 1985).

In a study of spectral reflectance, Herzberg et al. (1972) showed that 40% to 60% less opaque porcelain was required to mask an alloy surface covered by a gold coating agent than the bare alloy surface. A number of authors, and of course all of the manufacturers of the various coating agents, have also claimed that a gold covering is effective in helping to produce a more lifelike restoration (Vickery and Badinelli, 1968;

Rogers, 1980, 1982; Clayson, 1981; Hausselet, Schiwiora and Groll, 1982).

Others have maintained that these agents provide a minimal aesthetic advantage and have extremely limited applicability (Johnston, Mumford and Dykema, 1967; Johnston, Phillips and Dykema, 1971; McLean, 1979).

It has also been postulated that a gold coating can improve aesthetics by providing a barrier to the silver in high-silver alloys which can cause discoloration of the porcelain (Clayson, 1981; Tuccillo and Cascone, 1983).

Microporosity in some alloys resulting in bubbles in the porcelain at or near the interface has been recognised (Jarvis and Mumford, 1968; Southan, 1977; Eichner, 1983). Claims have been made that surface porosity can be sealed off by a coating layer, thus eliminating bubbles in the porcelain (Vickery and Badinelli, 1968; Jelenko and Co., 1968; Sperner, 1979; Rauter and Co., 1981).

On the other hand, Jarvis and Mumford (1968) reported that surface coatings were "of no value in preventing bubbles at the interface".

Southan (1977) showed excellent adaptation with few bubbles between opaque porcelain and two different gold coating layers, but he achieved a similar result when the porcelain was applied to uncoated alloy.

Brooks (1977) claimed that gold coating agents could exacerbate the problem of interface porosity in

that rather than filling deep recesses in a rough alloy surface, the gold particles bonded in a stacked manner, further increasing the depth of surface flaws, and thus restricting contact between the viscous opaque porcelain and the alloy substructure.

It has been suggested by McLean (1979) and Rogers (1980a) that coating layers prevent excessive migration of ions and oxidation which occur with base metal alloys. These authors considered that the best method of applying the gold layer was by electroplating as did Clayson (1981).

Electroplating had the advantage that the gold layer was applied in an even thickness. Also the gold surface could then be tin-plated to provide a reactive surface for bonding to porcelain (McLean and Sced, 1976; Rogers, 1980a), although it seems that this would somewhat negate the claimed aesthetic advantage of the gold layer.

One problem, however, is that the bond between the electroplated gold and the underlying alloy may not be very strong (McLean, 1977). Chong and Beech (1980) have reported a failure in an attempt to gold-plate a base metal. It has also been claimed that electrolytically plated surfaces are quite porous (Brooks, 1977a).

The effect that coating agents have on porcelain adherence has remained highly controversial. Some authors have claimed that these agents, if they have any

effect at all, cause weakening of the bond between porcelain and alloy (Johnston, Mumford and Dykema, 1967; McLean, 1979; Craig, O'Brien and Powers, 1983). Others have asserted that these agents, in fact, improve bonding (Stein and Kuwata, 1977; Kuwata, 1980; Rauter and Co., 1981; Rogers, 1982; Hausselt, Schiwiora and Groll, 1982; Degussa, 1983).

Shell and Nielsen (1962) found that an unspecified "metal conditioner" had no significant effect in shear bond tests.

Vickery and Badinelli (1968) using both shear and bend tests concluded that bond strength values could be more than doubled if appropriate trace elements were added to a gold surfacing system.

These authors also stated that a gold layer would prevent interaction between the porcelain and trace elements in the alloy necessary for good bonding, although these trace elements could diffuse through the gold layer with prolonged heating.

Stewart, Maroso and Schmidt (1978) found that gold conditioning agents masked the tin and indium present on the surface of gold alloys used for porcelain bonding.

Using a three-point bend test, Custer and Coyle (1969a) reported that a metal conditioner had no effect on the strength of the precious alloy-porcelain bond. However, porcelain bonding to cobalt-chromium based alloys was improved.

In another series of shear bond tests, it was found

that bond strength decreased by up to 84% when a noble alloy was coated with gold as opposed to oxidation of the bare alloy (Anthony et al., 1970). In the same paper, "no evidence of a significant amount of diffusion of oxidizable elements through the coating of gold" was indicated by x-ray emission spectroscopy analysis.

In contrast, Goeller, Meyer and Nally (1972) used electron probe microanalysis and concluded that diffusion, accumulation and oxidation of trace elements from the alloy into the ceramic was unaffected by gold coating agents. They also reported that bond strengths in a shear bond test were unaffected by gold coating agents.

Fairhurst (1977) devised a flexural bond test and used it to show that bond strength was increased when a bonding agent was applied to a base metal alloy. It should be noted that the alloy used was not recommended for use without the bonding agent.

The effect of a platinum-gold coating agent on the behaviour of a porcelain coating bonded to an alloy during flexure has been reported (Stein and Kuwata, 1977; Kuwata, 1980). It was shown that the porcelain cracks but remains adherent to the alloy when the coating agent is used whereas it is detached when no coating agent is used.

Hausselet, Schiwiora and Groll (1982) made a similar finding when they used Deck-Gold as the coating agent.

The problem with this type of test is that

clinically, an alloy-ceramic restoration has failed when the porcelain cracks even if it is not immediately detached.

Eichner (1979) reported that diffusion of trace elements from the substrate alloy did proceed through gold coatings and found that these agents had no significant effect on the strength of the alloy-ceramic bond.

Sperner (1979) reported that improved bonding resulted from using a gold coating agent.

Chong and Beech (1980) used a shear test to evaluate bond strength. They found that both a bonding agent and electrodeposition of gold could increase bond strength values for base metal alloys, although they failed to successfully gold-plate one alloy. It was noted that the bonding agent gave a larger scatter of results than did electrodeposition. They also found that bond strength values for the coated base metal alloys were similar to those obtained using an uncoated gold-palladium alloy.

In fact, they discovered that bond strengths correlated with the three different porcelains used rather than with the surface treatment. It was thus concluded that bond strength was dependent on the porcelain, provided the alloy surface was "amenable" to bonding.

Hausseilt (1982) and Hausseilt and Clasing (1982) have used three tests: a qualitative flexure test in

which a ceramic-coated alloy sheet is bent and the amount of ceramic which remains adherent is observed, a shear test, and a bend test in four-point loading. They have claimed that these tests demonstrated increased bond strength as a result of using a gold coating agent.

Schwickerath (1982) reporting the results of three-point bend tests, concluded that the effect of coating layers on alloy-ceramic adhesion could not be uniformly evaluated. Average bond strength values sometimes increased and sometimes decreased. In a later paper, however, Schwickerath (1982a) surmised that coating agents did, in fact, increase bond strength, and even cited his earlier paper (Schwickerath, 1982) in support of this assertion.

It has been claimed that underfiring of the gold metal conditioner will prevent proper porcelain adherence (Tuccillo and Cascone, 1983).

There have been many claims that a coating layer may provide a "buffer zone" between the ceramic and the alloy, thus decreasing residual stress in the porcelain and increasing compatibility between porcelain and alloy (Rogers, 1980, 1982; Hausselet, 1982; Hausselet and Clasing, 1982; Schwickerath, 1982a; Bertolotti, 1983; Degussa, 1983; Shoher, 1984). None of these authors has provided experimental proof of this assertion.

Rogers (1980) claimed that a gold-plated layer would be annealed during each porcelain firing procedure and aid in absorbing stresses resulting from differences

in coefficients of thermal expansion between alloy and ceramic.

Schwickerath (1982) claimed that the coating agents formed a "plastic-elastic" intermediate layer. It was suggested that this would allow more deformation of the alloy substructure before cracking of the porcelain would occur (Schwickerath, 1982a). In support of this, it was also claimed that a thicker layer of a coating agent was even more effective (Schwickerath, 1982a).

It has been theorised that stresses in porcelain caused by thermal expansion differences between alloy and porcelain could be reduced by plastic deformation of an intervening gold layer; this would be made possible by the very low yield strength of pure gold (Hausselet, 1982; Hausselet and Clasing, 1982). These authors maintained that this property would increase the compatibility range between porcelains and alloys.

Contrary to this, changes in elastic modulus and yield strength of intermediate layers have been shown to produce insignificant effects on stresses in bimaterial strips (Savolainen and Sears, 1969).

In addition, it seems that placing an easily deformable layer between porcelain and alloy might partially negate the stiffening effect that an alloy with high modulus of elasticity might have on the overlaying porcelain. It may also be disadvantageous if such a layer reduced compressive stress in the porcelain which can made it less susceptible to tensile failure.

make

CHAPTER 2PURPOSE AND SCOPE OF THE INVESTIGATION

The purpose of this investigation was to examine the efficacy of a gold coating layer in reduction of stresses arising in alloy-ceramic specimens. Porcelains with varying coefficients of thermal expansion were fired on to a palladium-based alloy with and without an intermediate gold coating layer. A thermal shock test was used to determine the compatibility of any particular porcelain-alloy combination.

It was hoped that this investigation would show whether a gold coating layer would reduce stresses in the porcelain and further, whether this effect (if any) was of practical significance in that it might allow a greater difference in coefficients of thermal expansion between alloy and ceramic.

CHAPTER 3MATERIALS USED

The materials used are listed in table 3.1.

Table 3.1 Materials Used

MATERIAL	NAME	MANUFACTURER	BATCH NO.
Alloy	Option	J. M. Ney Co.	4473.
			4497
			6100
			6101
Investment	Ceramigold	Whip Mix Corp.	P:0575306
			L:6909202
Gold coating agents	Wilkote	Wilkinson Co.	-
	Spectra-Seal	Unitek Corp.	-
	Deck-Gold (normal)	Degussa AG	-
Porcelains	Vita VMK 68 (545)	H. Rauter GmbH & Co.	587
	Vitadur (350N)	H. Rauter GmbH & Co.	325

3.1 ALLOY

Option is recommended by the manufacturer as a substrate alloy for ceramic-alloy restorations, especially those subject to high stress. Its composition as given by Bagby, Marshall and Marshall (1984) is shown in Table 3.2.

Table 3.2 Composition of Option Alloy

ELEMENT	CONTENT (%)
Pd	79
Cu	9
Ga	9
Au	2
B	1

Some of the important properties of the alloy, as given by the manufacturer, are listed in Table 3.3.

Table 3.3 Properties of Option Alloy (as given by manufacturer)

PROPERTY	VALUE
Ultimate tensile strength	1275 MPa
Yield strength	1147 MPa
Bond shear strength	139 MPa
Elongation	8%
Hardness (Vickers)	425
Modulus of elasticity	93,752 MPa
Density	10,600 kg/m ³
$\alpha_{(20-500^{\circ}\text{C})}$	0.68% (14.2 x 10 ⁻⁶ /K)
Melting range	1170-1190°C
Recommended casting temperature	1260°C

Some points about the data given in Table 3.3 should be noted. First, the manufacturer's figures have been converted to SI units. The yield strength value has been given by the manufacturer without a specified percentage offset, thus limiting its usefulness. The bond shear strength value given does not specify either

the test or the porcelain used to obtain it. It is thus a meaningless figure.

The manufacturer's instructions for the use of Option are as follows:

1. "Use an investment developed especially for Ceramometal castings. A vacuum or static pour is used". (It is not clear what is meant by a static pour).
2. "High heat burnout at 1300°F (704°C) is recommended".
3. "Use a multi-orifice gas-oxygen torch. A clay crucible is recommended. Do not use casting flux".
4. Cast by centrifugal or air/vacuum method seven seconds after a rolling button has been observed.
5. "If cast into a carbon containing investment, no pickling is required".
6. Finishing only by aluminium oxide stones or wheels to prevent contamination of the casting, followed by pressure blasting with $60\text{ }\mu\text{m}$ aluminium oxide. Castings are then treated with an ammoniated or non-ammoniated detergent solution in an ultrasonic cleaner followed by an ultrasonic rinse in distilled water. They can then be dried with a clean tissue.
7. Metal conditioning. Insert castings into furnace preheated to 650°C and raise to 1010°C without use of vacuum. Maximum temperature is held for five minutes or until brown oxide is formed on surface.

If a black oxide forms, the casting is replaced in the furnace at 1010°C without refinishing until a brown oxide forms. An alternative metal conditioning treatment of 1040°C for a shorter period of time will also develop the brown oxide layer.

In this investigation, 50% new and 50% used alloy was used for each casting. This has been shown not to have any detrimental effects on alloy properties (Moffa et al., 1973; Clayson, 1981; Rasmussen and Doukoudakis, 1984).

3.2 INVESTMENT

The investment, Ceramigold, is a phosphate-bonded investment, containing graphite, recommended by the manufacturer for casting of all dental alloys.

The manufacturer has stated that when the suggested liquid/powder ratio is used, the investment has the properties listed in Table 3.4. Once again figures given by the manufacturer have been converted to S1 units.

Table 3.4 Properties of Ceramigold Investment
(as given by the manufacturer)

PROPERTY	
Working time	2 - 4 minutes
Ready for burnout (minimum)	45 minutes
Setting expansion	1.0%
Thermal expansion	1.2%
Compressive strength, wet (2 hours)	6.2 MPa
Compressive strength, dry	20.7 MPa

The salient features of the manufacturer's instructions for use of the investment are:

1. Casting ring should be lined with a wet asbestos or wet non-asbestos ring liner.
2. The recommended liquid/powder ratio is 16ml/100g.
3. The suggested liquid concentration is 75% Ceramigold liquid/25% water.
4. Add liquid to bowl and then powder, and hand spatulate for about 15 seconds until no dry powder remains. Mix should begin to show signs of thinning down.

5. At slow speed (200-500 rpm) mix under vacuum for 90 seconds - then invest, no need to hold under vacuum. Larger rings may be invested under low vibration.
6. Slightly overfill and then allow to bench set for at least 60 minutes.
7. Place in cold furnace and raise furnace temperature to that recommended by alloy manufacturer in not less than one hour, more for large moulds. Maximum temperature should be held for one hour or more for large moulds.
8. Cast according to standard technique for the casting machine.

3.3 GOLD COATING AGENTS

All three gold coating agents used were composed of a gold powder and a liquid. The powder is basically colloidal gold, though the manufacturers of Deck-Gold and Spectra-Seal claimed some unspecified additives. The liquid is an organic base to facilitate application of the gold.

The manufacturers' instructions for Wilkote and Spectra-Seal were similar although the instructions for Spectra-Seal were much more comprehensive:

1. Prepare the alloy for application of gold coating by grinding with a stone and cleaning with tap water. (The Wilkote instructions simply refer to a "prepared and cleaned surface of the casting", not

specifying whether any metal conditioning procedures should be used).

2. Powder and liquid are mixed to a medium consistency.
3. Coating agent is brushed on in a thin coat and cross brushed to assure good coverage.
4. With the furnace temperature at 1060°C dry the framework at the muffle opening until vapours are no longer visible.
5. Introduce framework into furnace.
6. Spectra-Seal: Reset furnace temperature to 1070°C and remove framework as soon as this temperature is reached.

Wilkote: Leave framework in furnace until desired mirror finish is obtained.

7. Spectra-Seal: Repeat the procedure with an increased temperature of 10°C if finish appears underfired; grind off Spectra-Seal and repeat at 10°C lower if finish appears overfired. Pictures of an under-fired, properly fired, and over-fired surface are provided.

Wilkote: Do not over-fire to a dark brown-grey. Repeat if necessary to obtain desired mirror finish.

8. Application of porcelain can now proceed.

Instructions for Deck-Gold (normal) are similar, with these differences:

1. Framework should be cleaned for at least 15 minutes

in an ultrasonic cleaner.

2. Pre-dry the framework, after gold application, for 3-5 minutes in a warm furnace chamber. Then place in furnace at 400°C and raise to 600°C. Remove framework and allow to cool. Gold application can be repeated if desired.
3. Place framework in furnace at 980°C and hold for 2-3 minutes, then remove and allow it to cool.

Deck-Gold is recommended for use on all Degudent bonding alloys. Spectra-Seal is recommended for use on Degudent-Universal alloy. Wilkote is recommended for all Wilkinson bonding alloys. In the instructions for Wilkote, mention is also made of high palladium-silver alloys and low gold-platinum alloys, thus its suitability for these alloys is implied.

3.4 PORCELAINS

Vita VMK 68 (no. 545) is a dentine porcelain powder designed for use in alloy-ceramic restorations. The recommended firing temperature varies from 960-980°C depending on the furnace being used (Rauter and Co, 1981). The manufacturer states that it has a coefficient of linear thermal expansion of $13.8 \times 10^{-6}/K$ in the range 20 to 600°C (Eggert, 1984).

Vitadur-N (no. 350N) is a dentine porcelain powder designed for use in porcelain jacket crown construction. The recommended firing temperature varies from 940-1020°C depending on the furnace being used (Rauter and Co,

1981a). The manufacturer states that it has a coefficient of linear thermal expansion of $6.5 - 6.8 \times 10^{-6}/K$ in the range 20 to 600°C (Eggert, 1984).

A range of porcelains with varying coefficients of linear thermal expansion were made by blending VMK 68 and Vitadur N in the proportions given in Table 3.5. Increasing the amount of Vitadur-N in the blend would progressively reduce its coefficient of thermal expansion.

Table 3.5 Porcelain Blends

VMK 68 (% by weight)	Vitadur-N (% by weight)
100	0
85	15
82.5	17.5
80	20
77.5	22.5
75	25

CHAPTER 4EXPERIMENTAL METHODS4.1 PREPARING THE ALLOY SPECIMENS

A two-piece brass mould was machined to allow injection forming of a wax pattern sphere 8 mm in diameter with a sprue former 2.5 mm in diameter and 15 mm in length (Figure 4.1). The mould was filled with molten wax under pressure using a Jofre air pressure wax injector, model 4050. Eight to ten of the wax patterns so formed were bar-sprued together for investing.

The first castings produced from these wax patterns had a large number of surface defects caused by "back-pressure porosity". This is often a problem with phosphate-bonded investments because of their low permeability at the casting temperature. In subsequent pattern assemblies, wooden toothpicks were incorporated as formers to provide mould venting after burn-out (Figure 4.2 a). As can be seen, the vents were not continuous with the mould cavities but were still effective in overcoming this problem (Figure 4.2 b).

The pattern assemblies were invested according to the investment manufacturer's instructions. Casting rings 64 mm in diameter were lined with Whip Mix non-asbestos ring liner, which was then wetted by immersion in distilled water. Using the recommended liquid/powder ratio, the investment was hand spatulated and then vacuum

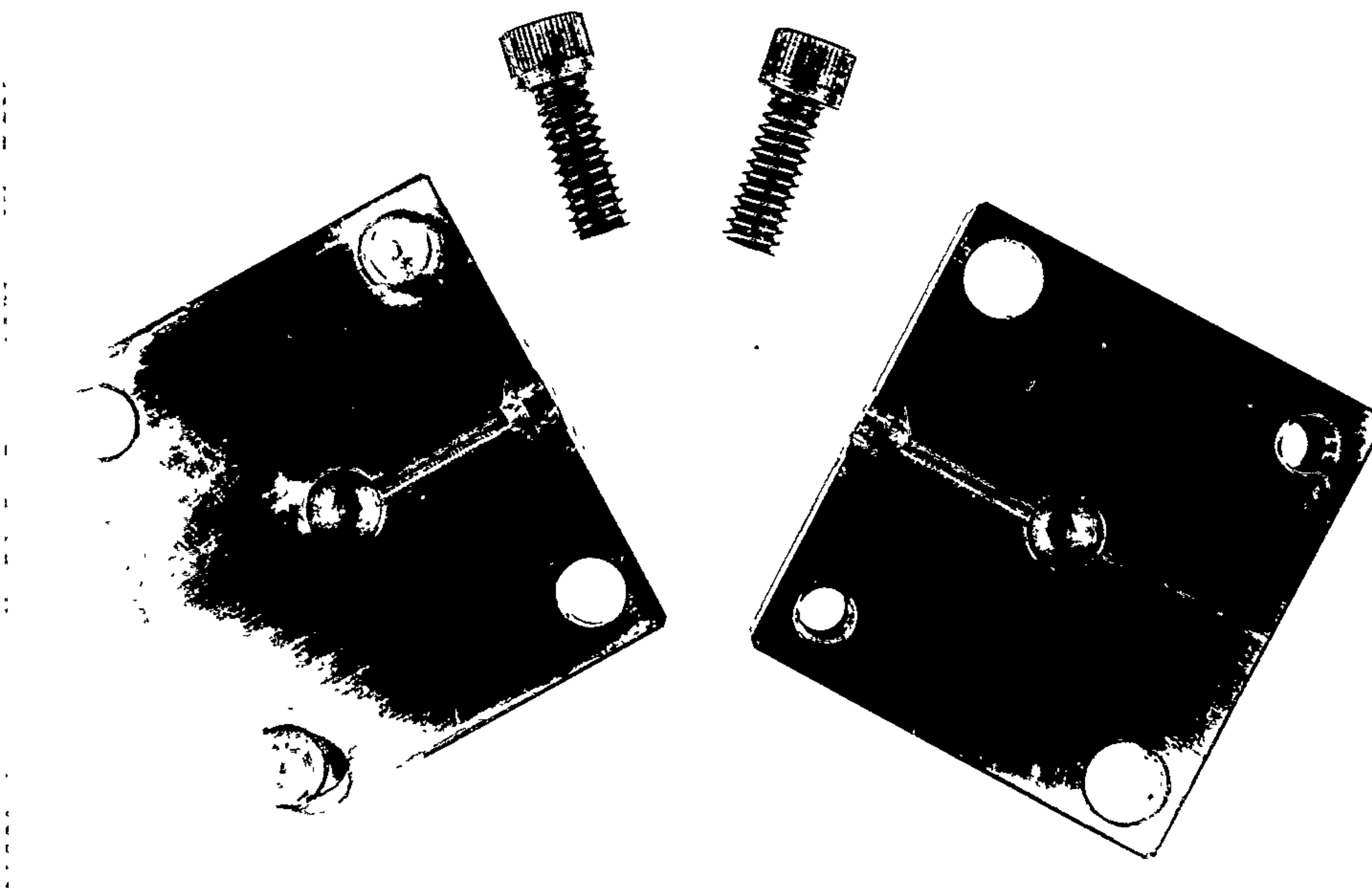
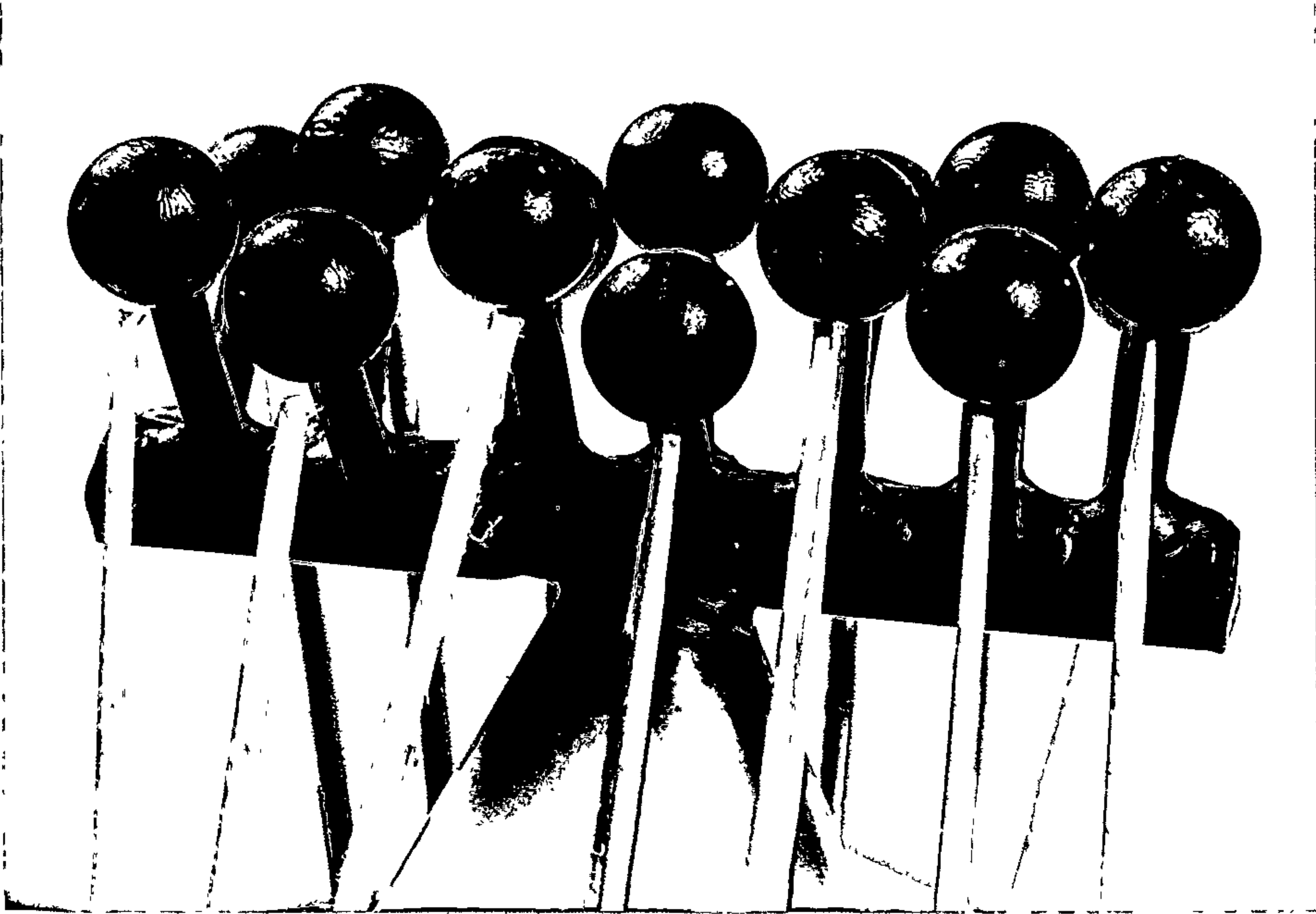
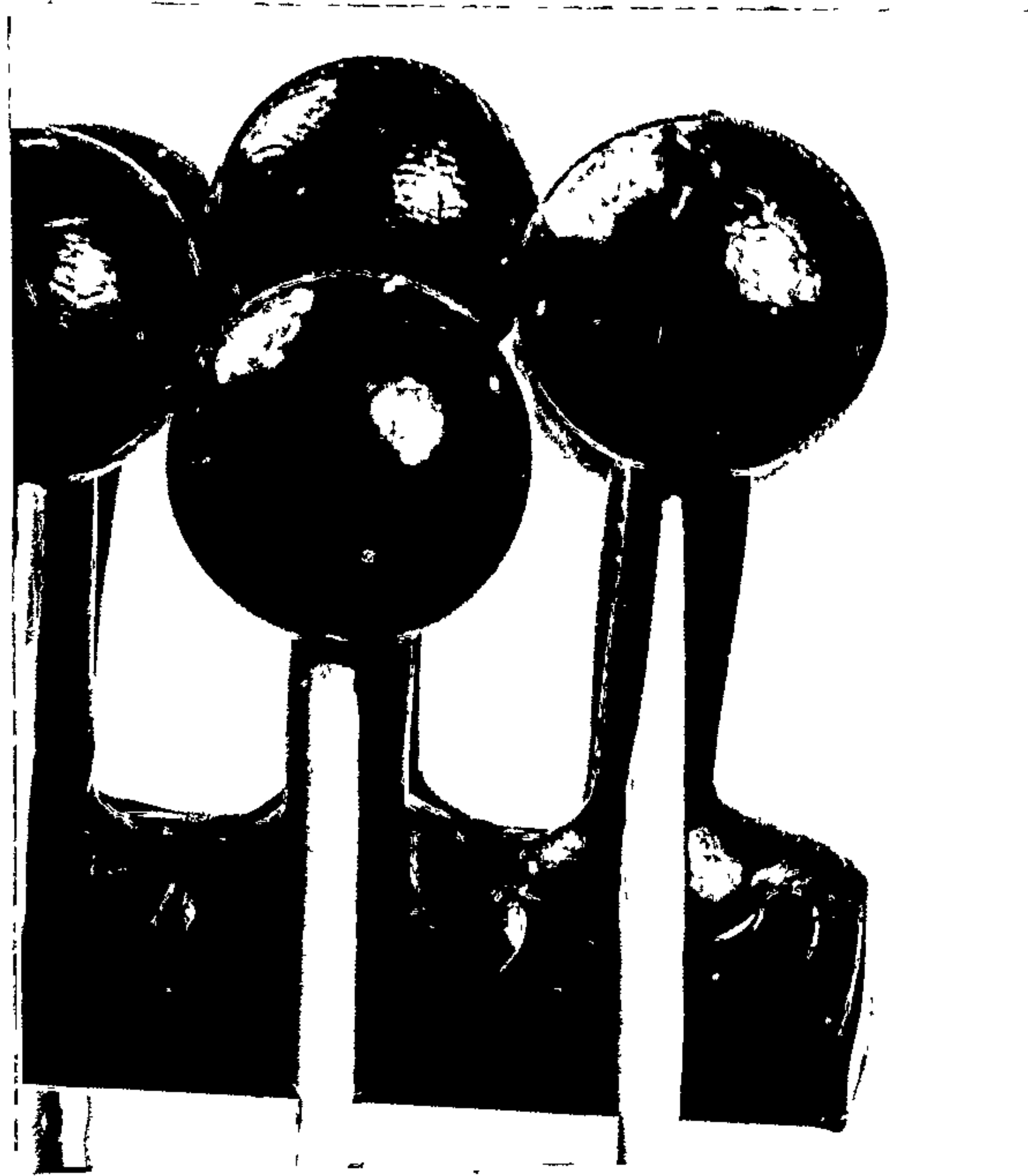


Figure 4.1 Brass mould for injection forming of wax pattern



a



b

Figure 4.2 a. Wax pattern assembly ready for casting
 b. Detail photo showing vent formers not
 in contact with wax pattern

mixed in a 500 mL Whip Mix Vac-U-Mixer using a Whip Mix Power Mixer, model B, at 425 r/min. for 90 seconds. The casting ring was then filled under low vibration without vacuum and the mould allowed to bench set for one and a half hours.

The mould was then placed in a Carbolite furnace, model no. GPB2, and the temperature raised from ambient to 750°C in 1 hour 50 mins., then held at that temperature for one hour.

Casting was carried out in a Kerr Centrifico casting machine, fitted with a clay crucible. As a gas-oxygen torch was not available a multi-orifice oxy-acetylene torch, adjusted to give a slightly carburizing flame, was used to melt the alloy.

After casting, the mould was allowed to bench cool until the button stopped glowing, then it was quenched in water.

After recovery of the casting (Figure 4.3), the spheres were cut off the assembly, together with a sprue section about 8 mm long, which was retained for ease of handling. In addition, the 3 mm section of sprue next to the sphere was reduced to a diameter of about 1 mm to allow maximum porcelain coverage (Figure 4.4 a). Any surface irregularities were smoothed with aluminium oxide stones. Specimens were then pressure blasted with 60 µm aluminium oxide powder and ultrasonically cleaned first with a detergent solution and then with distilled

water, after which the spheres were not touched (Figure 4.4 a).

The specimens thus prepared were 7.9 ± 0.1 mm in diameter. This was considered to be representative of a large full coverage pontic which might be encountered in clinical practice.

The cast specimens were then divided arbitrarily into two groups of equal number. One group, which was to receive direct porcelain application, was degassed according to manufacturer's recommendations; this resulted in the formation of a brown oxide surface layer (Figure 4.4 b). The other group, which was to have a gold coating layer applied, was not degassed.

Initially, Wilkote was used for all testing. Later, Spectra-Seal and Deck-Gold (normal) were used for comparison. Attempts to follow the manufacturer's directions for the application of Wilkote resulted in only a patchy cover of gold. After some experimentation, the following procedure was used to obtain a more consistent and satisfactory result:

1. Brush on thin coat of Wilkote.
2. Dry in furnace opening and place in furnace at 1040°C .
3. Remove and allow to cool.
4. Apply second coat, cross-brushing.
5. Dry in furnace opening and place in furnace at 1060°C to achieve a mirror finish (Figure 4.4 c).

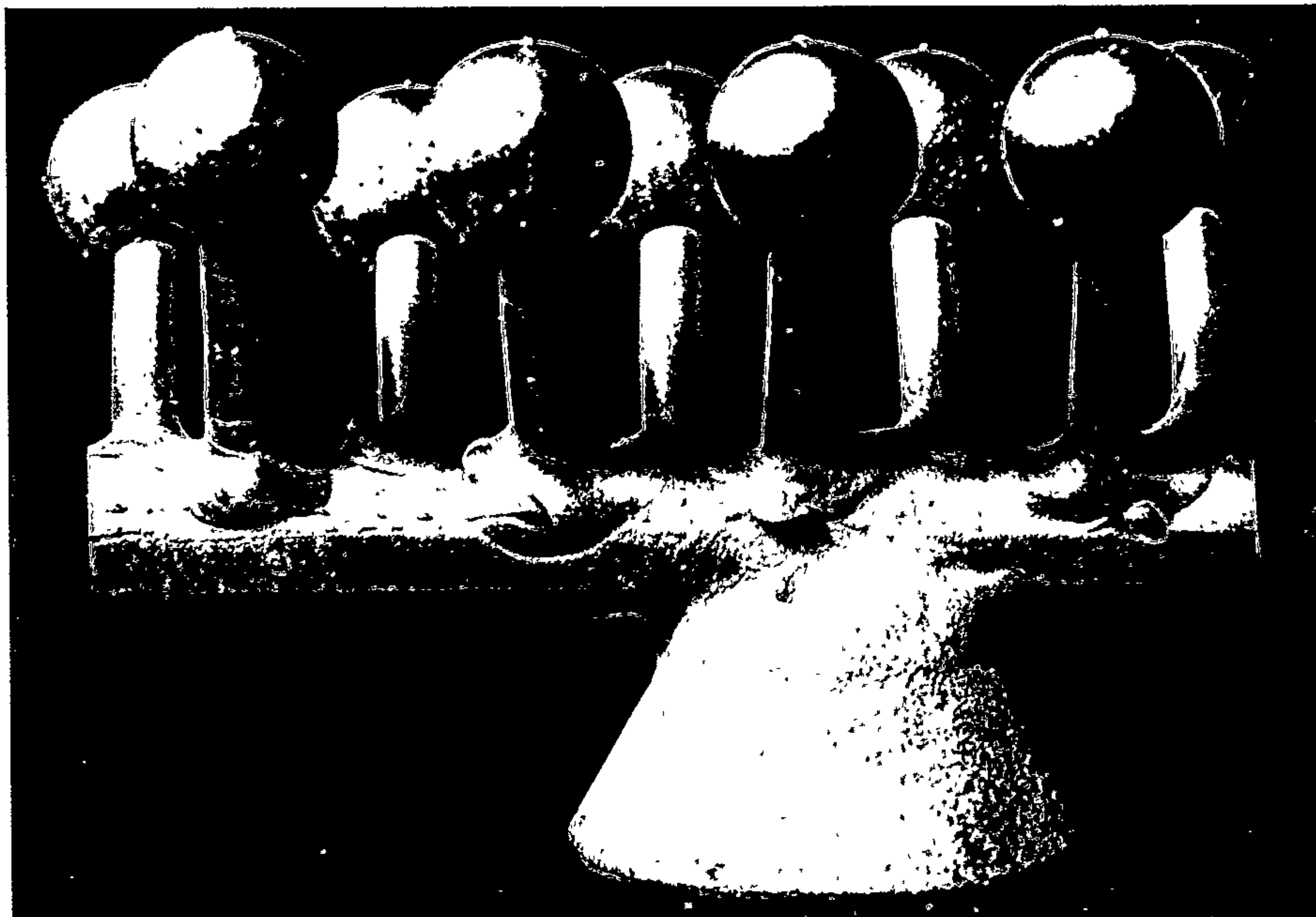


Figure 4.3 Casting recovered from investment

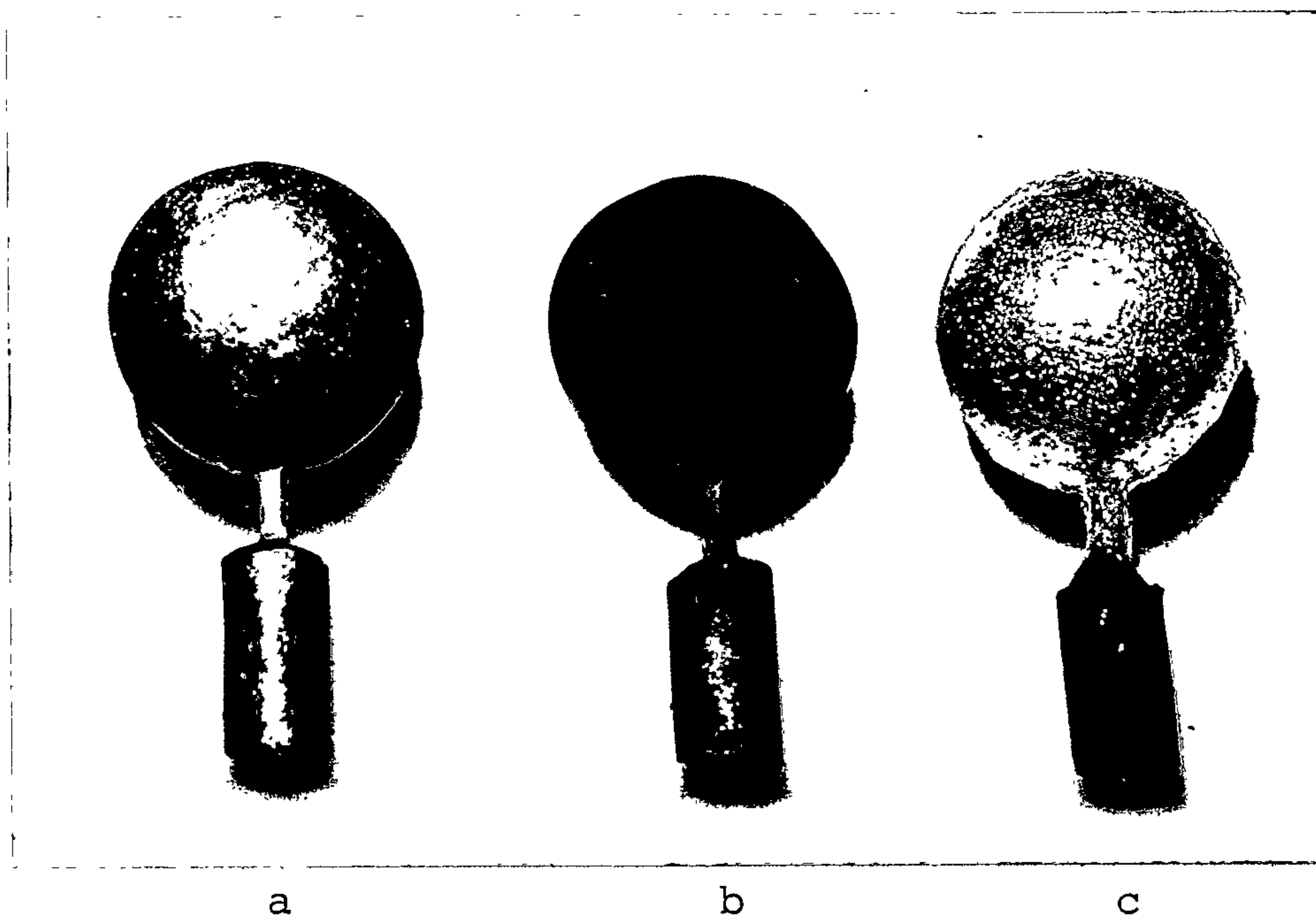


Figure 4.4 a. Cast sphere with modified sprue after pressure blasting
b. Cast sphere after degassing
c. Cast sphere after application of Wilkote

4.2 PREPARING THE TEST PORCELAINS

In initial experiments, the two porcelain powders were mixed in varying amounts and bonded to some of the alloy specimens in order to determine, approximately, the minimum percentage of jacket crown porcelain necessary to cause rupture of the porcelain. This done, a total of five combinations of the porcelains above and below the critical composition to cause fracture were selected for further testing (Table 3.5).

The porcelain powders were weighed on a Mettler PC4400 balance and 50 g of each combination was placed in a four-fluted powder mixer, 10.5 cm in diameter and 8.5 cm deep, specially constructed for this investigation (Figure 4.5). Each combination of blended powders was tumbled in the powder mixer by a 1/12 HP geared electric motor, at 10 r/min for a minimum of 12 hours.

4.3 MEASUREMENT OF THERMAL EXPANSION

In order to measure the coefficients of thermal expansion of the test porcelains used in this investigation, two rectangular bars of each porcelain blend were fabricated. Dry porcelain powder was poured into a five-piece steel mould constructed for this study (Figure 4.6 a to d). The mould had a cavity with a base measuring 37.5 x 3.5 mm, and a hardened steel plunger of similar dimensions was machined to fit the mould cavity.

The porcelain was condensed using a Hounsfield Tensometer adjusted to apply a force of 10 kN which

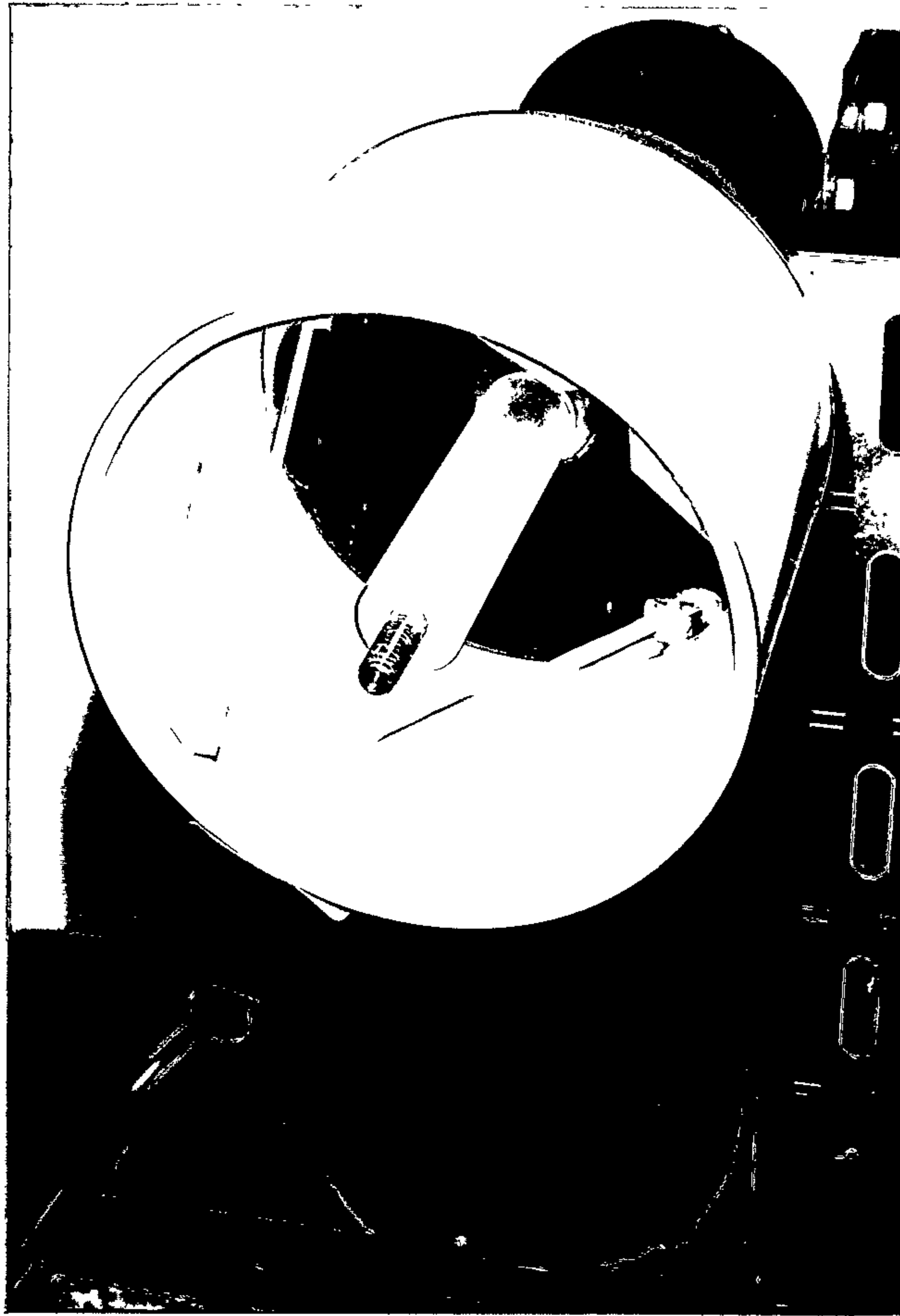
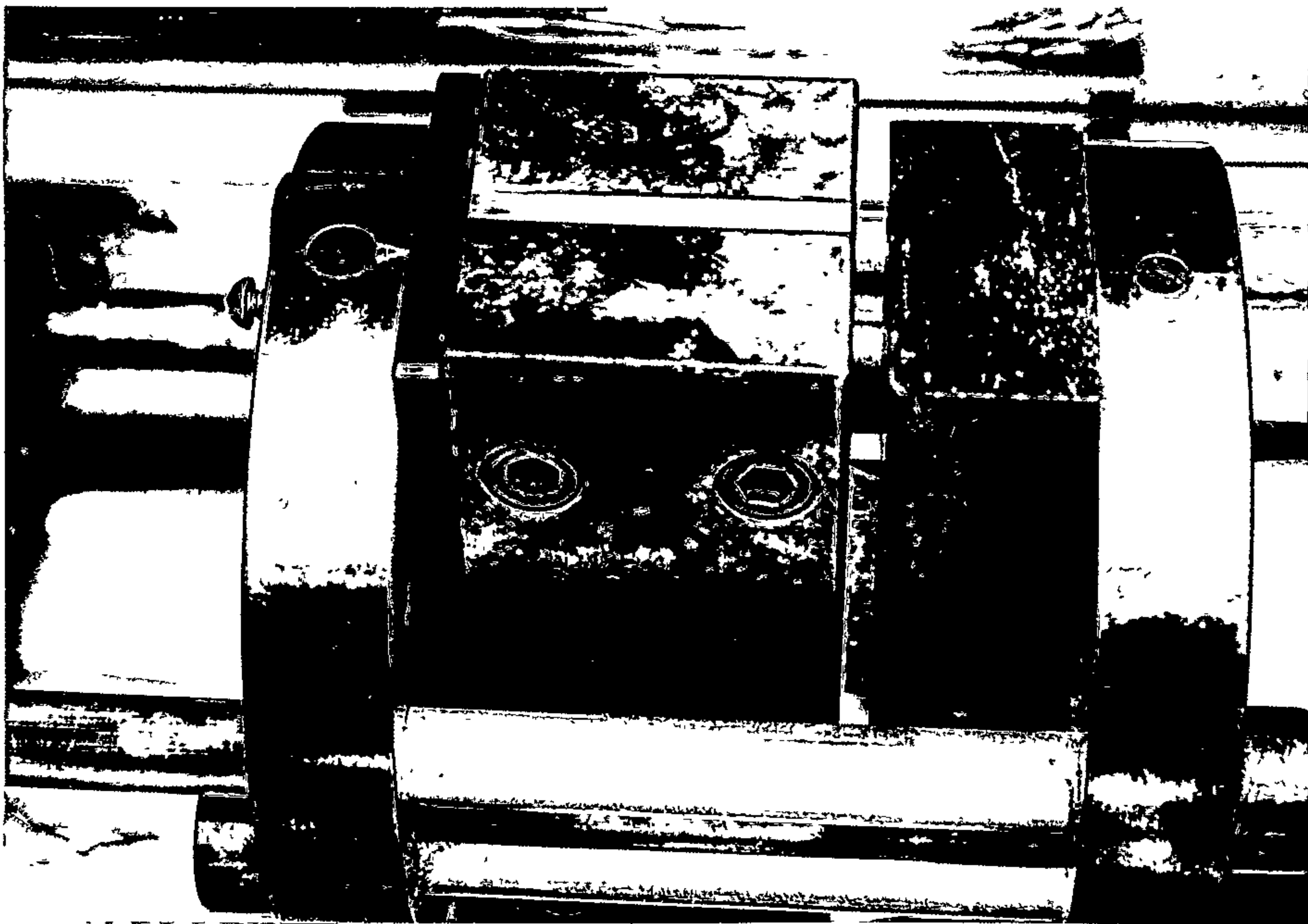
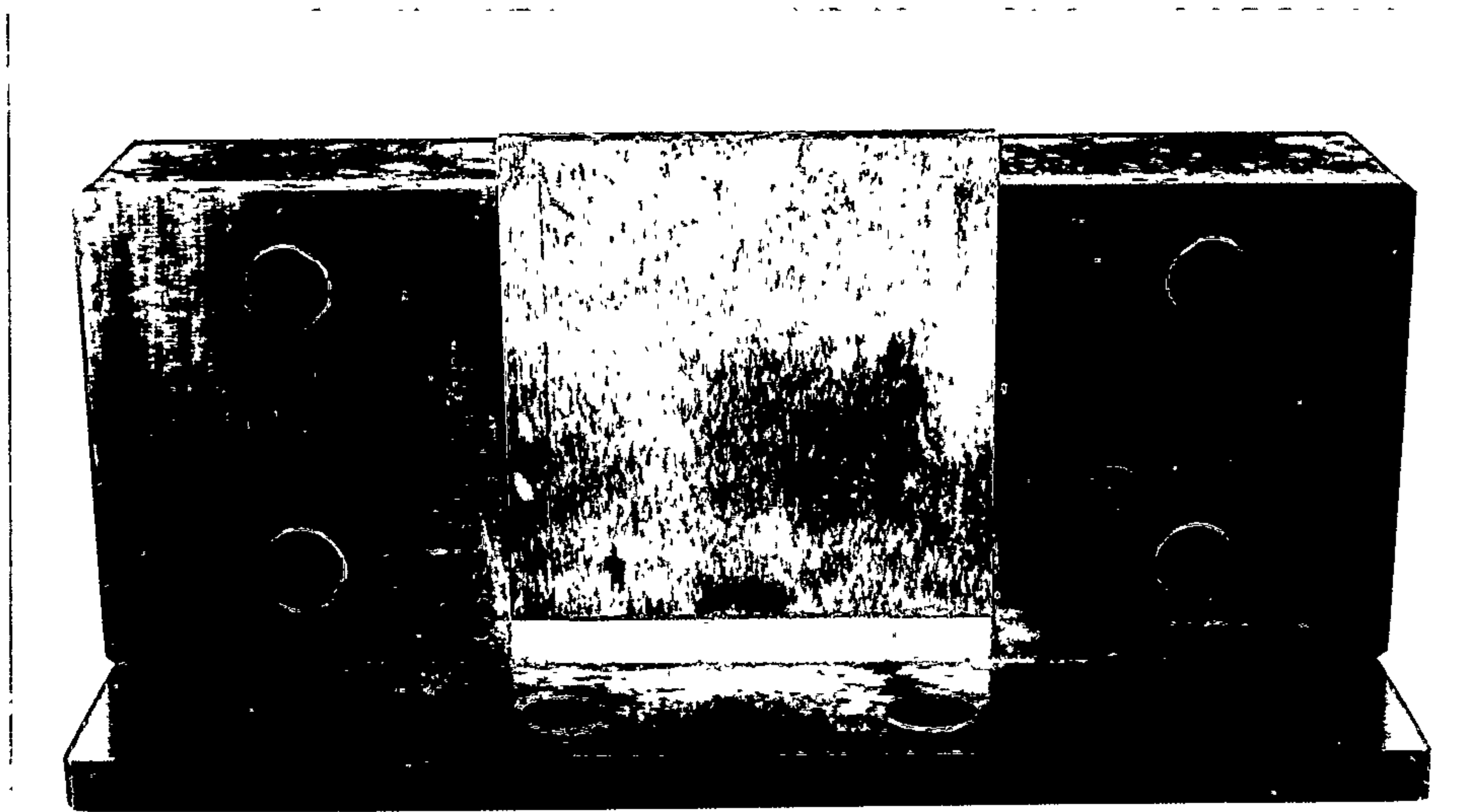


Figure 4.5 Mixer for porcelain powder



c



d

Figure 4.6 c. Mould with plunger in Hounsfield Tensometer
 d. Mould showing condensed prefired porcelain bar

exerted a pressure of approximately 75 MPa on the powder. The resulting bar, before firing, measured 37.5 x 3.5 x 3.5 mm. The bars were then placed on platinum foil and fired through the same cycle as that used for the thermal shock test (section 4.4) in a Ney Mark III vacuum furnace. After firing, the bars were trimmed to a length of 20.00 ± 0.05 mm using an Isomet 11-180 low speed saw. The specimens so produced were well condensed, uniform and straight (Figure 4.7).

An alloy specimen of similar dimensions was made by pouring wax into the rectangular mould, investing the wax pattern and casting according to the manufacturer's instructions. This bar was also trimmed to 20.00 ± 0.05 mm and sharp edges were rounded.

Thermal expansion measurements were made with a horizontal vitreous silica dilatometer (Leitz, type P11) fitted with a platinum wound furnace (Figure 4.8). A current limiting controller prevented overloading and possible fusing of the platinum element during early stages of heating.

A temperature rise of $5^{\circ}\text{C}/\text{min.}$ from 20°C to 600°C was used for all specimens. During cooling, attempts were made to control the temperature drop from 600°C to 20°C at a rate of $5^{\circ}\text{C}/\text{min.}$

Linear expansion of the specimen was transferred by the vitreous silica pushrod to a Schaevitz linear variable differential transformer (LVDT). Its output was calibrated with an Applied Measurement signal conditioner

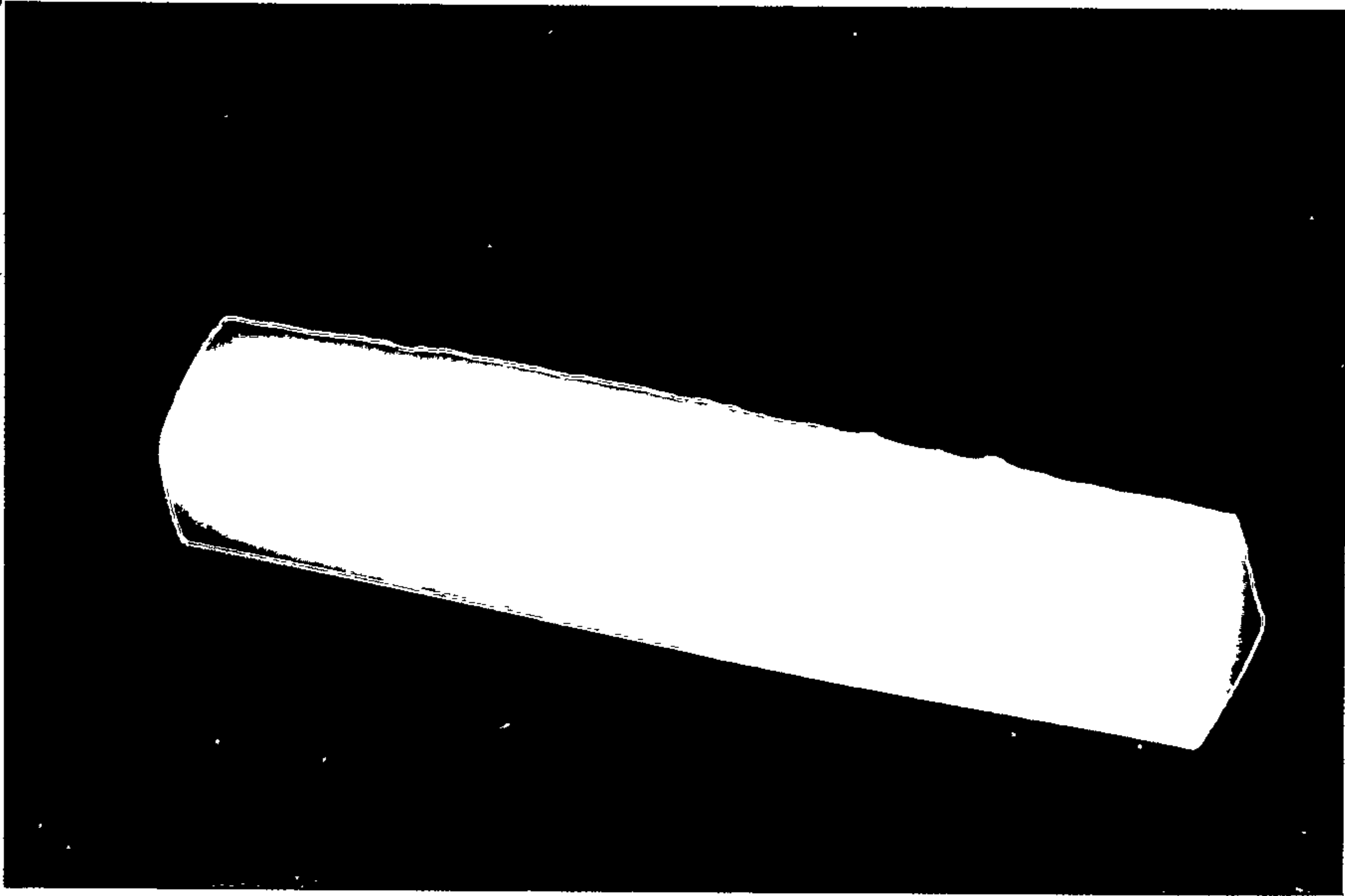


Figure 4.7 Fired porcelain bar prepared for the dilatometer

and connected to one axis of a W and W, Model 314 X-Y recorder.

A chromel-alumel thermocouple was positioned so that its bare hot junction was in contact with the midpoint of the specimen. Specimen temperature was determined from the e.m.f. of the thermocouple, which was connected to a YEW digital thermometer, type 2809. The linearized output from the thermometer was connected to the other axis of the X-Y recorder, which thus drew a thermal expansion curve for the specimen.

Outputs of the furnace control thermocouple and the specimen thermocouple were also connected to two Y-t recorders, to provide a record of the heating rates of furnace and specimen during each test.

Figure 4.9 is a schematic diagram of the dilatometer apparatus. Before testing began, the accuracy of the dilatometer was checked by recording a thermal expansion curve for an aluminium specimen of known thermal expansion.

The calibration of the X-Y recorder was checked, and adjusted if necessary, after each cycle.

Each porcelain specimen and the alloy specimen were run through two cycles. This was necessary, as it was found that in many cases the first run gave unreliable results.

Some of the porcelain specimens were put through a third cycle in order to determine the reproducibility of the thermal expansion curves. In all cases, results of

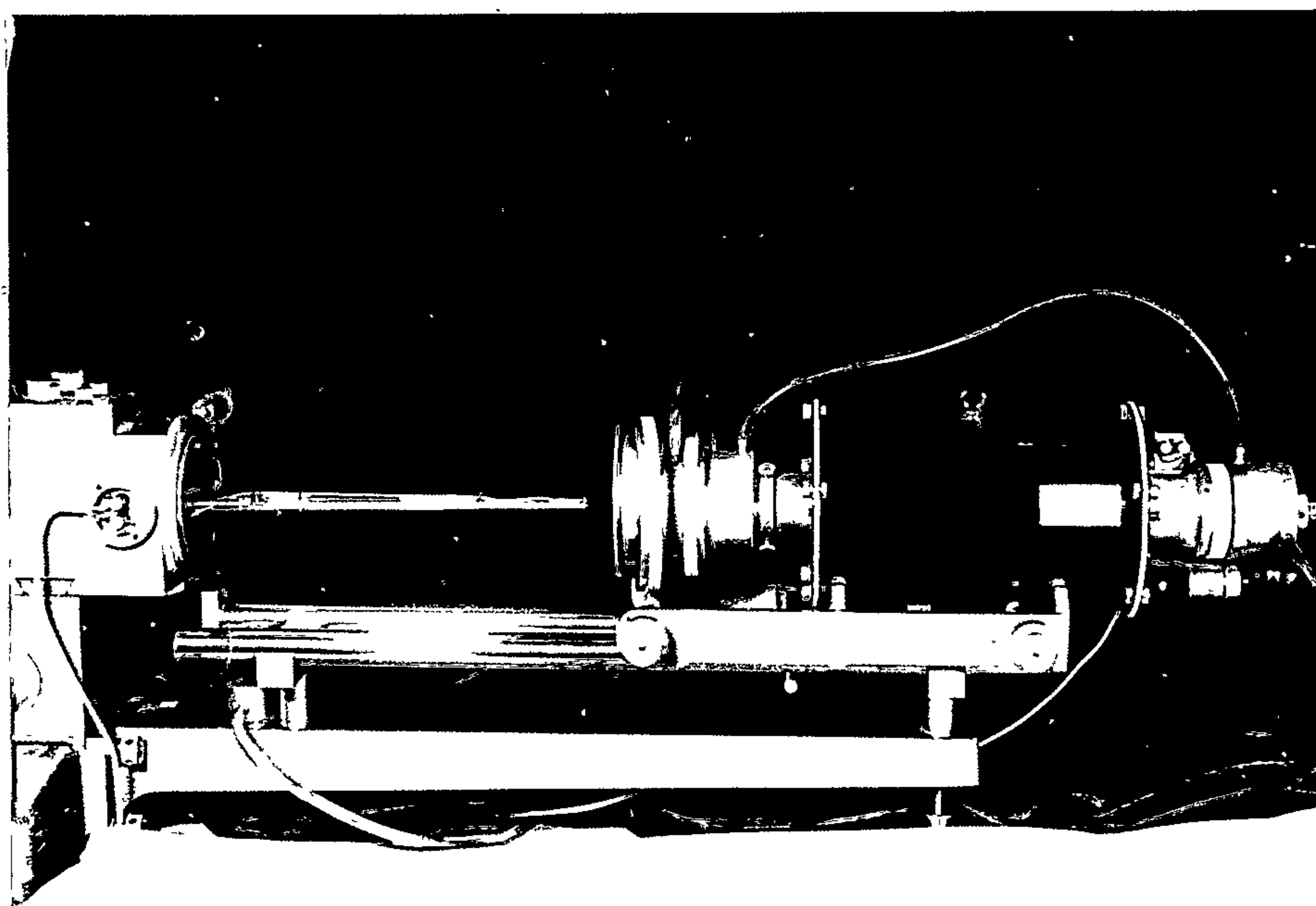


Figure 4.8 Dilatometer head and tube

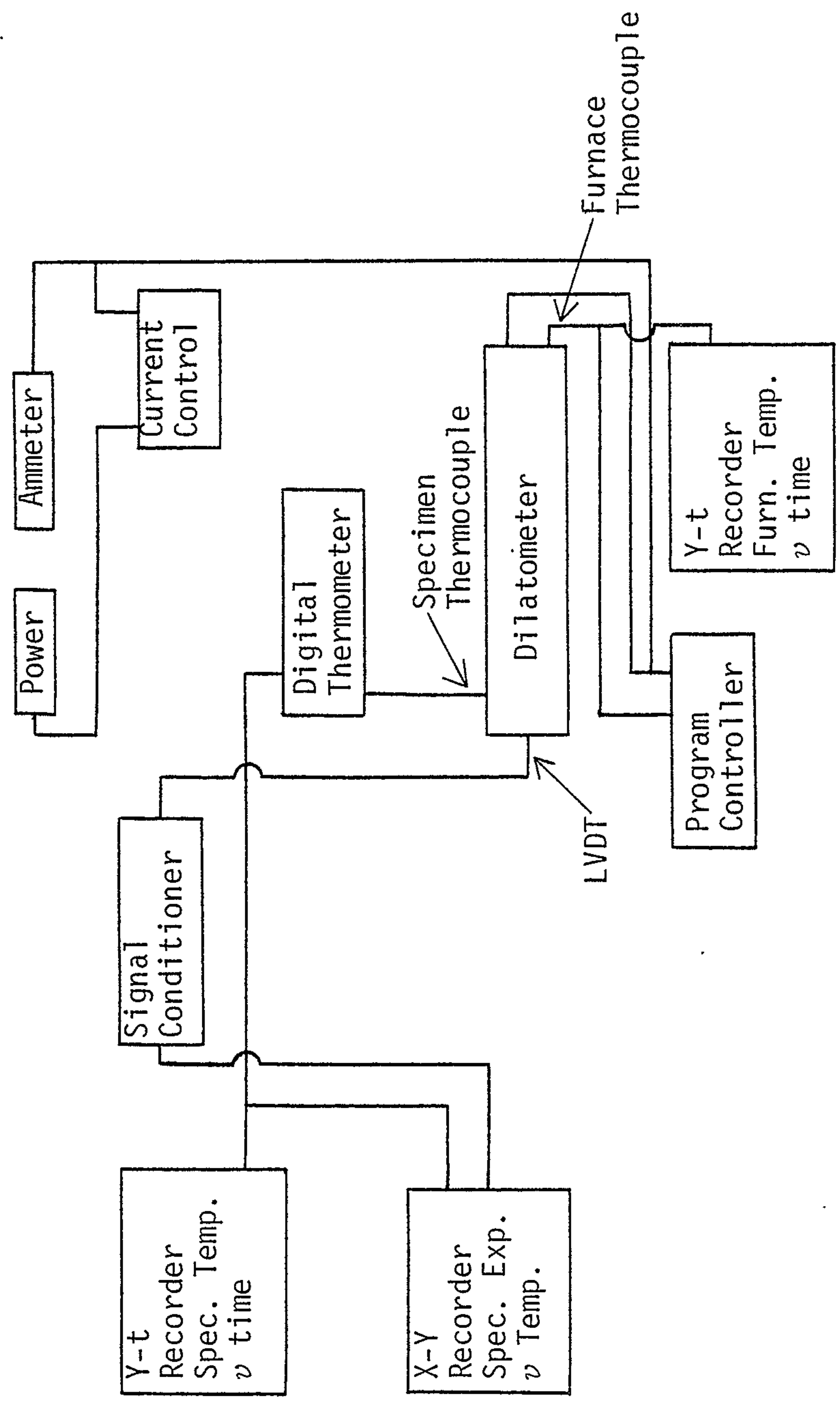


Figure 4.9 Schematic diagram of the dilatometer apparatus

the second and third runs showed good agreement.

Before the tests, each specimen was wrapped in two strands of platinum wire to reduce contact of the specimen with the dilatometer tube and so to minimise friction. A small hemispherical vitreous silica endpiece was placed at the end of the bar furthest from the hollow pushrod, with the flat end of the endpiece abutting the specimen. A conical vitreous silica endpiece, with point fitting into the pushrod was placed at the other end of the specimen. These endpieces were used in order to avoid inaccuracies which may have arisen from non-parallelism of the ends of the bar. Figure 4.10 shows the arrangement of the specimen in position in the dilatometer.

A figure for the linear coefficient of thermal expansion (α), for the test materials could be calculated from the curve according to the following formula:

$$\alpha(t_1 - t_2) = \frac{Y_2 - Y_1}{K \cdot L_0 (t_2 - t_1)} + \alpha_{VS}$$

where $Y_2 - Y_1$ = change in length

K = magnification factor

L_0 = specimen length

$t_2 - t_1$ = change in temperature

α_{VS} = coefficient of thermal expansion
of vitreous silica

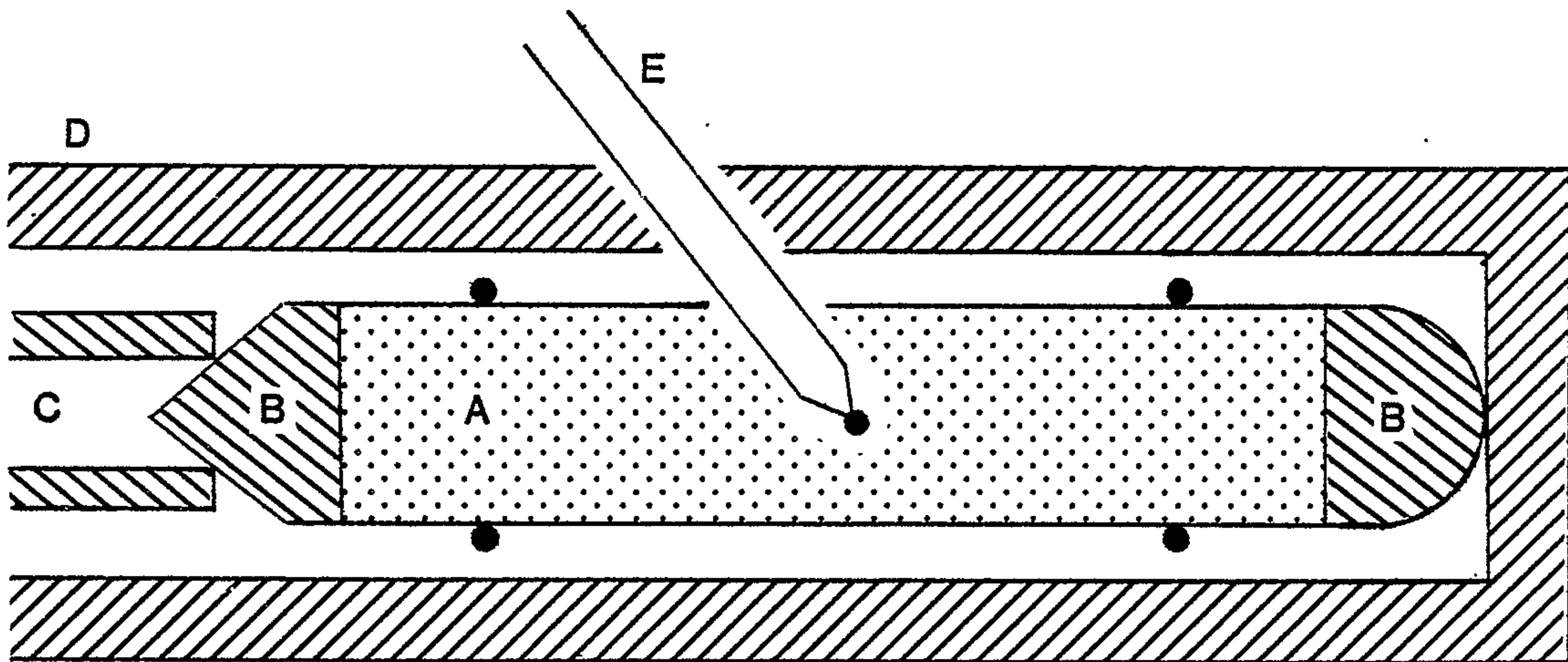


Figure 4.10 Schematic diagram of specimen in dilatometer

Code

A Specimen with Pt wire loops in section

B Vitreous silica endpiece

C Pushrod

D Dilatometer tube

E Specimen thermocouple

Since this instrument actually records the difference in linear thermal expansion between the specimen and an equal length of vitreous silica, to obtain an absolute value for the coefficient of thermal expansion of the specimen it is necessary to add, as a correction, the coefficient of thermal expansion of vitreous silica itself.

4.4 THERMAL SHOCK TEST

Each of the five test porcelain blends was measured into 1.5 g portions on the Mettler PC4400 balance to produce ten compound spheres for each blend, five with and five without the gold coating agent. The porcelain powder was mixed with Vita Modelling Liquid and applied to the alloy spheres with a le Cron carver. The spheres were vibrated by running the le Cron along the sprue in order to condense the porcelain and excess liquid was removed with a clean tissue.

The specimens were placed at the opening of a Ney Mark III vacuum furnace, which had been preheated to 450°C, to dry. They were then placed in the furnace and the temperature raised. A vacuum of 700 mm Hg was applied at 600°C and the temperature was then increased to 960°C at a heating rate of approximately 40°C/min. Two specimens with the same test porcelain were fired together in each cycle, one with and one without the gold coating agent. This reduced the possibility of problems resulting from inconsistencies between firing cycles.

This regimen also lowered the possible effect that increasing operator skill might have had on porcelain application technique. When the furnace had reached 960°C, the vacuum was released and the specimens were removed and allowed to bench cool (Figure 4.11). Any defects caused by porcelain shrinkage were noted. The thickness of porcelain after firing was approximately 1.5 mm, a thickness commonly found in alloy-ceramic restorations.

The spheres were examined under 20x magnification after 24 hours and note was made of any crack development, or rupture, of the porcelain. The type of failure that had occurred in the ruptured specimens was also noted. All specimens were re-examined after eight weeks.

The porcelain with the highest coefficient of thermal expansion that still failed the thermal shock test was identified. Compound spheres using this test porcelain and the test porcelains with percentages of Vitadur-N directly above and below it were produced using the other two gold coating agents. Results of these tests were similarly noted.



Figure 4.11 Cast sphere with fired porcelain

CHAPTER 5RESULTS5.1 THERMAL EXPANSION

The accuracy of the dilatometer was established by comparing the expansion curve obtained from an aluminium test rod to points plotted according to figures derived from data given in the Metals Handbook (Lyman, 1964). This comparison appears in Figure 5.1.

It was found that curves plotted from first run heating of the porcelain bars were not reliable and these were discarded. Second run heating curves were reproducible both for individual bars and between bars made from the same porcelain blend. Average curves obtained from second run heating of the two porcelain bars of each blend and from the thermal expansion curve of Option alloy from 20 to 600°C are plotted in Figure 5.2.

Attempts to obtain reliable contraction data for the porcelain bars proved unsuccessful because, with this apparatus, there was no adequate method of achieving a uniform cooling rate.

Table 5.1 gives values for the linear coefficient of thermal expansion from 20 to 400°C ($\alpha_{(20-400^{\circ}\text{C})}$) and from 20 to 550°C ($\alpha_{(20-550^{\circ}\text{C})}$) for the test porcelains and the alloy. α has been calculated only up to 550°C because a change in the slope of the porcelain thermal

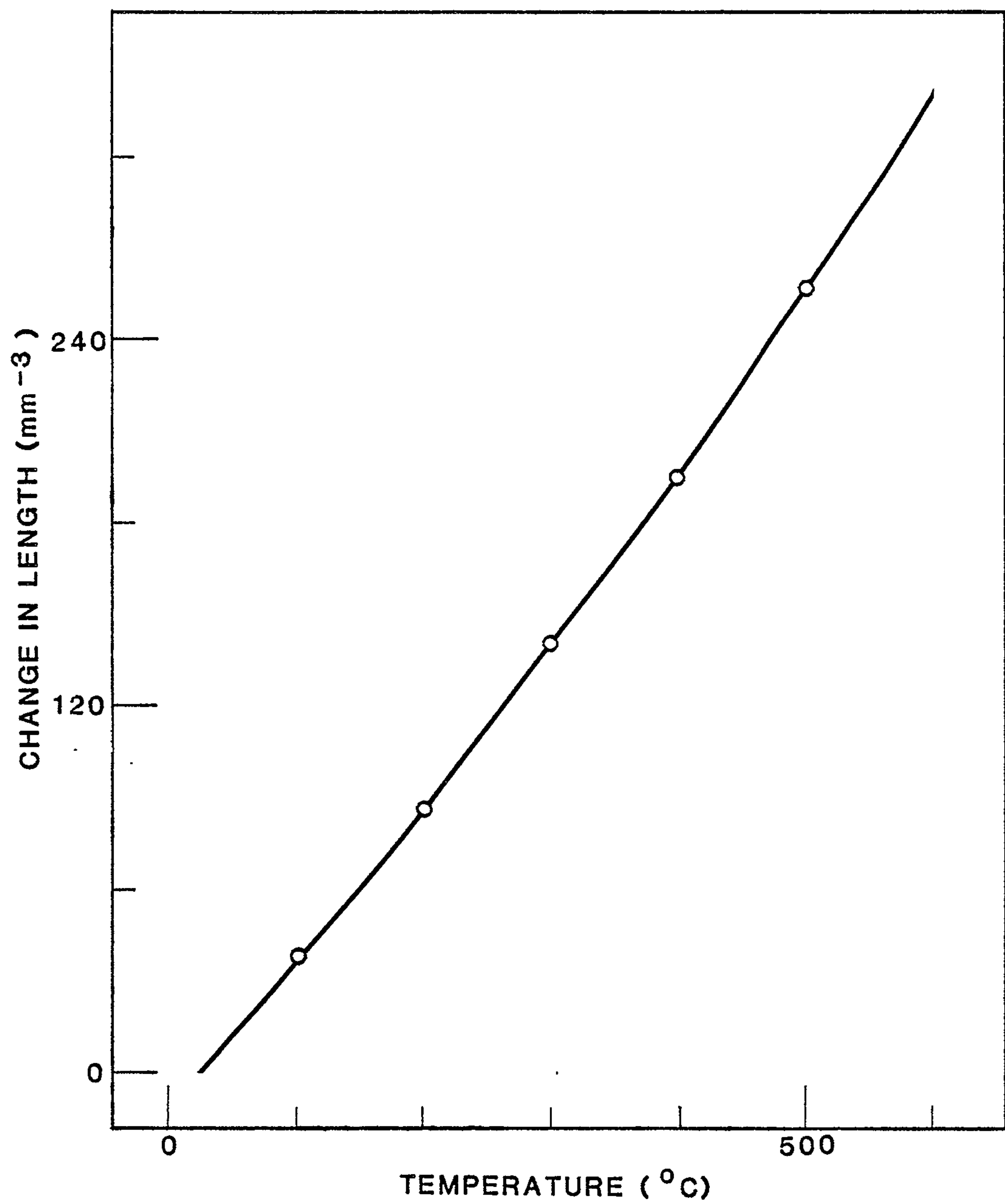


Figure 5.1 Thermal expansion curve for aluminium. Plotted points are derived from Metals Handbook (Lyman, 1964).

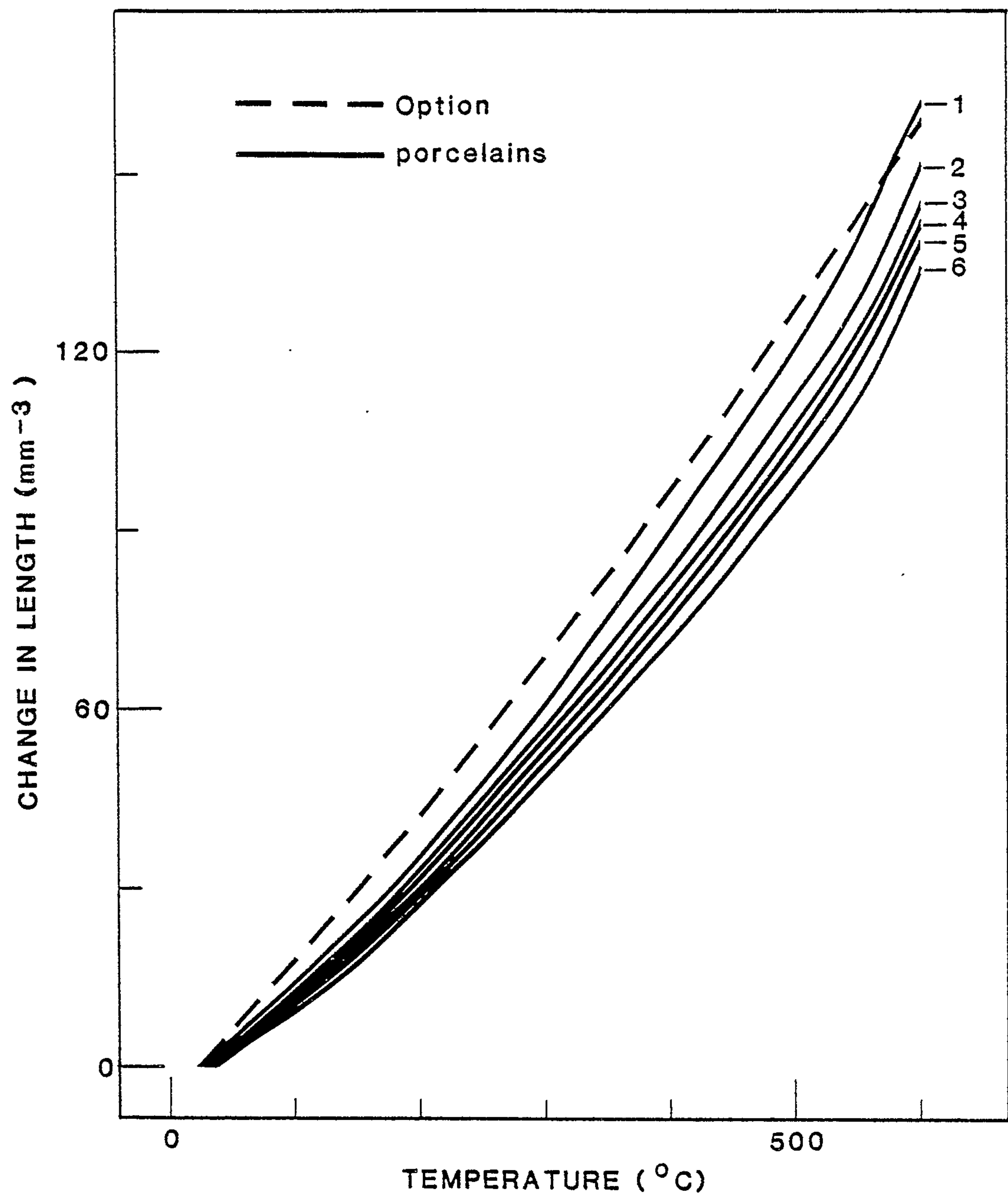


Figure 5.2 Composite graph of the thermal expansion curves for the alloy and the test porcelains

Code

1	VMK 68	4	80% VMK/20% Vitadur
2	85% VMK/15% Vitadur	5	77.5% VMK/22.5% Vitadur
3	82.5% VMK/17.5% Vitadur	6	75% VMK/25% Vitadur

Table 5.1 Linear coefficients of thermal expansion.

COMPOSITION	$\alpha_{(20-400^{\circ}\text{C})}$	$\alpha_{(20-550^{\circ}\text{C})}$
OPTION	13.4	14.0
VMK 68	12.6	13.6
85% VMK/15% Vitadur	11.7	12.6
82.5% VMK/17.5% Vitadur	11.3	12.2
80% VMK/20% Vitadur	10.9	11.8
77.5% VMK/22.5% Vitadur	10.5	11.4
75% VMK/25% Vitadur	10.1	11.0

expansion curves indicated that the glass transition range of the porcelains began not far above this temperature.

5.2 THERMAL SHOCK TEST

Cracking or rupture of the porcelain constituted a failed specimen. Figure 5.3 shows an example of cracking and of rupturing.

Table 5.2 compares the results of the thermal shock test after 24 hours and after eight weeks for specimens with no gold coating layer and for those fabricated with Wilkote. In all cases five specimens were tested.

Table 5.3 compares results obtained using Wilkote, Spectra-Seal and Deck-Gold (normal).

All ruptured specimens except one exhibited cohesive failure of the porcelain, in which some porcelain remained bonded to the alloy and no metallic surface was exposed. The exception was a specimen using Wilkote and 20% Vitadur-N porcelain in which rupture of the porcelain also exposed two areas of gold surface (Figure 5.4).

It can be seen that the three gold coating agents used gave similar results.

Under the conditions applying in this investigation, the gold coating agents proved to be of no benefit in reducing susceptibility to thermal shock.

A positive thermal expansion mismatch of $1.8 \times 10^{-6}/K$ for $\alpha_{(20-550^{\circ}C)}$ between the alloy and porcelains used in this investigation was critical.



a



b

Figure 5.3 a. Cast sphere with cracked porcelain
 b. Cast sphere with ruptured porcelain

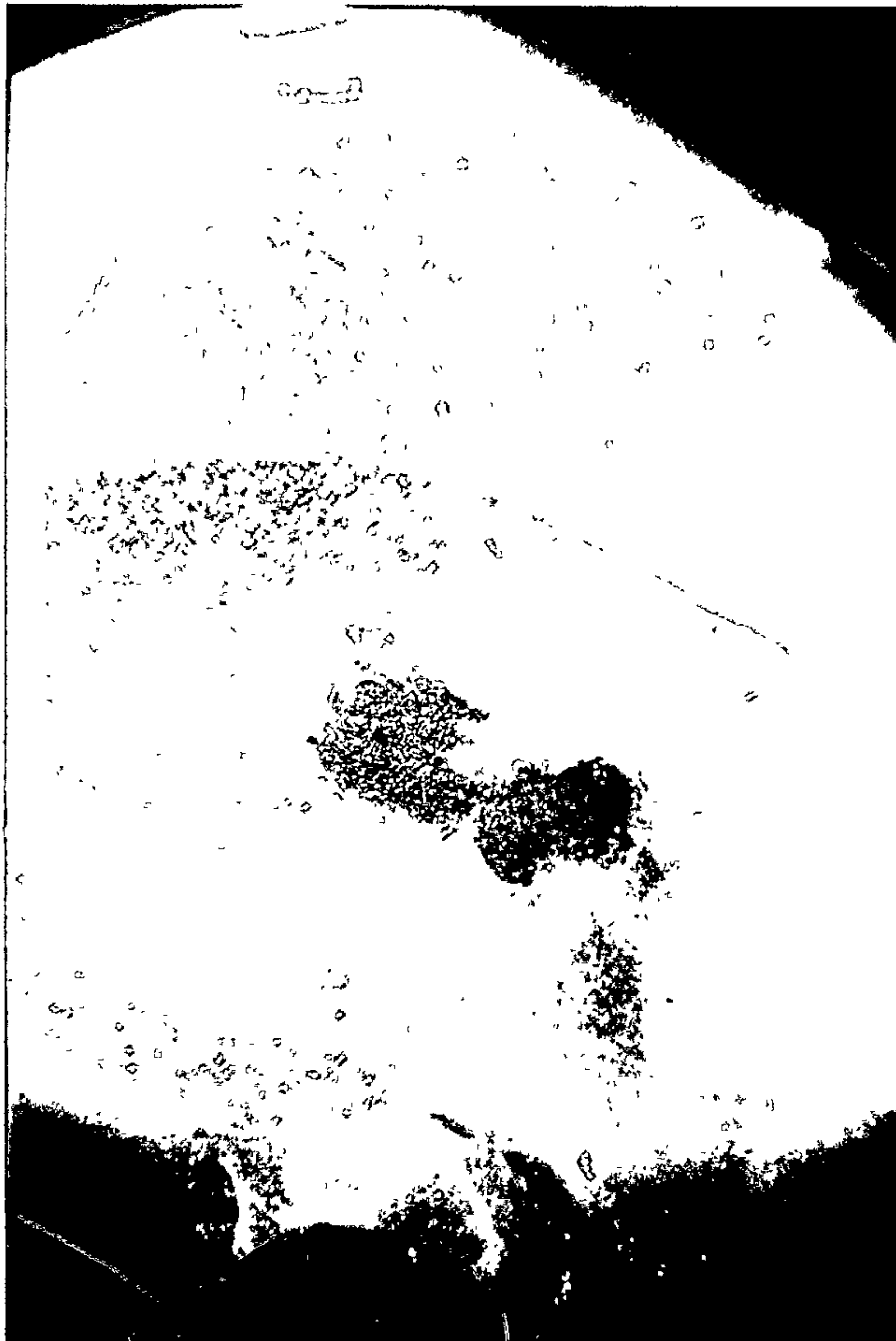


Figure 5.4 Cast sphere with ruptured porcelain showing exposed Wilkote

Table 5.2 Results of the thermal shock test on specimens with and without Wilkote.

Porcelain Blend	No. of Failed Specimens			
	No Gold Coating		With Wilkote	
	24 HRS	8 WKS	24 HRS	8 WKS
85% VMK/15% Vitadur	0	0	0	0
82.5% VMK/17.5% Vitadur	0	2	0	3
80% VMK/20% Vitadur	4	5	3	5
77.5% VMK/22.5% Vitadur	4	5	4	5
75% VMK/25% Vitadur	5	5	5	5

Table 5.3 Comparison of the effect of the three coating agents on the thermal shock test.

Porcelain Blend	No. of Failed Specimens		
	Wilkote	Spectra-Seal	Deck-Gold (Normal)
85% VMK/15% Vitadur	0	0	0
82.5% VMK/17.5% Vitadur	3	3	2
80% VMK/20% Vitadur	5	5	5

CHAPTER 6DISCUSSION6.1 THERMAL EXPANSION

The dilatometer used for this investigation proved to be a reliable method of plotting thermal expansion curves of the alloy and porcelains that were tested. A simple calculation could then be used to find a linear coefficient of thermal expansion for the temperature range of interest.

If such a dilatometer is to be used to plot thermal contraction curves modifications will be necessary so that furnace and specimen temperature can be lowered in a controlled manner.

Examination of the thermal expansion curves in Figure 5.2 shows that the thermal expansion of the alloy is more linear than the thermal expansion of the porcelain specimens. Thus it is inappropriate to refer to coefficients of thermal expansion without specifying the particular temperature ranges.

It was also noted that there was a marked increase in the expansion of the porcelain specimens in the vicinity of 550°C . This probably indicates the glass transition temperature range.

The regular decrease of thermal expansion of the test porcelains with increasing amounts of the jacket crown porcelain suggests that this is an effective method

of modifying the thermal expansion of a bonding porcelain for testing purposes.

It should be remembered that the dilatometer data relate to thermal expansion, whereas the important property in the thermal shock test is thermal contraction. Also, the dilatometer data were obtained at a heating rate of $5^{\circ}\text{C}/\text{minute}$, whereas the cooling rate in the thermal shock test is much higher, which, as has been discussed in Chapter 1, will have a marked effect on the actual thermal contraction of the porcelain.

For these reasons, the value of the thermal expansion curves lies in a comparison amongst them, rather than from the absolute figures.

6.2 THERMAL SHOCK TEST

The test attempted to produce conditions which would induce maximum stresses in the porcelain. As has been stated, the spherical geometry of the specimen causes maximum stress; bench cooling imposes maximum thermal shock; and stress relief through alloy creep is not possible. Thus, the ability of a gold coating layer to relieve stress when it was most needed was examined.

It was found that none of the gold coating agents used was effective in reducing residual stress between the alloy and porcelain.

The one example of mixed failure (i.e. cohesive and adhesive) appeared to be the result of applying the gold coating agent too thickly in two areas.

Failure of the porcelain was considered primarily to be the result of increased residual stress induced by an increased disparity between the thermal contraction of the alloy and the thermal contraction of the porcelain.

Another factor which may have caused porcelain failure was a decrease in the strength of the bonding porcelain as a result of the addition of the jacket crown porcelain. It was thought, however, that the addition of the jacket crown porcelain was likely to have little effect on porcelain strength (Southan, 1984).

It should also be acknowledged that the addition of the jacket crown porcelain might have caused a change in the glass transition temperature of the porcelain which would affect the amount of residual stress at room temperature.

Neither of these factors affect the validity of the investigation in determining the ability of a gold coating layer to reduce stress.

The delayed failure exhibited by some specimens (i.e. those which were intact after 24 hours but had cracked by eight weeks) indicates that at ordinary temperatures stresses are not dissipated with time. Further, it would seem that moisture contamination from the atmosphere was enough to promote static fatigue in the porcelain. A similar finding has been reported by Walton and O'Brien (1985). This is significant because restorations which appear to be successful in the laboratory may later fail.

Some possible explanations for the failure of a gold coating agent to act as a "stress release zone" can be advanced.

1. The gold layer may not be thick enough to allow plastic deformation independent of the alloy substrate in order to reduce stress in the porcelain. Thus residual stress may be purely the result of the bulk properties of the alloy and the porcelain despite the intervening gold layer. If the gold were thick enough to relieve stress by plastic deformation, problems of bonding the porcelain to the gold or the gold to the alloy might be encountered, as exemplified by the mixed mode of failure observed for one specimen.
2. Variations in the thickness of the gold coating layers as a result of the brush technique of application might reduce the possibility of lowering stresses by this means. In this regard, the advantages of applying an even layer by electroplating might be useful in reducing localised areas of stress concentrations.
3. At high temperatures, migration of ions from the alloy into the gold coating layer could be expected to take place rapidly. This would have the effect of alloying the gold which will increase its modulus of elasticity and its yield strength, which

in turn could make it ineffective as an agent in reducing stress. Even if the modulus of elasticity remained below that of the alloy, Tesk et al (1983a) have shown that this would have very little effect on stresses arising between the alloy and the porcelain.

4. Another factor which might compromise the ability of a gold coating to reduce stress is the relatively high coefficient of thermal expansion of pure gold. Brandes (1983) gives a value for $\alpha_{(20-500^{\circ}\text{C})}$ of $15.2 \times 10^{-6}/\text{K}$.

CHAPTER 7CONCLUSIONS

The following conclusions can be drawn from the results of this study:

1. The dilatometer apparatus used in this study is a reliable method for plotting thermal expansion curves of alloys and porcelains.
2. Thermal expansion of alloys and especially porcelains do not follow a linear relationship with temperature.
3. The thermal expansion of porcelain used for bonding to alloy substrates can be lowered in a controlled manner by the addition of jacket crown porcelain.
4. Residual stress in alloy-ceramic specimens is not reduced with time at room (or mouth) temperature.
5. Gold coating agents have an insignificant effect on residual stress in alloy-ceramic specimens.

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