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Development of a microwave system for processing zirconia

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Development of a Microwave System for Processing Zirconia.

A thesis submitted in fulfilment of

the requirements for the award of the degree

Master of Engineering (Honours)

from

University of Wollongong

by

Stuart John Street, B.E(Hons)

Department of Materials Engineering

1994

"Exploring is delightful to look forward to and back upon, but it is not comfortable at the time, unless it be of such an easy nature as not to deserve the name."

Samuel Butler
Erewhon.

Acknowledgments.

This body of work would not have been possible without the efforts of numerous people, to all those that helped I am indebted.

Thanks must firstly go to my academic supervisor Sharon Nightingale for maintaining an open door policy with regards to help and guidance throughout the entire project. I would also like to thank all of the technical and research staff, in particular Nick Mackie deserves credit for showing me how to drive the SEM, despite continual traumas of the unit. The computer facilities of Masoud Samandi were also greatly appreciated.

Last but not least, a special mention should be made of my friends and fellow students, for putting up with my whingeing during the problem stages and for providing ample opportunities to forget about them. In particular I would like to thank Tahnee Smith, for her angelic last minute help and her generous hospitality, plying me with food and coffee on numerous unexpected visits. Thanks Mum!

Abstract.

The development of a 2.45GHz multimode oven is described. Difficulties were encountered in developing the temperature measurement and control system and the attainment of a uniform heating zone. On the strength of the development work, a number of recommendations to improve the microwave system were made.

Suitability of the oven for processing of zirconia was investigated. Evaluation was carried out by a series of comparative experiments, with 3.0mol% Y-TZP, using conventional and hybrid microwave heating.

It was demonstrated that the zirconia could be sintered, aged, and thermally etched with the microwave oven, and that binder burnout of the green compacts was successful.

Interpretation of the experimental data, to determine whether the material properties were process or merely microstructure dependant, was unresolved due to the uncertainty of temperature measurements.

CONTENTS

CHAPTER 2 SINTERING

CHAPTER 3 MICROWAVE TECHNOLOGY

CHAPTER 4 EXPERIMENTAL METHOD

4.3 Microwave Equipment Description

CHAPTER 5 SYSTEM DEVELOPMENT

5.3 Development of Temperature Measurement and Control

CHAPTER 6 EVALUATION OF MICROWAVE SYSTEM FOR PROCESSING OF ZIRCONIA

Chapter 1 Introduction.

Processing of ceramics with microwave energy provides both technical and economic advantages. As an emerging technology it holds the potential of enabling advanced ceramics to be processed which can not be done so feasibly with conventional techniques. Of the processing stages which have been investigated, sintering has attracted the greatest amount of interest as an application for microwave heating.[1]

One of the main attractions of utilising microwave energy for sintering of ceramics is the potential for tailoring of microstructures, in particular structures that may not be obtainable with conventional techniques. The incentive being that microwave sintering may lead to ceramics with superior properties. Apart from improved properties, the principle reasons for research are often cited as the development of new materials and greater process control.[2,3]

The unique nature of microwave sintering is ascribed to the manner in which the heat is generated.[4,5] Heat is generated volumetrically due to the interactions of the microwave energy with the material, the nature of the interactions is dependant on the materials' dielectric properties. This is the fundamental difference between sintering with microwaves and conventional heating techniques. Several ceramic materials have been successfully microwave sintered including alumina,[6] silicon nitride,[7] silicon carbide,[8] and titanium diboride.[9]

The dielectric properties of many ceramic materials, are such that at low temperatures they are effectively transparent to microwaves,[10] and therefore require more elaborate methods for processing. "Hybrid" heating has found broad acceptance[11,12,13] as a processing method for these materials. Hybrid heating relies on external heat, from a more receptive material, being conducted to the ceramic. The aim is to heat the ceramic to a temperature where it can efficiently absorb the microwave energy.

One ceramic that displays such behaviour is zirconia. Microwave sintering of zirconia is complicated, not only by its dielectric properties, but also by its low thermal conductivity. Different techniques adopted to successfully sinter zirconia, include hybrid heating,[11] the use of high frequency microwaves,[14] and concentrating the microwave field by using single mode cavities.[15]

Sintering of zirconia, as with other ceramics, has been claimed to be enhanced by using microwave energy.[3,11,13,16,17] Evidence cited for the enhanced sintering includes reduced sintering temperatures and higher densities. Although believed to be due to reduced activation energies the fundamentals of this microwave heating phenomenon are yet to be fully understood.[3,18]

Interpretation of the enhanced densification that is observed is hindered by difficulty in attaining accurate temperature measurement in a microwave field.[19] The measurement of temperature is a keystone to understanding the fundamentals of heating yet, there is doubt over the accuracy which can be provided with current temperature measurement devices.

The initial objectives of this research were to develop and commission a microwave system which would enable an investigation of the enhancement phenomenon of a microwave sintered Y-TZP. Development of the microwave system was necessary for accurate measurement and control. Previous research,[20,21] including projects involving the author,[22,23] have successfully sintered zirconia based materials. However, for these works, temperature measurement and control were very limited.

"What posssessed me was dread, and the misery of anticipating the unavoidable."

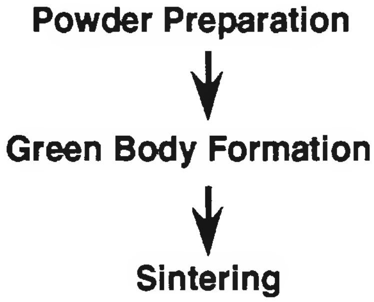
William Trevor
Worst Journeys
The Picador Book of Travel.

Chapter 2 Sintering.

2.1 Introduction

Generally ceramic articles are manufactured in three stages, figure 1.

Figure 1: Typical Ceramic Processing Route.



In this basic process route material densification occurs in the green body formation and sintering stages.

Sintering describes those processes whereby powder consolidation occurs by heating. Although mankind has been sintering ceramics for thousands of years, research into the processes did not begin in earnest until the 1920's.[24] A continued and ever accelerating amount of research has seen the level of understanding in ceramic sintering grow from the infancy it was still in the late 1970's,[25] to be a reasonably well understood and controllable process,[26] even at an industrial level. However there is still debate over some of the theories and models used to predict and evaluate sintering behaviour.

2.2 Sintering Process Variables.

Sintering is controlled by the properties of the compact and the process variables. Richerson[27] lists the main process variables as, time/temperature cycle, atmosphere, furnace design, and the materials of construction for the furnace and heating elements.

The sintering schedule is the easiest of the process variables to control. Modern temperature measurement devices and controllers enable a very accurate control to be maintained over the sintering schedule. The traditional approach to sintering has been that of time at peak temperature, although the rate of heating and cooling has also been an integral part of the schedule.

The heating and cooling affect the mechanical integrity of the sintered body. If the rates are too severe, thermal shock can occur resulting in failure. The time at peak temperature also affects the final density and the extent of grain growth.

Rate controlled sintering (RCS) is argued to be a more efficient[28] process than traditional sintering, yet results in a finer and more uniform microstructure.[29] Densification using the RCS technique follows a predetermined density-time profile, the required temperature being the minimum needed to maintain this profile. RCS can avoid some of the problems associated with traditional sintering such as gas entrapment, pore entrapment, irregular microstructure and excessive grain growth. Huchkabee et al[29] claim that during the intermediate and final stages of sintering there is minimal excitation of undesirable transport mechanisms, resulting in minimal grain growth.

Poppi and Vincenzini[30] optimised sintering, at reduced costs, using a technique they called integral thermal process (ITP). The ITP technique is based on the thermal stresses a body can withstand during heating and cooling. Maximum heating and cooling rates are adopted so as to eliminate the "dead times" of sintering. The heating and cooling regions were argued to be ineffective scheduling, contradicting the underlying basis for RCS.[28,29] The effect of the ITP approach on material properties and microstructure was not investigated.

Rapid rate sintering can lead to microstructural benefits,[31] where higher than conventional temperatures are used for relatively short periods. Rapid rate sintering enhances densification yet retards grain growth. The diffusion paths for rapid rate sintering are complex and open to interpretation[32,33] although temperature gradient driven diffusion is thought[34] to be responsible for the high densification rates.

The sintering atmosphere may have either very negligible or very drastic effects depending on the material being sintered. The physical and chemical characteristics of the sintered body are most strongly effected. The atmosphere has little effect on the driving forces, but may be more significant to the transport mechanisms. The atmosphere needs to be carefully selected, not only to match the material, but to suit the final desired properties of the body. Sintering of zirconia is usually carried out in air or inert atmospheres to prevent reduction, however for aesthetic reasons zirconia is often sintered under reducing conditions. Zirconia sintered under reducing conditions loses oxygen, ie (ZrO_{2-X}). The greater the oxygen loss the darker the appearance of the zirconia.[35]

If sintering is one of the most critical steps in ceramic manufacturing then furnace design is one of the most critical process variables. Sheppard's[2] review of sintering technology highlights that furnaces are becoming more sophisticated to meet the increasing demands required for sintering. The aims of sintering, maximum density and highest quality at lowest cost, are more difficult to attain for the advanced engineering ceramics than the traditional ceramics. Considerations for furnace suitability include temperature capability, temperature control, temperature uniformity and atmospheric control.

Improvements to furnaces have come by changed furnace design, faster firing capabilities, greater flexibility and control, and the introduction of fibre insulation. Sheppard still sees many challenges to be met in furnace design, in particular energy efficiency and the problem of noxious emissions.

As the specifications for material performance are pushed higher and higher the ability of conventional sintering techniques to meet these demands is becoming more constrained. Alternative sintering techniques can provide a means of attaining these aims, and in many cases provide a unique solution. Table 1 lists some of the possible alternative sintering techniques, however, currently many of these only have limited commercial acceptance.

Table 1

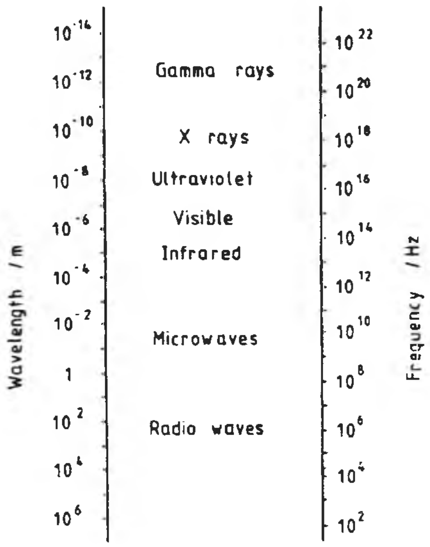
Alternative Sintering Techniques.
Hot Pressing
Hot Isostatic Pressing
Reaction Sintering
Plasma Sintering
Microwave Sintering.

Chapter 3 Microwave Technology.

3.1 Introduction.

Microwave heating is defined as "the heating of a substance by electromagnetic energy operating in the frequency range 300MHz to 300GHz".[36] Due to statutory requirements only a few set frequencies are available. In Australia these are 2.45GHz for all domestic and the majority of commercial uses with 915MHz being designated for the remaining commercial systems.[37]

Figure 2, the electromagnetic spectrum. From Binner.[1]



From the initial discovery of dielectric heating in the 1940's the level of interest in microwave heating has grown considerably, an indication of this growth can be seen by the increasing number of published papers.

As a fundamentally new heating technique, microwaves, have been shown to offer many unique solutions to a variety of processing problems. However, the uses of microwave technology are not universal and many of the fundamentals are still not fully understood. Hence, continued research into all facets of microwave heating is still required.

3.2 Advantages of Microwave Technology.

Microwave technology has been periodically reviewed[4,37,38,39] and as such the processing advantages are well documented. However, many of these optimistically omit the material dependency or the difficulty in achieving them in practise. Table 2 lists some of the possible advantages to be gained by using microwave technology.

Table 2

Advantages of Microwave Technology
instantaneous power control
no thermal inertia
volumetric heating
selective heating
faster and more efficient heating
adaptability and ease of use
higher yield rates
enhanced material properties
material synthesis
economic savings

3.3 Microwave Heating Mechanisms.

Microwaves, being part of the electromagnetic spectrum, obey the laws of electromagnetism. Microwaves can be transmitted, reflected and absorbed. They are also coherent and polarised. Microwave heating results due to the interaction of the material and the incident radiation. These processes are well documented[10,40,41] and as such will only be briefly discussed.

A material will either reflect, as in the case of most metals, absorb or transmit microwaves. The nature of the interaction mechanisms will be dependant on material characteristics, namely its dielectric and magnetic properties. The behaviour of a dielectric material in an electromagnetic field can be described by the complex permittivity (ε^*) and the complex permeability (μ^*), (Appendix A equations 1 and 2).

Heating arises when energy is lost from the incident radiation to the material. Transfer mechanisms include ionic conduction, dipole rotation, magnetic losses, interface polarisation, molecule twisting and bending, and resonance phenomena.[4] Dipole rotation and ohmic loss are the two main heating mechanisms.[1]

Dipole rotation results in heat generation due to dielectric losses. Dielectric losses arise due to friction and conduction when the dielectric material is in an oscillating electric field. Friction losses are conventionally described by the loss tangent ($\tan \delta$), (Appendix A equation 3).

Molecularly, friction arises due to the intermolecular bonds opposing the rotation of the dipoles. This creates hysteresis between the induced field and the resulting polarisation. At 2.45GHz, for most materials, the loss factor increases with increasing temperature, however heating is most efficient when ε'' is at its maximum rather than $\tan \delta$.

Figure 3, loss tangent. From Paoloni.[42]

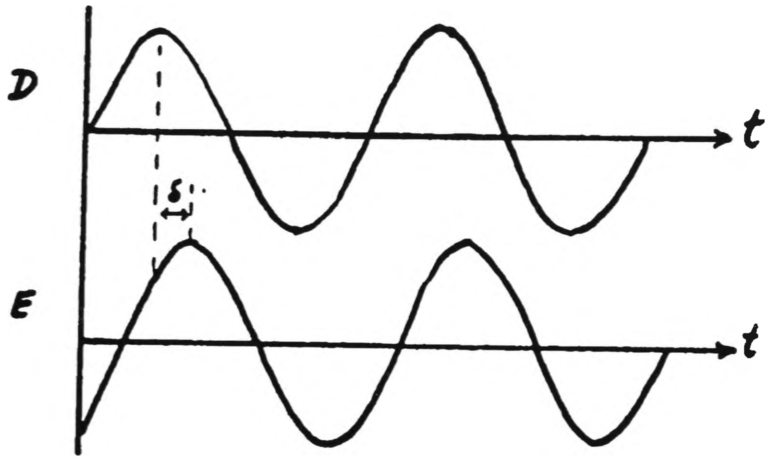
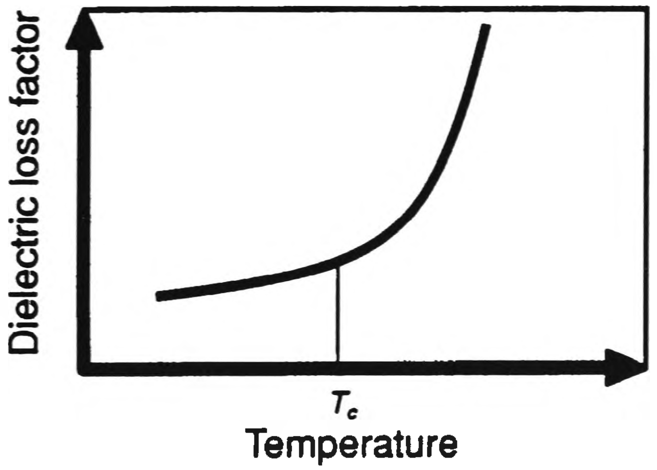


Figure 4, variation of dielectric loss factor with temperature. From Hamlyn and Bowden.[43]



Power absorption by a material is dependant on frequency, particle size and shape, density and the temperature.[1] As the microstructure changes during processing, so to does the material properties, which inturn effects the rate and uniformity of heating. As the frequency is increased, the power absorption increases, (Appendix A equation 4) however, the penetration depth decreases.

Increasing temperature generally results in an increase in the loss factor, however penetration depth decreases, (Appendix A equation 5). The loss factor is not only dependant on temperature but also changes in impurities, where conduction tends to be enhanced by reducing the energy gap between the valence and conduction bands.

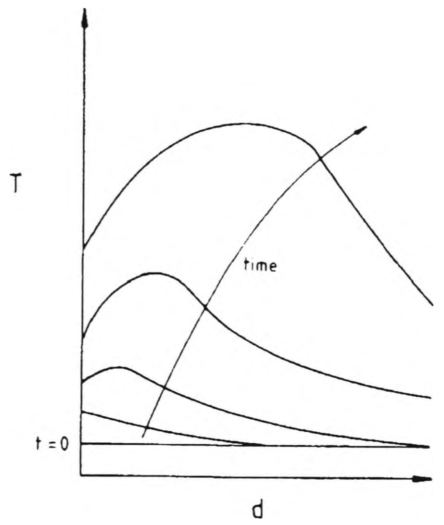
The extreme case of the loss factor increasing with temperature is thermal "runaway". As already stated, generally the lossiness of a material increases with temperature. A lossless material over a narrow temperature range may become extremely lossy. The process behaves in a self perpetual manner, in that increasing temperature increases the lossiness allowing for the material to absorb more of the microwave energy.

Kenkre et al[44,45] used physical considerations to model thermal "runaway". The model postulates that materials consist of two heating species. Type 1 species absorb energy through a Debye mechanism and are responsible for the low temperature heating. The second species however, exist in potential wells which need to be overcome to enable them to absorb the microwave energy. As the temperature increases, more type 2 species can overcome the potential well and absorb energy, resulting in a temperature rise. This feedback effect allows for thermal "runaway" to be desribed with a suitable non-linear component, (Appendix A equation 6).

The greater the energy required to overcome the potential well, the greater the dependancy of the initial heating on the type 1 species. The proportion of the bound to free absorbers is a simple thermal balance. The model was applied to several materials and found to be in good agreement with the experimental data.

The nature of the heating mechanisms allows inverse temperature profiles to be attained with microwave heating, (figure 5). The size of the inverse temperature profile depends on the power level, electric field intensity and material properties such as lossiness, and thermal and electrical conductivity.The inverse temperature profile can be limited by careful insulation to stop heat losses from the surface, or by combination heating.

Figure 5, inverse temperature profile. From Binner.[1]



Deepak and Evans[46] carried out a theoretical investigation of temperature profiles within a ceramic body heated by microwaves. Although their work required simplifications and estimates of material properties, such that their conclusions were at best semi-quantitative, they were able to draw several conclusions about microwave heating. Their calculations predict that both the temperature and temperature profiles could be controlled by the incident power levels and the insulation. It was also concluded that the temperature and temperature profiles were sensitive to the dimensions of the body and its orientation in relation to the microwave field.

Microwave-matter interactions are dependant not only on the field uniformity but also material characteristics. Predicting heating behaviour can often be complicated because materials in general are not truly homogeneous. Uniform heating within a system is more easily facilitated with precise processing and design.[5]

3.4 Microwave Design Considerations.

Tinga[4] describes microwaves as a highly ordered and controllable form of energy. However, careful design is still required to enable the system to be, not only controllable, but efficient.[2]

Two common features of all microwave appliances are that they have a source of microwaves and an applicator. Microwaves can be generated by a magnetron or a klystron and the applicator a resonant or oversized cavity. The connection between the two being either a coaxial cable or a waveguide.

Magnetrons are relatively compact and efficient (60-65%) power convertors, and their low cost of manufacture has made them the most popular source of microwaves. Operating lives of a magnetron are generally in the order of 2000 hours,[47] although with care this can be extended to in excess of 4000 hours.[48]

Although magnetrons are fairly efficient convertors, remaining power dissipates as heat in the anode and cathode, (figure 6). Heat can be removed in smaller models by simple air cooling, the magnetron is mounted in finned (figure 7) heat sinks with an air blower. Higher power models require water cooling.

Figure 6, schematic diagram of magnetron. From Rowe.[47]

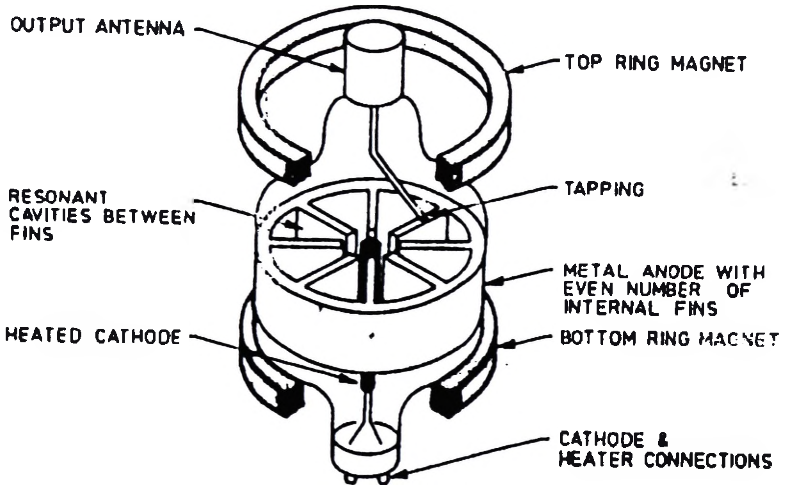
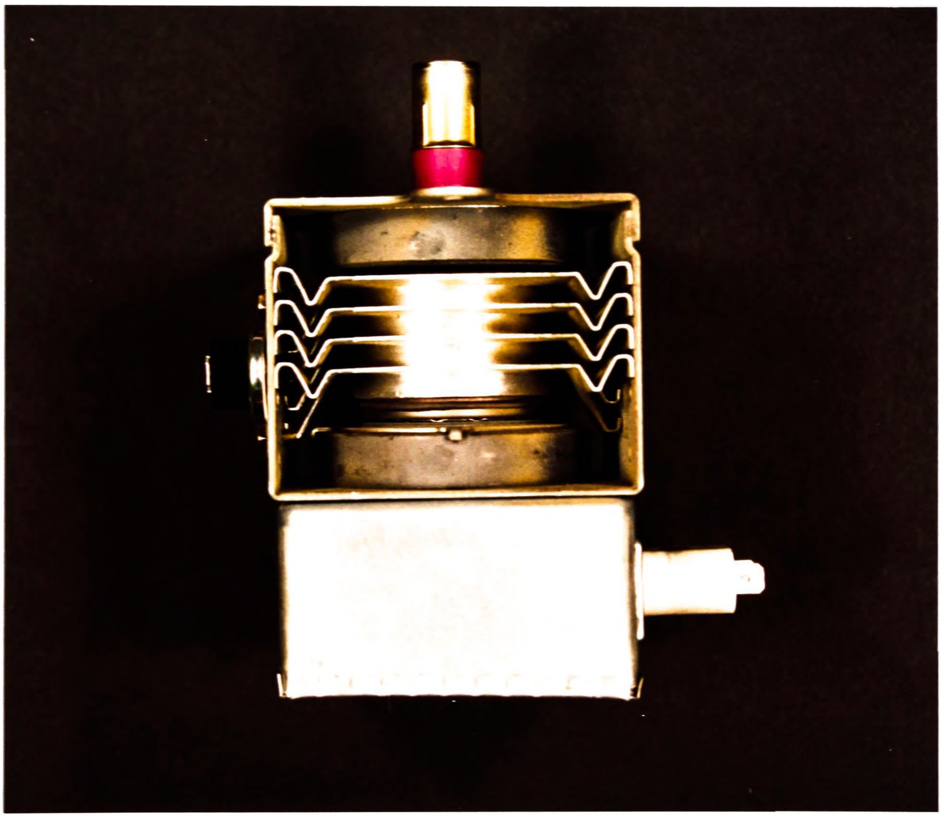


Figure 7, cooling fins on a low powered magnetron.



Domestic model magnetrons typically deliver 500-900W[47] while large industrial models are capable of delivering in the order of 10kW at 2.45GHz. Generally, the higher the frequency the greater the power attainable from the magnetron. Choice of magnetron is dependant on the exact application. Domestic magnetrons operate optimally for loads of approximately 300ml water,[49] but can handle varying loads, including the empty cavity situation.[41] Low loading is undesirable and continued use shortens the life of the magnetron considerably as power can be reflected back from the applicator to the magnetron.[47] The initial warmup period of a magnetron can also cause problems when very short exposure times are required.[49] Varying warmup times hindering reproducibilty.

The most commonly used means of transmitting power from the antenna of the magnetron into the applicator is the rectangular waveguide.[50] Rectangular waveguides, particularly at low frequency, are able to handle greater power loads than other guides due to their size. The waveguides need to be matched to the magnetron, which requires that the waveguide has set dimensions. Standard[51] waveguide dimensions for 2.45GHz include 72.14 x 34.04mm^2, 86.36 x 43.18mm^2 and 109.22 x 54.61mm^2. The higher the magnetron frequency the greater the losses. Typical losses in a metallic waveguide at 2.45GHz are less than 10%.[52] Losses occur due to skin effects and surface roughness and at higher frequency due to reduced waveguide size.[50] Ideally the waveguide should be smooth so as to reflect the microwaves into the applicator with as little mismatch and loss as possible. Non-metallic waveguides exhibit low loss, hence providing a possible means of overcoming the problems of metallic waveguides at high frequency.[50] However, the majority of waveguides and applicators are constructed from magnetic and highly conductive metals.[51]

The design of the applicator is dependant on its intended use, hence consideration should be made to the size of the material, its characteristic properties, the operating frequency and power, and the process type.[51] Impendance matching, field uniformity, safety and construction materials are also of importance.

The four types of applicators[52] are;

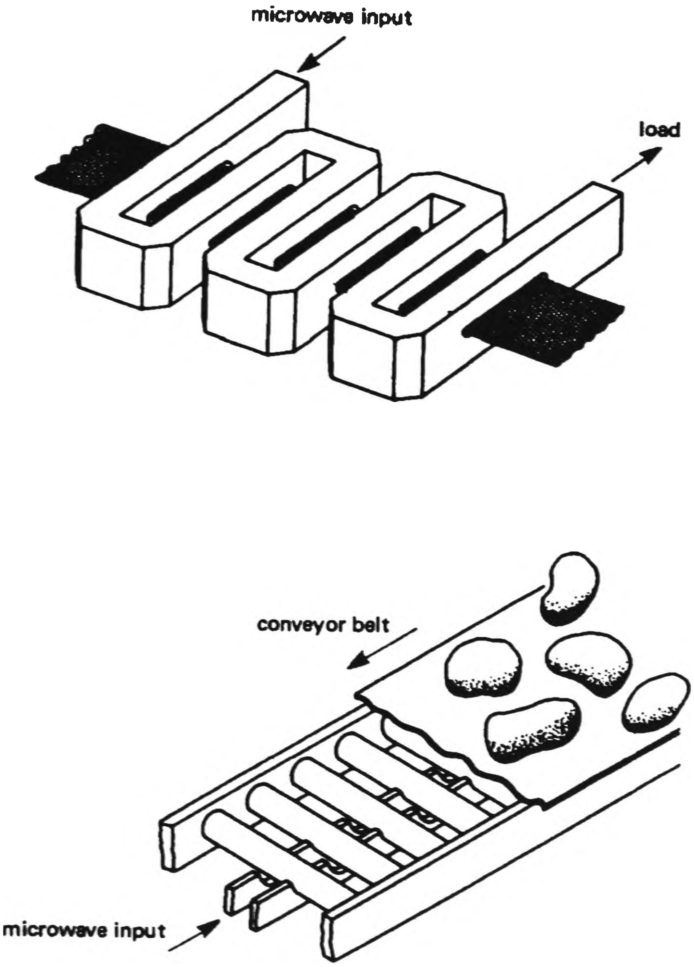
i) resonant cavity

ii) travelling wave applicator

iii) free space applicator

iv) slow wave applicator.

Figure 8, applicator designs. From Gardiol.[52]



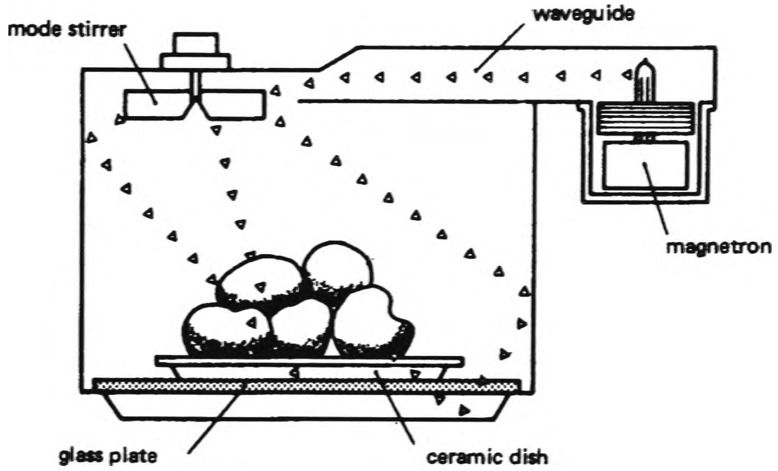
Resonant cavities can either be multimode (oversized) or singlemode cavities. The dimensions of a multimode cavity are such that they are considerably greater than the wavelength and the material. Multimode cavities are suitable for large volume and irregularly shaped materials. Small loads in a multimode cavity are not efficient, thus a single mode cavity is often more suitable. Single mode cavities can provide very rapid heating, however, the field tends to be unidirectional.[51] Although it has been shown that single mode cavities are successful on a laboratory scale there is some doubt over their industrial viability.

Energy utilisation in the large multimode cavities tends to be very high,[4] 50-95%. Multimode cavities exhibit spatial resonant behaviour, power can vary considerably with position. In single mode cavities this is not a problem as the field is well defined.[51]

Mismatching of the impedance between the magnetron antenna, waveguides, applicator and process material, place a load back on the magnetron. Minimising the impedance protects the magnetron from reflected power and allows for greater heating efficiency. Ideally the impedance should be as low as possible (V.S.W.R < 1.5). A common method of matching a system is by the use of "tuners" placed between the magnetron and the applicator, which alters the distribution of power. However, for some applications it focuses the field too sharply.[49]

To overcome the problem of small multimode cavities (domestic models) a turntable and/or a mode stirrer can be used,[47] as shown in figure 9. The turntable moves the material through the varying field so as to create a stastically uniform field, while the mode stirrer perturbs the field. Spatial behaviour could be overcome by using multiple frequencies, however this would be difficult due to limited frequency allocations.[37] Multiple frequencies have also been suggested as a means to overcome the problem of heating low dielectric loss materials.[3,53]

Figure 9, domestic oven with mode stirrer. From Gardiol.[52]

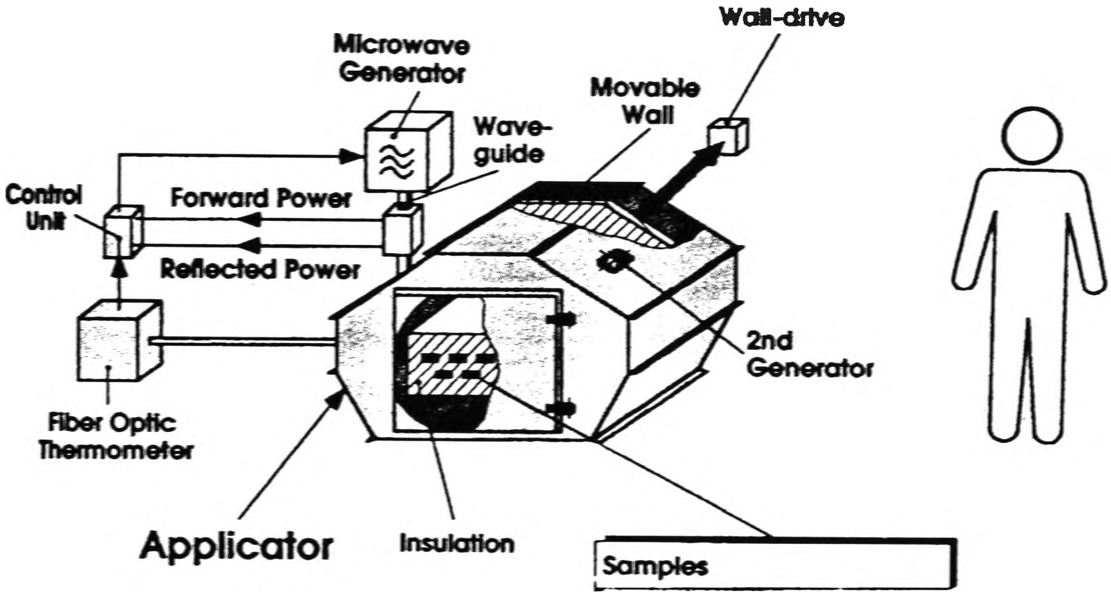


Careful design is necessary for all components in the system. A poorly designed cavity is unlikely to be efficient regardless of the tuning system. Raytheon[49] designed and constructed a complete microwave system which was shown to be far superior than previous models which had been adapted from other uses. Specialised chambers, power units and control systems enabled processing to be carried out with minimal problems that had been encountered previously.

Senise[48] designed waveguides and applicators so as to allow multiple low power magnetrons to be connected into a single system. The modular approach is claimed to have several advantages including the ability to use lower cost magnetrons rather than a single more expensive larger powered unit. This approach is used by the University of Florida[3,54] for high temperature processing of materials. A total of 8 magnetrons and mode stirrers are used to provide a maximum of 6.4kW operating power at 2.45GHz.

Schuh et al[6] successfuly used a multimode applicator with a moving wall at 2.45GHz, see figure 10. During processing, one wall of the applicator oscillated creating a statistically average field. Qualitative field distribution measurements indicated that gradients were minimal.

Figure 10, large multimode oven with moving wall. From Schuh et al.[6]



For uniform processing, field uniformity and concentration need to be controlled. Patil et al[55] performed reaction sintering at 2.45GHz with 3kW of power using a single mode applicator. The single mode applicator was chosen because of the need for high field strengths which the material required. Although the material was placed in the field at the point of maximum strength the field uniformity varied enough to form a temperature gradient during processing.

Hendrix and Martin,[56] using low frequency microwaves (915MHz), were able to improve field uniformity by using a waveguide splitter. The field uniformity improved as the microwaves entered the applicator 180° out of polarisation.

Heating rates may be varied by two techniques of power delivery. The magnetron can be run at varying power or at full power in a "chopped" time sequence, where the power cycles on and off. The "chopped" time sequence is used in most domestic models,[47] where typical cycle times are between 10 and 30 seconds. Although this technique is acceptable for domestic use, many industrial applications require variable power to allow for uniform heating, especially if thermal "runaway" is likely.

To limit the possibility of thermal "runaway", heating needs to be kept uniform throughout the material and power must be carefully controlled.[51] Uniform heating can be difficult for a material with low thermal conductivity. The development of a hot spot within the sample is undesirable since conduction to the bulk maybe slow enough that locally the temperature can reach the critical point for the onset of thermal "runaway". Holcombe and Dykes[57] showed that for many ceramic materials to avoid thermal "runaway", the incident power level must be variable. The thermal "runaway" phenomenon highlights the need for accurate control of the microwave energy, where the control of the system is only as accurate as the measurement of the system parameters themselves.

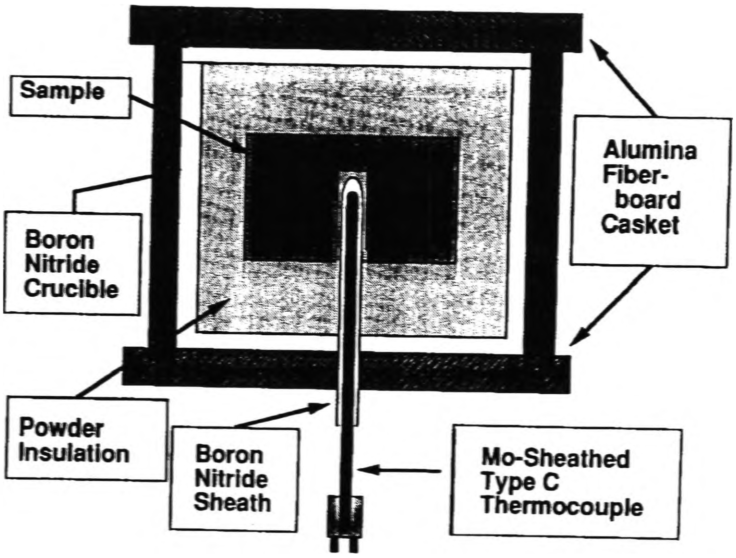
3.5 Microwave Measurements.

A fundamental requirement in the operation of any process system is that of accurate measurement of the system parameters. In microwave applications these include field strength, field uniformity and temperature.

Temperature measurement and control has been widely[4,19,58,59] recognised as the main problem in microwave processing. Although many techniques have been proposed, the two most commonly used are the thermocouple and the infrared optical pyrometer.

A typical thermocouple arrangement for use in a microwave field is shown in figure 11. Shielding of the thermocouple is required to insulate it from the microwave field. The temperature, indicated from an uninsulated thermocouple, will fluctuate wildly as a signal is induced in the thermocouple which varies with the field. Not only is the true temperature masked, but the thermocouple, acting as an antenna, leaks microwaves to the outside environment.

Figure 11, typical thermocouple arrangement. From Tiegs et al.[7]



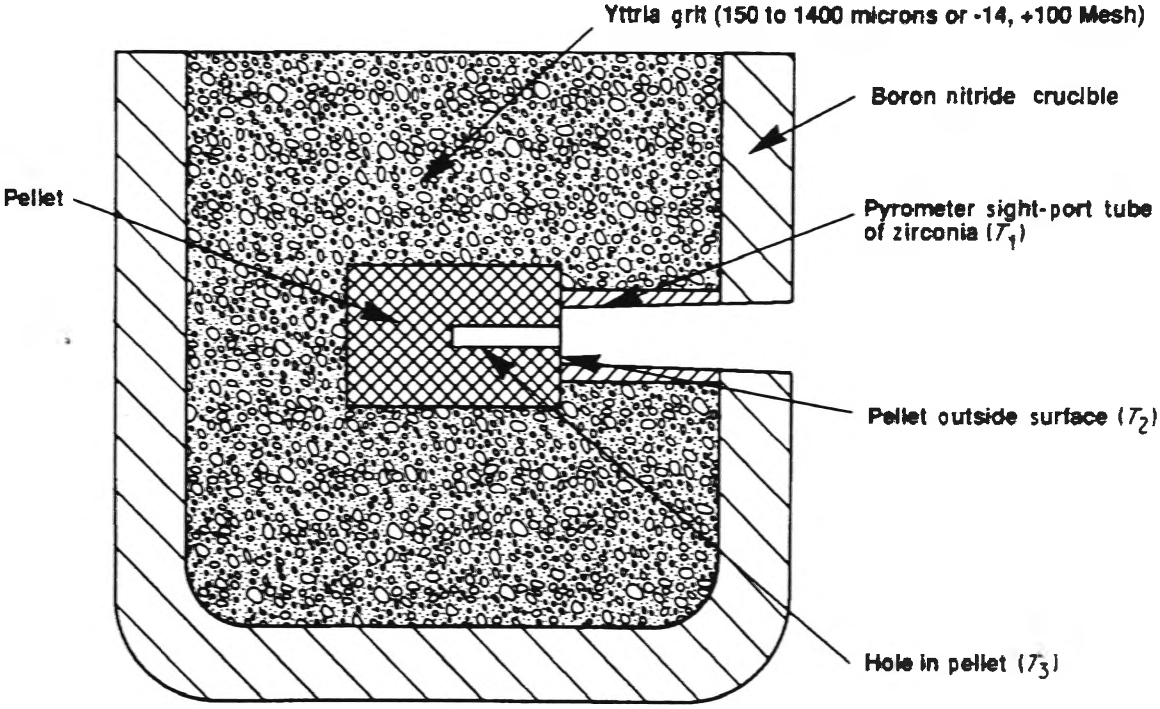
Boron nitride,[7,57,60] molybedunum,[11,61] and platinum[62] are common shielding materials. An alternative approach[19] to the solid sheath for shielding, is to wire wrap the thermocouple. The wire is earthed to the cavity with the pitch kept to less than one quarter of the wavelength.

The difficulty associated with using a thermocouple is that it perturbs the microwave field. The field uniformity is altered sufficiently that as Tinga[4] argues, an accurate local temperature cannot be measured. Also Meek et al[19] found the presence of a thermocouple results in inferior sintering.

Field effects can be avoided by measuring the temperature while the field is off, or by using a non-evasive technique such as an infrared optical pyrometer.

Infrared pyrometers, being non-evasive, avoid the field pertubation and arcing problems that occur with thermocouples. The pyrometer also has the advantage of much higher operating temperatures, with commercial models operating up to 3000°C. However, apart from cost, pyrometers however are not trouble free. Technical consideration has to be taken of the clear optical path required, which is usually provided by means of a port into the cavity. The dimensions of the port are such that it becomes a high impedance path for the microwaves, hence preventing leakage. Another limitation of the infrared pyrometer is that it only measures the surface temperature. Figure 12 shows the pyrometer arrangement used by Holcombe and Dykes.[57]

Figure 12, sample and insulation arrangement for optical pyrometer. From Holcombe and Dykes.[57]



Buchta et al[63] observed that during microwave processing the temperature reading indicated when using a pyrometer (operating at 1.64μm) changed, although the true sample temperature remained constant. It was summised that the difference was due to the emissivity of the sample changing during processing. This highlights an operating limitation of single wavelength pyrometers in that they are sensitive to changing emissivity. In general as a material is heated its emissivity will also change, therefore temperature readings need to be continually updated with the emissivity.

Meek et al[19] compared three temperature measurement techniques: the thermocouple, the infrared pyrometer and d.c resistance. It was shown that neither the pyrometer nor the thermocouple gave accurate temperature readings. Large discrepancies often existed between the two values, figures 13 and 14.

Figure 13, comparison of pyrometer and thermocouple temperature. From Meek et al.[19]

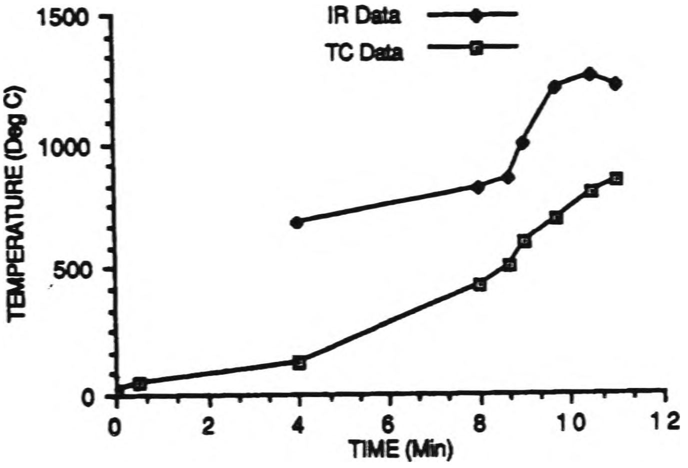
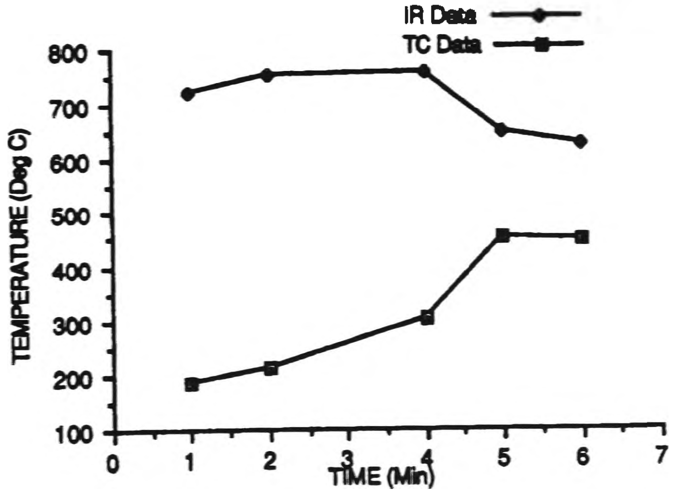


Figure 14, as for figure 13 but at a faster heating rate. From Meek et al.[19]

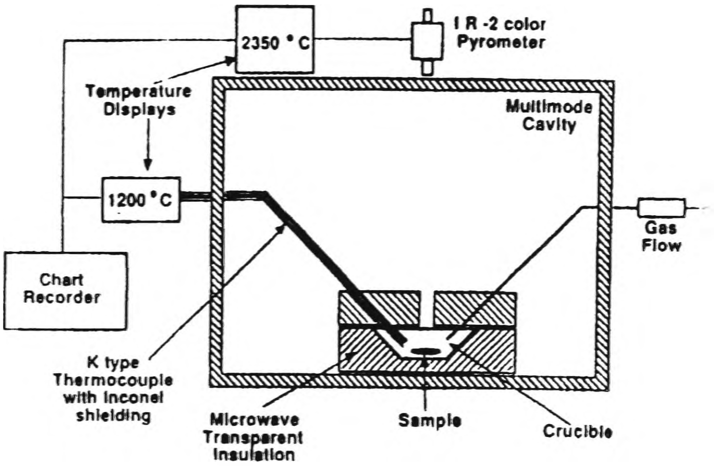


It was concluded that temperature measurement was difficult in microwave applications due to the nature of the process, and that other non-evasive techniques would perhaps be more suitable. Non-evasive techniques for measuring temperatures in microwave heating include d.c resistance,[19] material power absorption,[58] and fibre optic probes.[13]

Fibre optic systems are fast gaining popularity for determing temperature in a mirowave field.[6,13] Being transparent to the microwaves, they exhibit none of the field effect problems of the thermocouple, yet offer the advantage over the infrared pyrometer in that they contact the sample. Cost and fragility in fibre optic systems is the only hinderance in their widespread adoption.

Often, due to the inherent limitations of the individual techniques, temperature is measured using two different systems, commonly a thermocouple and a pyrometer,[19,54] as shown in figure 15.

Figure 15, dual temperature measurement arrangement. From Clark.[3]



Temperature can be predicted based on the power the workload absorbs, (Appendix A equation 7).[18] However, this technique depends on there being no spatial temperature distribution and no heat loss from the surface of the sample. Apart from the field strengths, knowledge of the dielectric loss changing with temperature is also required.

An alternative approach to measuring temperature in a microwave field was taken by Bond et al.[64] They constructed a gas thermometer which was connected to a pressure transducer, the bulb size being about 6mm in diameter and 10mm in length. With this arrangement temperatures up to 500K (softening point of Pyrex) were measured. The reproducibility of this system was ±0.5K. Construction of the thermometer in silica raises the upper working limit to levels more suitable for ceramic processing.

Doubt over the accuracy of current temperature measurement techniques raises the question of validity of data interpretation for those phenomena reliant on temperature measurement.

The measurement of power is important as it provides a means by which the efficiency of a system can be checked. Each microwave system is unique in that the power available to the process material is dependant on: the power output of the magnetron, the type and dimensions of the applicator, and the state of tuning of the waveguide.

A terminating power meter is the easiest direct method to measure power.[50] The terminating power meter is most often used with the four port directional coupler to measure the forward and reflected power in a waveguide. A system can only be as precise as the accuracy of its control and measuring equipment. The main sources of error or uncertainty in power measurement arise from: 1) power monitor linearity, 2) flange repeatibility, and 3) drift and noise effects on instrumentation.[50]

Measurement of the absolute temperature rise in a quantity of water can be used to determine the available power, (Appendix A equation 8). This technique is commonly used[47,65,66] due to its shear simplicity. Errors can arise if the volume of water is not sufficiently large enough to absorb all of the microwave energy, (typically 1 to 2 litres of water is used). The equation used to calculate the available power makes no allowance for the change in heat capacity and the dielectric loss as the temperature increases during heating.

Water can also be used to determine the field uniformity within an applicator.[6] The field within an applicator is mapped by measuring the temperature rise in varying positions. This method only gives an indication of the field uniformity since the size and dielectric properties of a material influence the field patterns. A simple indication of the field uniformity can be seen using hydrated silica gel,[67] egg whites and other such materials which change colour on heating. Field gradients are then easily distinguished by varying colors.

The increasing demands made, not only on research but also industrial heating applications, has made automation an integral part of the process system. Arnold's[50] review of the practicalities of automation design for microwave systems, highlights two main advantages over manual measurement and control systems. Automation has facilitated the successful adoption of new measurement techniques. Faster data acquisition, linked with complex computer routines providing statistical processing, allow for more accurate measurement and control of microwave processing. Apart from the technical advantages automation can provide obvious economic benefits. The ease and adaptability of automating a system is often cited as one of the main advantages for using microwave energy as a source of heating.

3.6 Microwave Heating Applications.

Microwave heating can be broadly categorised into industrial, scientific, medical and domestic applications. Significant interest in possible industrial applications was generated after Raytheon had developed commercial (1951) and domestic (1961) microwave ovens.[68] An extensive review of the history and development of microwave heating applications is given by Osecphuk.[39]

Possible applications for microwave heating are widespread and varied.[37,41,68] Applications have often arisen due to accidental discoveries of material interactions with microwaves.[69,70] Major commercial users include industries from, agriculture, food, chemical, paper and textiles, medical and ceramics, whilst future users may come from the pyrometallurgy, automotive and mineral extraction industries.

Within the ceramics industry microwave heating can be utilised in all facets of production. Microwave technology has been sucessfully adopted on an industrial scale in many ceramic processes, in same cases providing a unique solution. Table 3 lists ceramic applications for microwave heating.

Table 3

Ceramic Applications of Microwave Heating
Drying
Slip casting
Calcination
CVD
Joining
Sintering
Plasma assisted sintering
Material synthesis
Others.

Drying is the oldest industrial application of microwave heating.[59] Microwaves have been found to be very effective for the removal of water from ceramics at low moisture levels,[38,71] the volumetric heating making it very amendable to large objects. The benefits of microwave drying are an improved drying profile, (figure 16), and decreased drying times, (figure 17).

Figure 16, drying profiles for conventional and microwave heating. From Binner.[1]

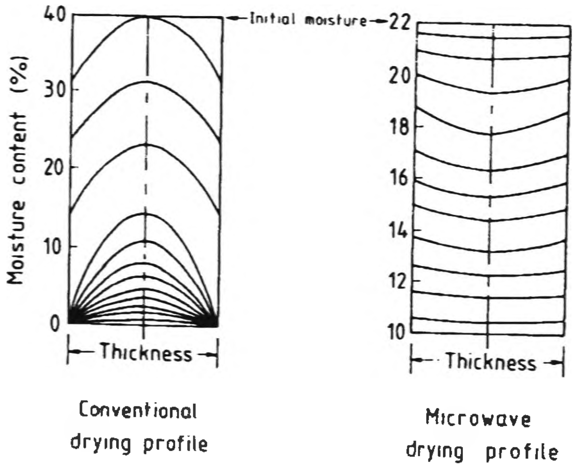
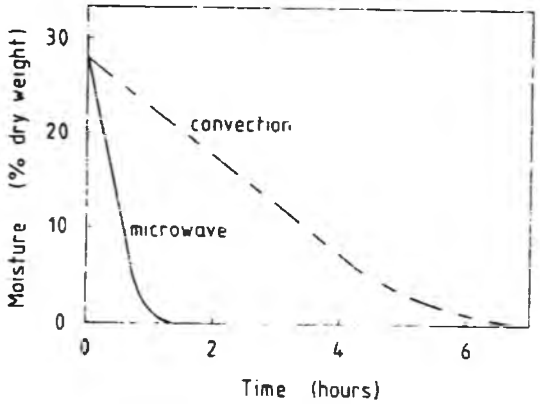
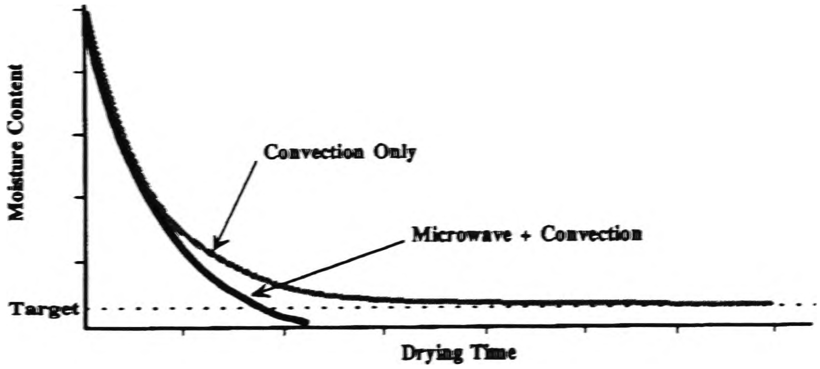


Figure 17, drying rates for conventional and microwave heating. From Binner.[1]



Hendrix and Martin[56] used microwaves combined with conventional heating to study the drying of electrical porcelain insulators. The aim of the trials was to increase the drying rates, (figure 18), without increasing energy costs, or producing case hardened insulators.The microwave system used was a batch oven operating at 915MHz with 6kW of maximum power. The feasibility of using microwaves for drying was shown by a reduction in drying times of 80-90%.

Figure 18, improved drying rates due to microwave heating.
From Hendrix and Martin.[56]

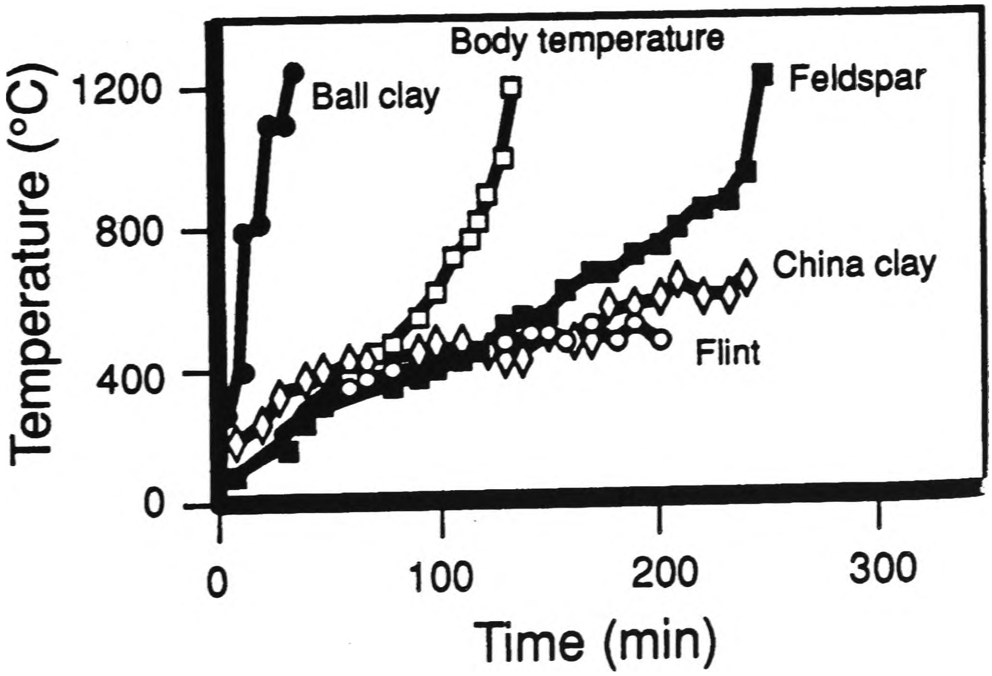


Both traditional and advanced ceramics have been successfully slip cast whilst microwave heated. It has been found universally, that microwaves improve the casting rate. Chabinsky,[68] working with sanitaryware, found that among other advantages the productivity improved by 10-40%. Binner[1] believes that for advanced ceramics this would be a minimum, finding improved casting rates of up to 300% for alumina. Relatively low levels of power are required, since heating rates which are too high cause control of the slip to be lost. Binner[72] found that only 90W of power was required, at 2.45GHz, to heat the alumina slips to 60°C. The degree to which a slip absorbs microwave energy has been found to be dependant not only on the solids content, but on the lossiness of the solids.[72]

Binder burnoff can be accomplished using microwave heating.[38] The binders, used to aid forming of the greenware, heat by either direct coupling to the microwaves for the lossy binders, or by conduction from the host ceramic. Moore and Clark[73] used pure and hybrid microwave heating at 2.45GHz to study the removal of polymethyl methacrylate from alumina compacts. In all cases conventional heating was superior to microwave heating in removing the binder. For microwave heating the efficiency of binder removal was found to be dependant on binder concentration, sample mass and the microwave power level. Work by researchers has shown that it is possible to combine several stages together, i.e. drying, binder burnoff and then firing. Sutton[69] utilised this approach on high alumina castables in which he developed a 2-stage firing schedule; the first stage to remove excess water, the second being the firing stage. The microwave heating schedule was 50% faster and up to 30% lower in energy costs compared to conventional gas fired schedules.

Hamlyn and Bowden,[43] using a 2.45GHz oven, investigated microwave heating of traditional earthenware ceramics. Their work found that earthenware ceramics could be successfully heated, with some constituent minerals being more receptive to irradiation than others, figure 19.

Figure 19, microwave heating of earthenware ceramics. From Hamlyn and Bowden.[43]



Drying, casting acceleration and binder burnoff are low temperature applications of microwaves. One high temperature use of microwave energy is that of material synthesis.

Dalton et al[74] used a 2.45 GHz oven to carry out combustion synthesis reactions, with microwaves igniting the process. They found that they could synthesise carbides, borides, silicates, nitrides, cermets and ceramic composites. By controlling the microwaves the combustion wavefront propagation was able to be controlled during synthesis. Higher temperatures allowed complete combustion, greater coupling and better densification. Substantial reduction in synthesis times can also be achieved by using microwaves, (Table 4).[72] Other high temperature processes that utilise microwaves are calcining, firing, melting and sintering.[38]

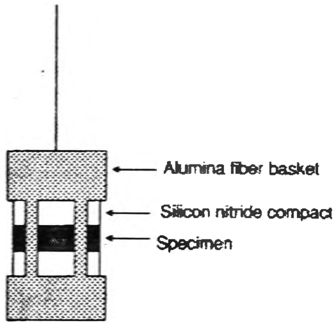
Table 4

Comparison of Material Synthesis Times

product	starting materials	microwave synthesis (mins)	conventional synthesis (hours)
KVO_3	K_2CO_3, V_2O_5	7	12
$CuFe_2O_4$	CuO, Fe_2O_3	30	23
$BaWO_4$	BaO, WO_3	30	2
$La_{1.85}Sr_{0.15}CuO_4$	La_2O_3,$SrCO_3$, CuO	35	12
$YBa_2Cu_3O_{7-X}$	Y_2O_3,$Ba(NO_3)_2$,CuO	70	24

Reaction bonded silicon nitride was produced taking advantage of the thermal gradients generated by microwave heating.[75] Thermal gradients were maximised within the sample by minimising the insulation against the samples outer edge, see figure 20. Higher internal temperatures allowed for larger samples to be fully nitrided compared to conventional heating. The microwave system was also found to have several other advantages. Greater control of the reaction rates was possible, since the sample temperature was very responsive to the power level and the turnaround time between processing samples was relatively quick, due to the volumetric heating nature of microwaves.

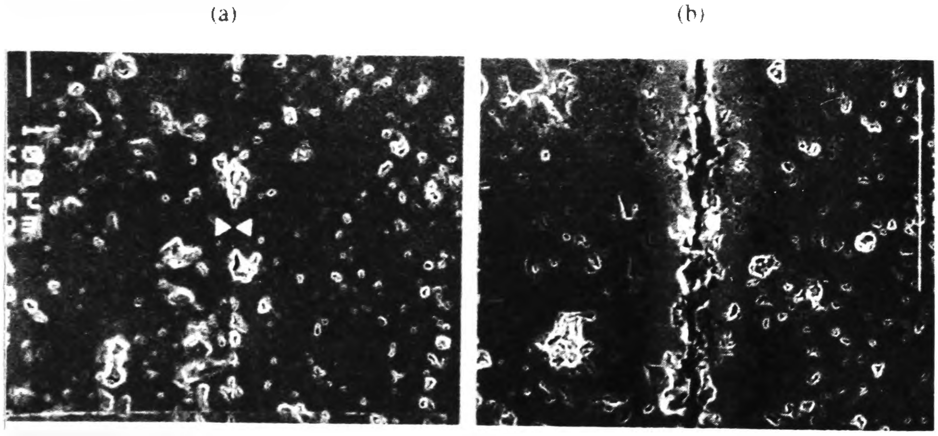
Figure 20, insulation casket design to maximise thermal gradients. From Thomas et al.[75]



Microwave heating has been successfully used to join ceramics in relatively short times. The presence of a glassy phase or interlayer aids the joining process with joint strengths being similar to the bulk material.[8,76,77]

Fukushima et al[77] directly joined low purity alumina in 3 minutes at a pressure of 0.6MPa. High purity alumina was joined by using a lossy interlayer. Al-Assafi and Clark[76]investigated the use a sol-gel as the interlayer in joining of alumina. Joining times were between 15 and 60 minutes using a maximum of 4kW of power, under 0.46MPa of pressure. The presence of the sol-gel was found to improve the join, (figure 21), the sol-gel enabling lower temperatures and shorter joining times to be used. The hardness of the alumina-gel-alumina joint was found to be greater than the bulk, compared to the direct alumina-alumina joint which was similar. The increase in the joint strength was thought to be due to the densification of the joint during heating.

Figure 21, microwave joined alumina showing joint. From Al-Assafi and Clark.[76]



(a) 99.5%-gel-94% alumina joint, (b) 99.5%-94% alumina joint. t=60 min, T=1350°C.

Reaction bonded silicon carbide has been successfully joined using both a single mode cavity and a commercial microwave oven with hybrid heating[8] with joining times of up to 45 minutes. Both joints were barely detectable by SEM. No pressure was used nor was there an interlayer material, however, joining was aided by the silicon which bled out of the bulk during heating.

Plovnick and Kiggans[62] used microwave energy to thermally etch TZP samples. Etching was carried out at 1200°C (100°C below their microwave sintering temperature) for times between 15 to 60 minutes in a 2.45GHz oven. Plovnick and Kiggans[62] drew the conclusion that microwave etching, was a faster process than conventional thermal etching, and that it provided a greater degree of resolution.

The versatility of microwave energy was demonstrated by Harrison et al.[16] Microwave processing was found to be feasible for all processing stages of PZT and PLZT including sintering.

3.7 Microwave Sintering of Ceramics.

Microwave sintering of ceramics is not a straightforward process. To achieve successful sintering numerous systems and heating techniques have been adopted. The complexity of the thermodynamics and electromagnetics has seen a qualitative approach taken to most developments.[4]

System designs vary considerably, with different approaches taken to the applicator, the frequency and power levels, all attempting to produce fast uniform heating. Uniform heating for sintering is difficult to attain. Tinga[4] argues that it "does not mean that microwaves are not suited to the process, but they are possibly being used in an insufficiently controlled heating environment."

Sintering of ceramics using microwave energy provides advantages that may not be available with conventional techniques (Table 5). Both traditional and modern engineering ceramics have been investigated for their potential to be sintered using microwave energy including alumina, titanium diboride, zirconia and composites such as alumina-silicon carbide and alumina-zirconia.

Microwave sintering of ceramics has disadvantages similar to other microwave heating applications. The microwave-matter interactions are not only materials dependant but also process dependant. Process/material parameters that have been found to effect sintering include insulation, workload:cavity ratio, field uniformity, dielectric properties (such as lossiness), and heating phenomena (such as thermal runaway and inverse temperature profiles).

Sutton,[69] whilst investigating the potential of microwaves for drying of high alumina castables, found that heating to high temperatures was possible. Effective loading and heating was found to be dependant on the mass and volume of the samples relative to the oven cavity size. Test work showed the importance of insulation, with full heating only being attained if the load material was surrounded by non-coupling insulation. Uninsulated the temperatures only reached 450°C, whereas with insulation the heating rate was faster and reached 1170°C. The chemical and mechanical properties of the microwave fired samples were similar to that obtained with conventional firing techniques.

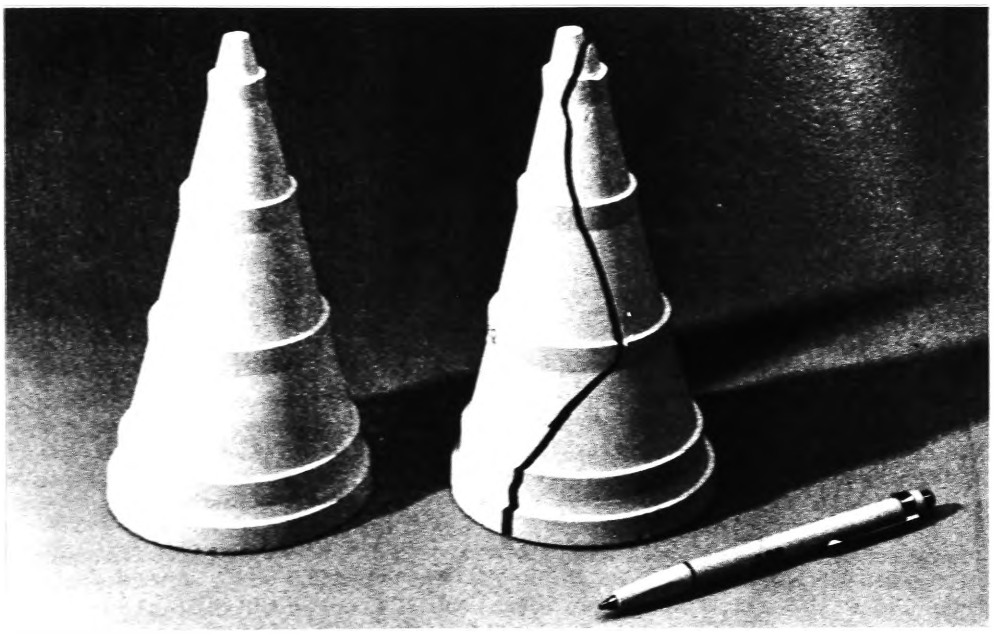
Table 5

Potential Advantages for Ceramic Sintering in a Microwave Field.
Volumeteric Heating
Efficient Energy Transfer
Faster Heating Rates
Greater Control of Microstructure
Superior Properties
Localised Heating
Reduced Processing Times and Temperatures
More Economical
Reduced Cracking and Thermal Stresses
Reduced Contamination

Microwave reaction sintering was used by Patil et al[55] whilst trying to produce zirconia dispersed mullite and $MgAl_2O_4$. A single mode cavity operating in the TM_{012} mode was used at 2.45GHz with a maximum of 3kW of power. Uniform heating was found to be dependant on properly insulating the samples, whilst thermal runaway was avoided by careful control of the input power. $MgAl_2O_4$ was successfully reaction sintered to a density of 96% T.D with a fine microstructure. The zirconia dispersed mullite composite was not completely formed, with unreacted alumina and silica being detected after sintering. Complete mullitization was not achieved possibly due to the insulation and the heating schedule adopted.

Field uniformity has often been shown to be the key to successful sintering. Relatively large alumina pieces were sintered at 2.45GHz by Schuh et al.[6] Crack free pieces with densities up to 98% were attained, however without the uniform field attempts to sinter crack free pieces were unsuccessful. Figure 22 compares alumina parts sintered in uniform and non-uniform fields. The cracked piece was a result of the development of hot spots during heating.

Figure 22, alumina sintered in uniform and nonuniform fields.
From Schuh et al.[6]



Researchers[17] at Oak Ridge National Laboratory overcame the problem of non-uniform fields in oven cavities by changing the ratio of the wavelength to the cavity size from 1:3 to 1:100. This was accomplished by increasing the frequency from 2.45 GHz to 28 GHz.

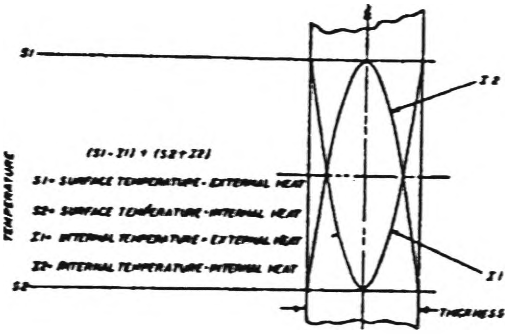
Finer microstructure and higher densities resulted when Tiegs et al[7] sintered silicon nitride at 28GHz compared to 2.45GHz and conventional sintering. Sintering at 2.45GHz was inefficient and produced samples which were often cracked. Greater field uniformity at 28GHz, rather than increased power absorption, was thought to be the origin of the improved sintering.

Cracked samples were also produced by Janney et al[11] when they tried to sinter yttria - partially stabilised zirconia. Cracking was due to thermal runaway in localised regions, producing tensile stresses at a catastrophic level. Thermal runaway was caused by the non-uniform field in the 2.45 GHz oven used, which producied "hot spots" in the zirconia. Zirconia has a low thermal conductivity, hence localised heat is slow to conduct throughout the bulk. Its dielectric nature also changes from a poor to an excellent absorber of microwaves over a small temperature range. Localised regions have loss tangents which increase rapidly, producing thermal runaway. Figure 23 shows the difference between zirconia samples sintered directly in the 2.45GHz oven and the more uniform field of a 28GHz oven.

Figure 23, Y-PSZ sintered at 2.45GHz and 28GHz. From Janney et al.[11]

A different approach to improve field uniformity is by the use of susceptors. Silicon carbide rod susceptors were used by Kimrey et al[60] to overcome the poor field uniformity whilst processing at 2.45GHz. Using 2.6kW of power in an untuned cavity the lossy rods lowered the Q factor of the cavity, resulting in a more uniform field and providing hybrid heating conditions.

Figure 24, effect of hybrid heating on temperature profile. From Tinga.[4]



The hybrid heating approach is one means to overcome the problem of low dielectric loss that many ceramics have at low temperatures.[11,12] A ceramic with a low dielectric loss will not heat up efficiently unaided, if at all, as it cannot sufficiently couple with the microwave energy. Several different approaches can be taken to overcome the low dielectric loss of ceramics, the three most common techniques involve;

1) coupling agents (doping)

2) susceptors (hybrid heating)

3) increased microwave frequency.

Dopants are a common means to increase and control the absorption of microwave energy by low loss ceramics.[59] The degree of doping needs to be finely balanced between that of increasing the dielectric loss and producing sintered samples with inferior property values. It is widely recognised[5] that the type and level of dopant needs to be chosen so as to be not detrimental to the final sintered product.

Meek et al[78] studied sintering of several ceramic materials (e.g alumina, zirconia and yttria) with varying dopants. The dopant was used as a susceptor to aid heating and as a glassy second phase to act as a crack inhibitor. Heating was observed to occur in three stages. Initially the insulation heated up followed by heating of the dopant. When the bulk heated up sufficiently, due to conduction, it began to couple to the microwave energy itself.

Sintering produced numerous samples with cracks, either due to thermal shock or poor pressing. Properties of the microwave sintered samples were comparable to those produced by conventional sintering. It was concluded that doping provided a means to enhancing or accelarating sintering of ceramics using microwave energy.

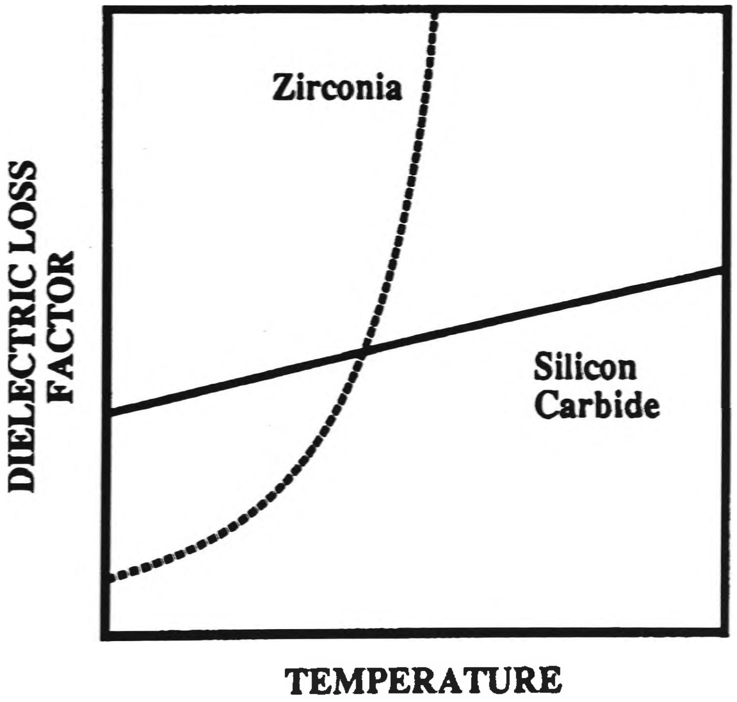
Some ceramics lend themselves to the doping process more readily than others. Silicon nitride, a good example of a ceramic suited to doping, requires liquid phase techniques for sintering and has a low dielectric loss. Tiegs et al[7] investigated the effect of dopants whilst studying microwave sintering of silicon nitride. The dopant concentration was found to effect both the coupling efficiency and the sintered density. In general, as the dopant level increased so too did coupling efficiency and density. More efficient coupling was also shown to improve heating uniformity, reducing the likelihood of cracking. Lossy secondary particles were also used, producing similar results to the dopants. Heating was more uniform and higher sintered densities were achieved.

Many ceramic materials which have a low dielectric loss at low temperatures become quite susceptable as temperatures increase. Hybrid heating techniques rely on this typical dielectric behaviour, by providing external heating to the material until it is sufficiently hot enough to couple to the microwave energy.

Susceptors are one form of hybrid heating in which a lossy material is used to absorb the microwave energy to provide the initial heating. The susceptor acts as a "pump" to allow coupling at higher temperatures to occur. The advantages of the susceptor technique is that it reduces the inverse temperature profile that is associated with microwave heating. The energy the susceptors initially absorb however, means that it is not as efficient a process as pure microwave heating.

Cracking problems were overcome by Janney et al[11] when they adopted a hybrid heating approach to sintering. Silicon carbide rods were used as susceptors arranged as a ‘picket fence’ around the zirconia sample. Both zirconia and susceptors were then surrounded by insulation. Figure 25 depicts the change in the loss factor as temperature increases for silicon carbide and zirconia. Using low heating rates crack free samples were then successfully sintered to greater then 99%TD. Comparing microwave to conventional sintering they found that the microwaves produced samples with a smaller grain size.

Figure 25, schematic diagram of dielectric loss factors.From Janney et al.[11]



Wilson and Kunz[12] used silicon carbide susceptors in the sintering of Y-PSZ. The hybrid heating technique enabled samples to be successfully sintered to high densities (up to 98% T.D) in short times. Similar structural and mechanical properties to conventionally sintered samples were found, however, if the heating rate was too high badly cracked samples were produced. It was also found that as the zirconia began to couple efficiently and its temperature rose, the susceptor temperature began to fall. The microwaves preferentially couple to the material with the higher dielectric loss factor.

The low dielectric loss problem was also overcome by Kimrey et al[60] in their comparative study, not only by using susceptors but by increasing the frequency of the microwaves. Alumina with 10 to 70% zirconia was successfully microwave sintered, using lower (sintering) temperatures, (figure 26), and producing finer grain structures compared to conventional sintering. Silicon carbide rod susceptors were used at 2.45GHz, while sintering at 28GHz was carried out with 200kW of power, in an untuned cavity. Microstructurally, there was little difference between 2.45GHz and 28GHz, however, the sintering temperatures were lowest for 28GHz, this is shown in figure 27.

Figure 26, density of sintered alumina. From Kimrey et al.[60]

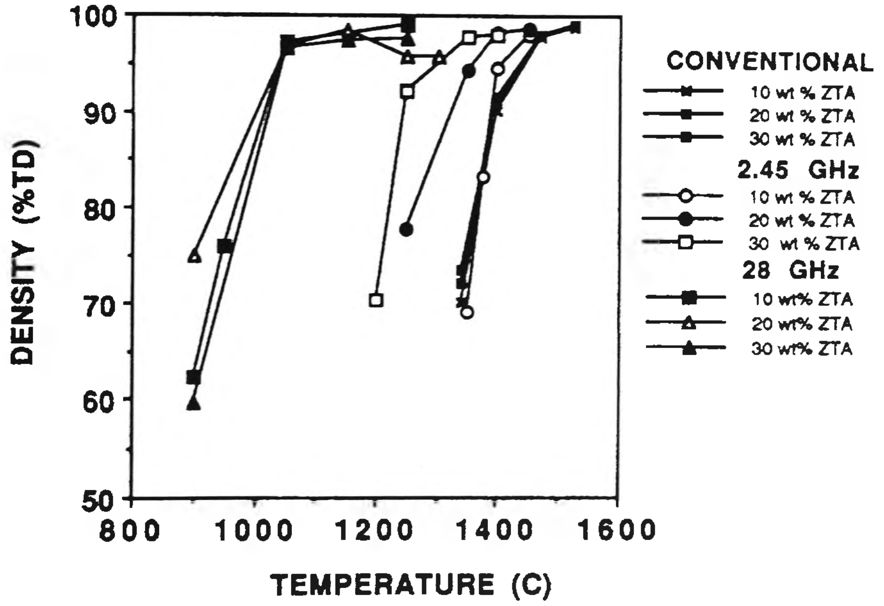
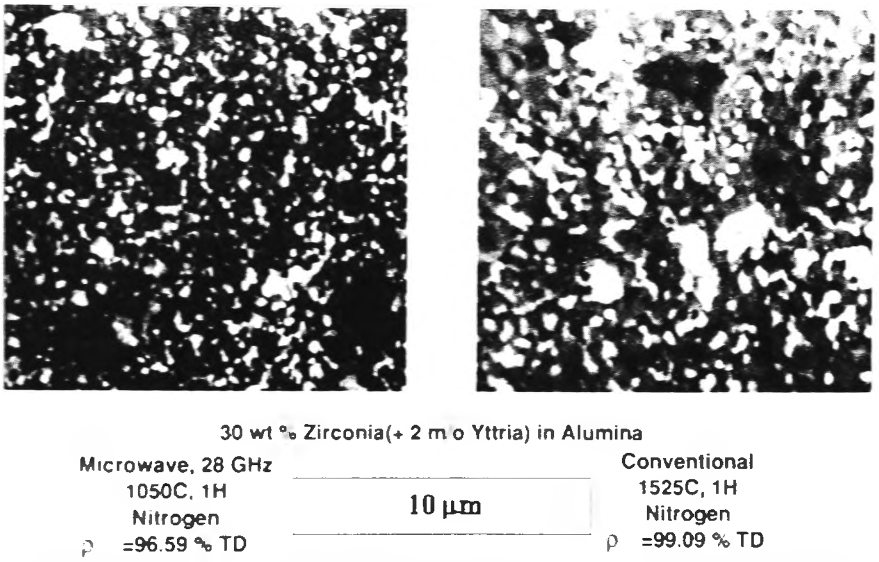


Figure 27, microstructure of ZTA. From Kimrey et al.[60]



Increasing the frequency allows for more energy to be deposited. However, as frequency increases the penetration depth decreases. Increasing the frequency also increases the dielectric loss and the field uniformity. Sintering studies on alumina showed the advantage of increasing the frequency, from 2.45GHz to 28GHz. At 2.45 GHz the alumina could not be sintered,[17] however, it showed an increase of 1000 times in absorption of microwaves between 1 and 100 GHz. Theoretical densities approaching 100% were obtained for sintering times of 1 hour at 28GHz, with equivalent properties to alumina that had been hot pressed.

An alternative method of sintering low loss ceramics is to concentrate the microwave field. Sintering is carried out in a single mode cavity at a point where the field is at a maximum. Dewan et al[79] describe a TM_{010} single mode cavity used successfully to sinter α-alumina and alumina-titanium carbide at 2.45GHz with 1kW of power. Sapphire tubes were used to alter the Q factor of the cavity, achieving a tuning range of 145MHz. Uniform heating zones were approximately 2.5cm in length allowing heating rates of 20°C/sec to be achieved.

A single mode cavity was also successfully used to sinter Y-TZP and Y-TZP/Al_2O_3 composites.[15] With careful control of the system, uniform heating rates and stable sintering temperatures were attained. Theoretical densities of greater than 98% were achieved for both Y-TZP and 20 vol%Al_2O_3/Y-TZP. The Y-TZP content was found to effect not only the heating rates but also the power requirements themselves. Increasing the Y-TZP content resulted in faster heating rates, due to its higher dielectric loss. Also, greater power was required during holding periods because of its lower thermal conductivity. Sintering of Y-TZP at 1450°C resulted in grain sizes varying between 0.2µm (edge) and 0.4µm (centre) due to an inverse temperature profile. Park and Meek[80] sintered zirconia-alumina composites to 100%T.D in 10 minutes at 1500°C. The sintered composite had small regular grains. Uniform heating was indicated by the grain homogeniety and the absence of the tetragonal to martensitic transformation.

Although numerous composites have been successfully microwave sintered,[81] differences in dielectric properties between the matrix and the secondary particles have to be considered. Often one phase will tend to retard the sintering process due to its lower dielectric properties[15] or its restrictive physical nature. Sintering of alumina-silicon carbide at 2.45GHz and 60GHz produced similar microstructures. However, a density of only 70% T.D could be achieved using silicon carbide whiskers due to network formation.[82] The use of silicon carbide platelets resulted in a higher density of 94% T.D, achieved in under 20 minutes. Differences in particle size have been shown to effect sintering in composites.[15] However, De´ et al,[54] studying the effect of particle size on microwave sintering of alumina, concluded the effect of particle size in microwave sintering to be analagous to that of conventional sintering.

It is argued that microwave energy can lead to enhanced or accelerated sintering compared to conventional techniques. The mechanisms that are responsible for the enhanced sintering, observed experimentally in alumina, zirconia and other oxide ceramics, are not fully understood.[18] Literature on microwave processing covers a broad spectrum of information on this topic. It ranges from authors postulating that experimental observations were likely to be due to microwave enhancement (with little or no other detail), to papers dealing solely with the phenomenon in more depth.

Harrison et al[16] found that microwave sintering did not clearly enhance the sintered properties of PZT and PLZT. Accelerated sintering is however implied. The microwave sintered samples had the highest density (98% T.D for PZT) and the smallest grain size, yet the shortest soak time and fastest heating rate (115°C/min). Sintering times were reduced from ~31.4 hours for conventional, to ~22 minutes for microwave sintering. The piezoelectric and mechanical properties were found to be dependant on grain size rather than processing technique.

Enhanced diffusion was used by Tiegs et al[7] to explain an increase in density, whilst microwave sintering silicon nitride. However, a decrease in sintering temperatures was not distinguished, it was summised that the absence of reduced sintering temperatures was due to the fact that the liquid phase was still required for sintering.

Less time and energy with an apparent difference in seal composition and bonding, was found by Meek and Blake[83] whilst investigating microwave sintering of ceramic-ceramic seals. From their comparative study they postulated that: i) microwave energy coupled differently and, ii) kinetics other than those in conventional sintering possibly operate.

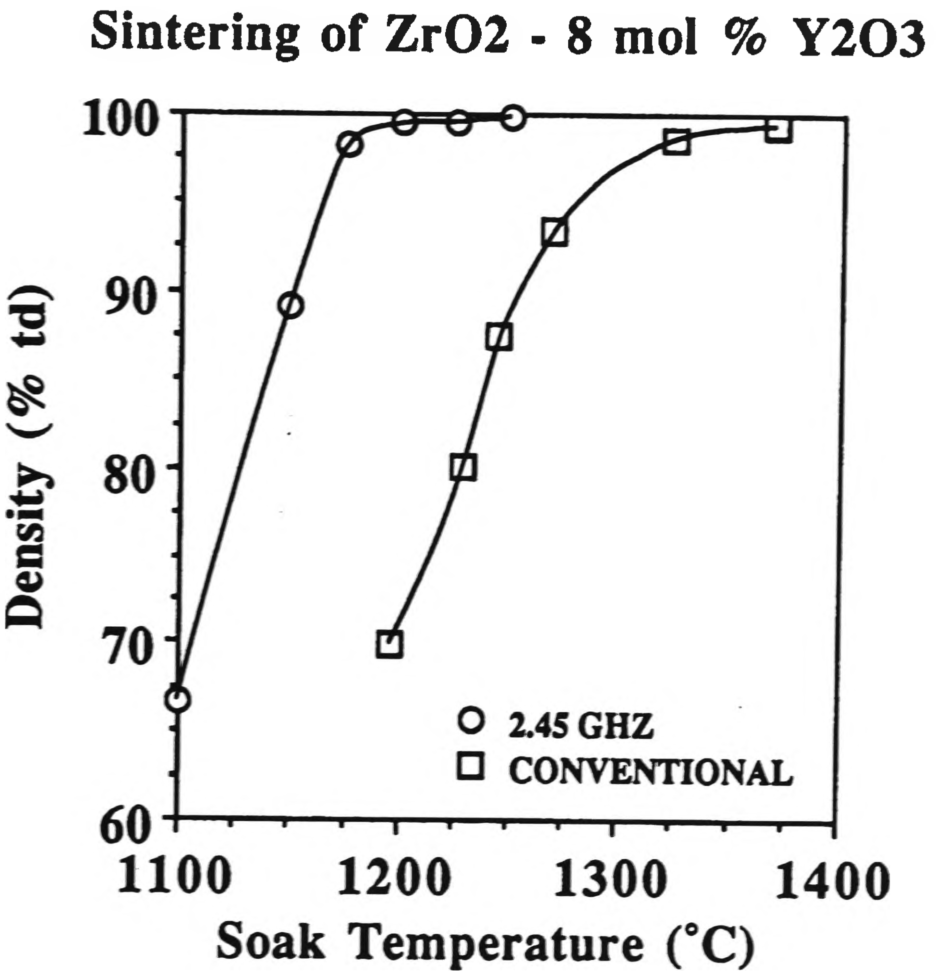
De´ et al[54] attributed the microstructure, from microwave sintered alumina studied, to be due to faster sintering mechanisms and enhanced densification. The microstructure of the microwave sintered samples were more uniform and homogenous than that produced by conventional sintering.

Meek[84] has suggested a model for the sintering of a dielectric in a microwave field, which describes the heating for a porous monolithic ceramic body. The model proposes that heating will occur uniformly throughout the body, provided porosity is evenly distributed. Uniform sintering is attained by the electromagnetic field preferentially coupling to those less dense regions. Not only is the power density greater in these regions, but the penetration depth is also greater. Energy therefore reaches and transfers to those regions which need it most to maintain uniform sintering. This model suggests that the pores and surface of the particles will be at higher temperatures. Evidence for this theory being the sole explanation of the enhanced sintering observed is inconclusive.[5] Johnson[85] argues that the temperature differential, between grain boundaries and a localised average, is minimal. Studying sapphires using heat flow calculations, he concluded that enhanced sintering due to microwave heating cannot be due to hot grain boundaries alone and that other mechanisms are required for an explanation.

Janney et al,[11] when comparing conventional to microwave heating observed enhanced sintering of zirconia, they summised the "microwave effect" was possibly be due to a lower activation energy for sintering. Figure 28 shows the comparison between microwave and conventional sintering.

Similarly, Samuels and Brandon[13] suggest that enhanced sintering is possibly due a reduction in the activation energy for grain boundary diffusion. In a comparative study of alumina-zirconia composites, enhanced sintering was observed in all trials, however, it was most prevalent at the lower sintering temperatures. The composition of the samples was found to effect the degree of enhancement, in that the greater the zirconia content, the greater the difference in sintering temperatures. This was argued to be because of zirconia having a higher dielectric loss compared to alumina, rather than the zirconia acting purely as a sintering aid.

Figure 28, comparison of conventional and microwave sintered zirconia. From Janney et al.[11]



Enhanced diffusion was observed,by Fathi et al,[86] in β-alumina in the presence of a microwave field. Enhancement was argued to be dependant on the bond strength of the ions, in that, the weaker the bonds the greater the effect induced by the microwave field. The bond strength of the mobile ions in β-alumina being relatively weak, allowing easy coupling to the microwaves.

Janney et al,[61] using a 28GHz oven, were able to determine that the activation energy for grain growth in alumina was lower using microwaves, relative to conventional techniques. In both cases the grain-growth kinetics were cubic, although the microwaves accelerate the kinetics to such an extent that at 1500°C they were nearly two orders of magnitude higher. The decrease in grain-growth activation energy (590 to 480kJ/mole) was less than that found previously by them for the activation energy for sintering (575kJ/mole to 160kJ/mole). Janney and Kimrey[14] believe that the mechanisms may be due to electric field effects on the crystal lattice or preferential coupling to point defects. Figures 29 and 30 show the decrease in activation energy due to the presence of the microwave field.

The often observed "microwave effect" may also be related to the frequency. Comparitive studies[60] indicate that as frequency increases so too does the microwave effect. However, greater field uniformity, power concentration from high frequencies and masking effects from hybrid heating at lower frequencies, can confuse the interpretation. Determining the exact origins and mechanisms of the enhancement is not straightforward.

Figure 29, activation energy for grain growth. From Janney et al.[61]

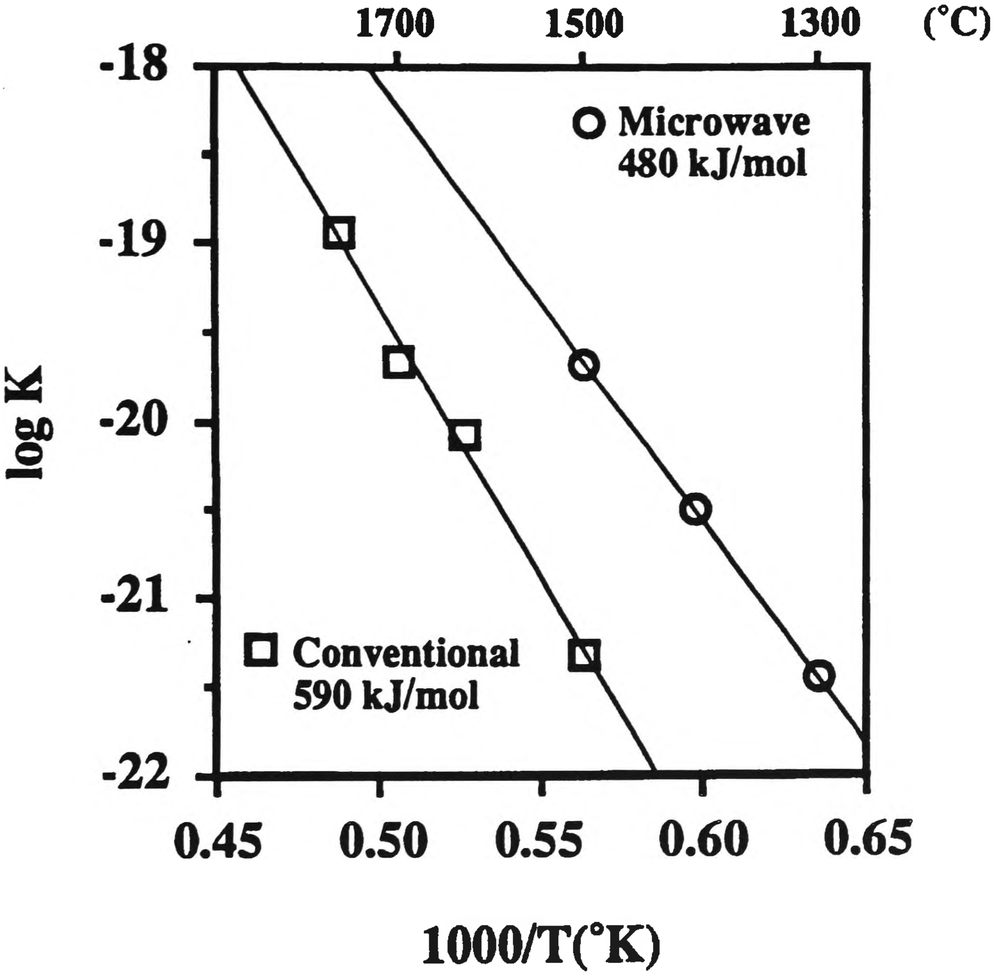
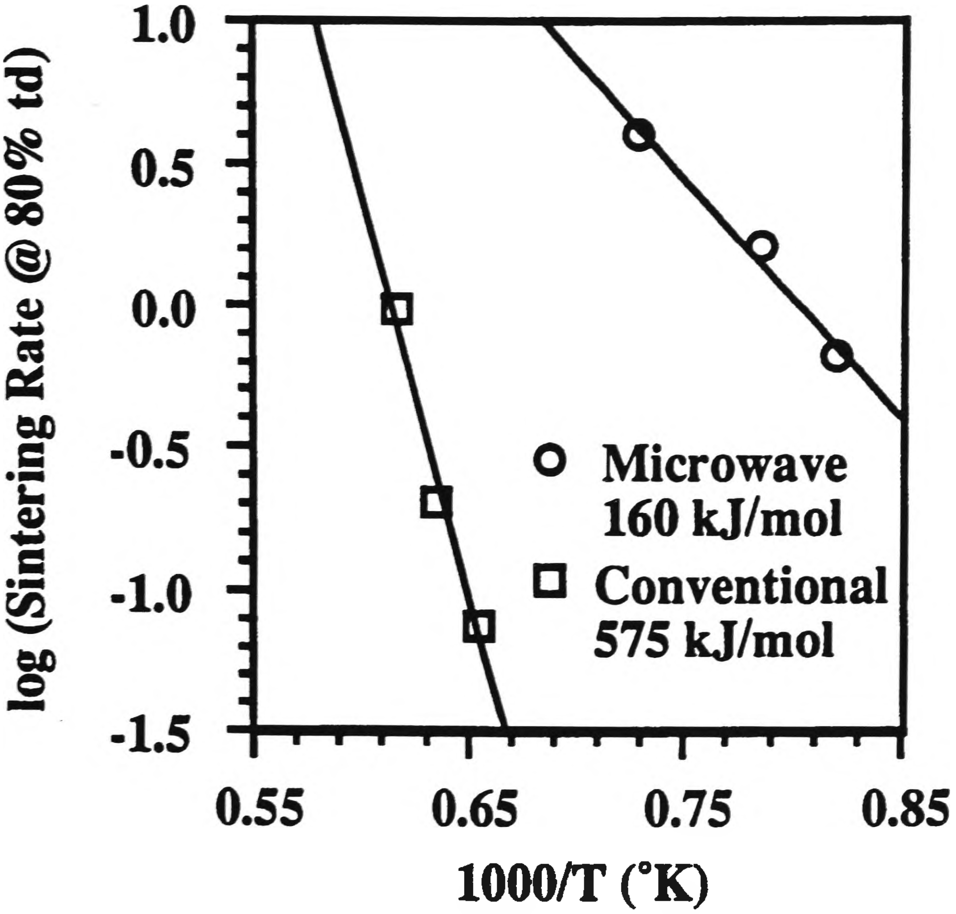


Figure 30, activation energy for sintering. From Janney et al.[61]



3.8 Economics of Microwave Applications.

The development of microwave applications has been directed by numerous factors, besides technical considerations.[39] Binner[1] realistically states that "ultimately , the deciding factor for microwave processing will be dependant upon economics."

Osepchuk's[39] review, with hindsight, highlights the over optimistic predictions of previous authors on the potential growth for microwave heating applications. The largest sector of users is, and has been for considerable years, the domestic market.

Domestic ovens created the initial driving force for studying industrial applications of microwave heating. In the 1970's,[87,88] due to the oil crisis, energy conservation was driving microwave technology development. Saddler's[88] study highlighted the postion of microwaves as a means of achieving more efficient use of energy in Australia. Out of the 48 profiles of efficient energy inovations, only 1 involved microwave technology.

However, the driving force for adoption of microwave technology may now be shifting. Gibbons and Blair[89] now see the motivation as being production of more competitive products in the market place and the lowering of environmental impacts, rather than energy supply driven as previously. This notion is upheld by a review of recent literature on microwave applications. In general, research appears motivated by non-economic reasons. Authors are stating new or improved products and greater process control as principle reasons for research.[2,3]

Although microwave technology appears to offer economic advantages, industrial growth has fallen short of expectations. The difficulty of growth forecasting in this industry is widely recognised.[1,39] Similarly the origins for this poor growth are widely known and accepted.[1,2,3,39,90] Growth is hindered by a scarcity of relevant support data, lack of commercial exploitation, limited frequency allocations, limited knowledge of material/microwave interactions and a perceived risk problem. Osepchuk's[39] review addresses the economic and risk problems, highlighting that many potentially successful microwave heating applications exist merely awaiting a suitable economic climate or improved design. Although commenting upon health risks Jauchem's[91] views could equally be said to be relevant to economics. Jauchem argues that many reports are not balanced and that many claims about the risks of microwaves were speculative. Microwave technology in general is considered to be a risk investment.[92]

Das and Curlee[93] raise the question as to the exact cost saving of using microwave heating. They conclude the final feasibility of microwave systems to be dependant on non-energy factors, such as lower labour costs and improved product quality.

The economic advantages of microwave heating have been found to include:

1) lower energy costs
2) reduced process floor space requirements
3) reduced process times
4) lower inventory
5) lower total production costs

The main disadvantage with microwave heating is that the initial capital costs are high, especially if the system needs to be custom designed.[4] Often the best approach is to implement microwave technology with a total system design.[92]

Energy savings have been quoted as being in the range of 50%[68] to 95%.[16] Difficulties arise in trying to compare figures cited in literature. Conflicting views are possibly due to assumptions which need to be made.[1,59] Microwave processing in itself is less energy intensive, however, the overall conversion of fossil fuel to microwave energy is inefficient.[2,68] Some figures are based on laboratory scale projects, and may only include direct energy savings, whilst others are for commercial units in full production. Eves and Synder[53] argue that because of the wide variation, especially within laboratory processing, the microwave ovens and test material need to be systematically characterised to allow for proper comparison.

Chapter 4 Experimental Method.

4.1 Hybrid Heating.

The dielectric properties of zirconia at 2.45GHz dictate that the best method of microwave heating is either with a single mode cavity, where the field is well defined and concentrated,[15] or by hybrid heating.[11]

A hybrid heating approach was developed in an earlier project[20,21] which was used to successfully heat zirconia. This technique has been used as the heating method for several other following projects, including those involving the author.[22,23] The technique developed involves using a microwave receptive material, (a susceptor), to provide external heating to the zirconia.

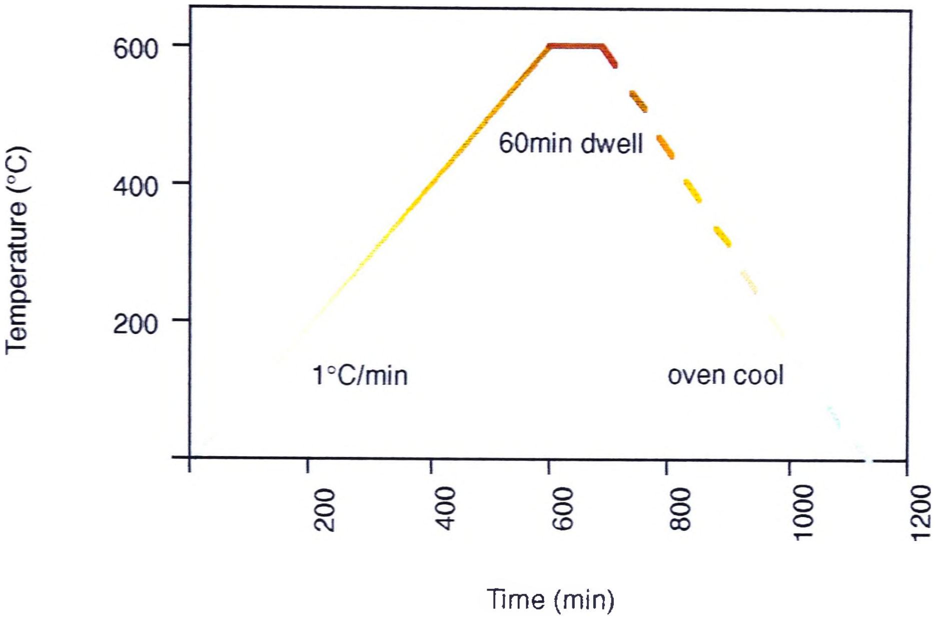
The susceptors consisted of 93% alumina, -325 mesh, and 7% graphite, mixed and lightly pressed into rods. The weight and diameter of the susceptors varied throughout the trials, but were initially 25g and 1" in diameter. The susceptors were used to surround the zirconia samples and then encased in a suitable insulation. This was similar to the "picket fence" arrangement of susceptors used at Oak Ridge National Laboratory.[11]

4.2 Preparation of Zirconia Samples.

Green zirconia samples were prepared from a spray dried 3 mol% yttria partially stabilised zirconia powder, SY-P Ultra 5.2 Z-Tech ICI. SY-P Ultra 5.2 is a co-precipitated spray dried powder, which contains organic binders. Typical characteristics of the "as received" powder are given in Appendix B.

Powder consolidation was carried out by dry uniaxial pressing. The powder was pressed into discs of 25.4mm (1") diameter and approximately 1.9mm in thickness at a pressure of 158MPa, with a dwell time of 20 seconds. The bulk density of the green zirconia samples was then determined by direct measurement, AS 1774.5-1989, prior to sintering.

Figure 31, heating schedule for binder burnout.



4.3 Microwave Equipment Description.

4.3.1 Commercial Microwave Oven.

A commercial microwave oven (Sharp Model R-2370), shown in figure 32, was used in both unmodified and modified states. The oven had a total output of 1300W, achieved with two magnetrons operating simultaneously. Power was fed down separate stainless steel waveguides (80mm x 40mm) into the top of the cavity, as shown in figure 33. The cavity was stainless steel and has internal dimensions of 35cm x 22cm x 37cm.

Figure 32, modified 1.3kW commercial microwave oven.

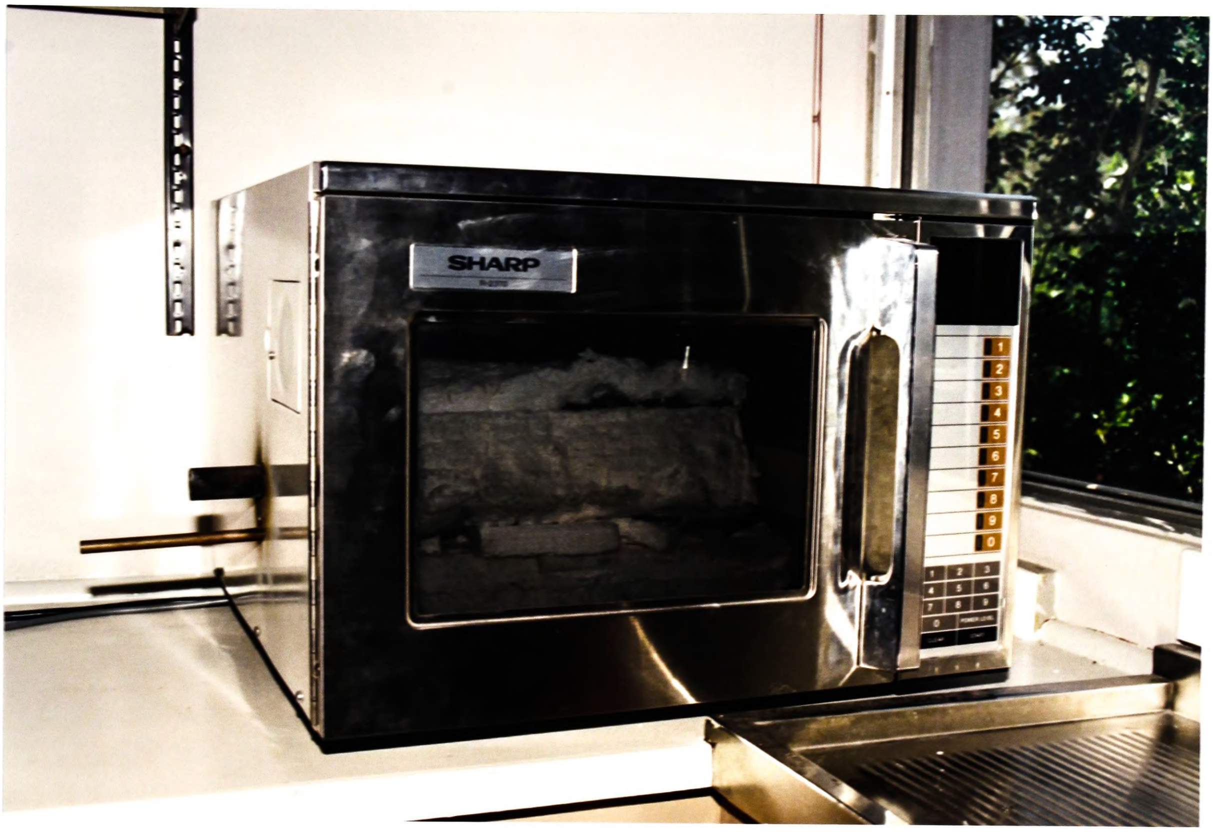
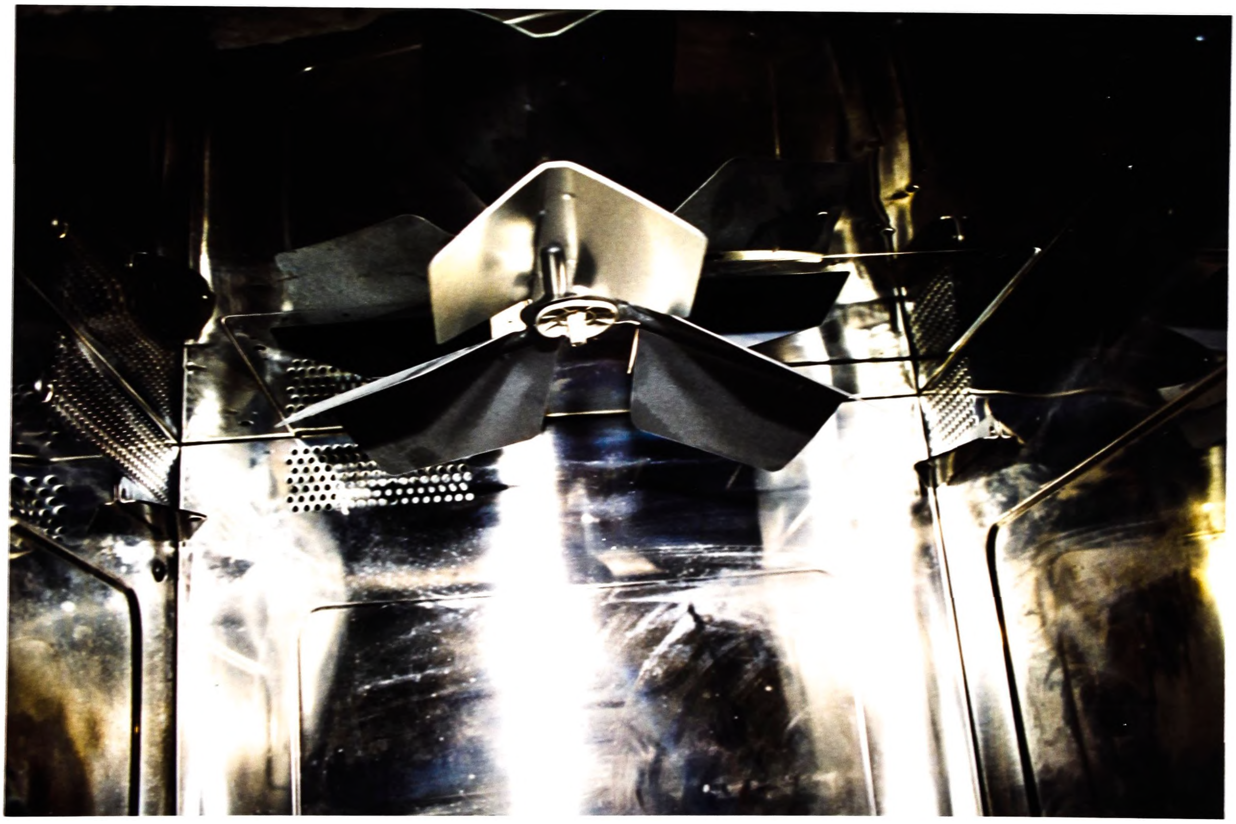


Figure 33, wave guides and mode stirrer in commercial oven.



A single mode stirrer lays beneath both waveguide ports to perturb the microwave field.

Power and time cycles were adjusted via a control pad on the front of the oven. Power levels operated using a chopped time cycle, in 10% increments which gave either full power or no power.

The only modification made to the oven was the installation of two ports. A 9.5mm (3/8") diameter copper tube was installed to allow for insertion of a thermocouple into the cavity whilst a second copper tube, 25.4mm (1") diameter, was installed for an optical pyrometer. There were no control loops for either temperature measurement or output power control from the magnetrons.

4.3.2 Custom Built Microwave Unit.

A custom built microwave oven was constructed. The system essentially consists of;

1) power supply
2) magnetron and microwave launcher
3) directional coupler
4) tuner
5) cavity.

Figure 34 depicts the entire assembled system.

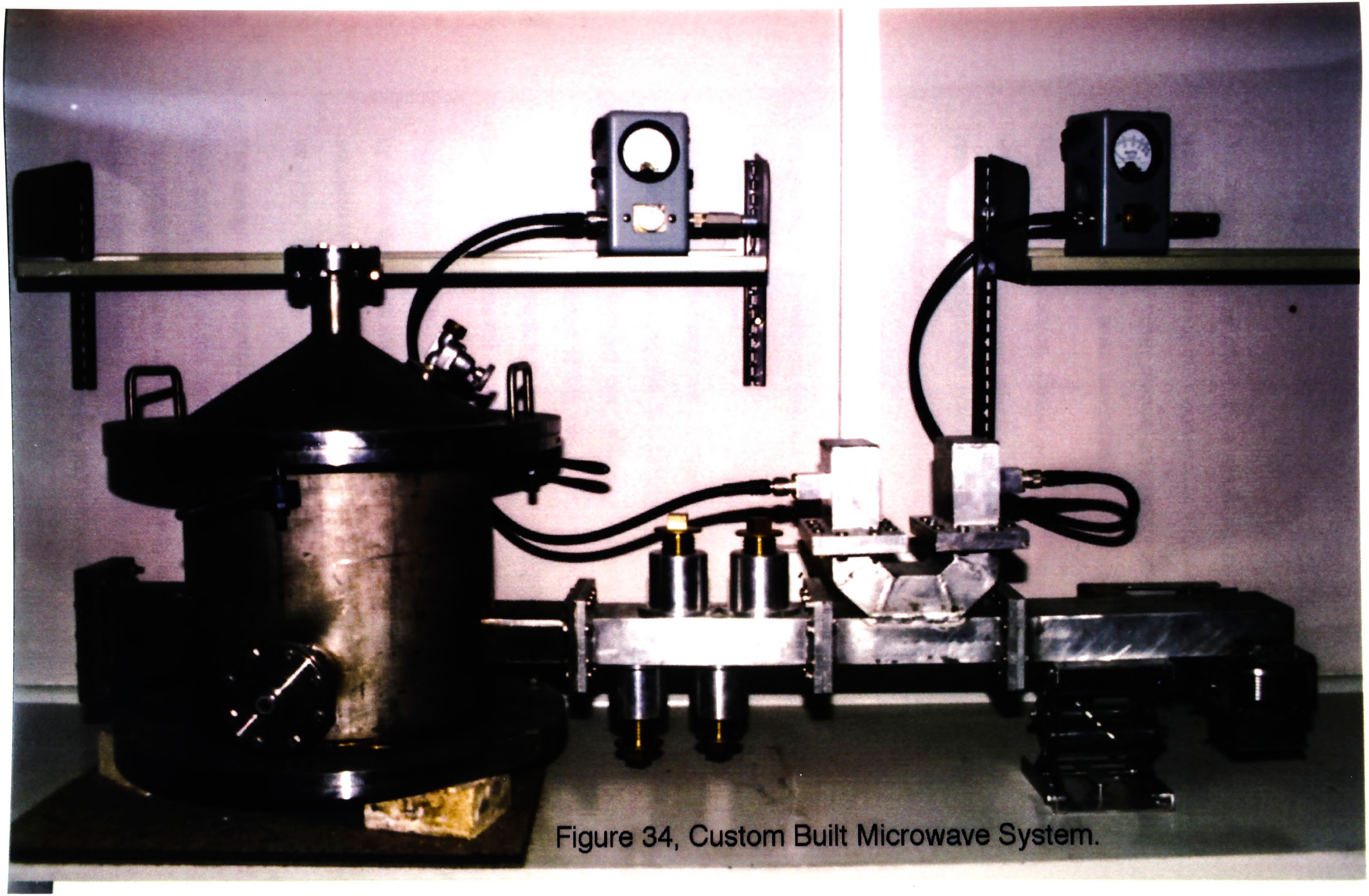


Figure 34, Custom Built Microwave System.

The magnetron was driven by a single phase 240volt power supply, which was capable of driving the magnetron at 1200W. Variable control of the power was achieved by either manual adjustment of a potentiometer, or an input signal, 0 to 5 volts, which overrided the manual control.

The 1.2kW magnetron, (National Electronics), generated the microwaves which were propagated into the initial waveguide section (the microwave launcher). The magnetron operated at a fixed frequency of 2.45GHz, the drift from the magnetron was expected to be minimal, being of the order of ±25MHz. The microwave launcher, as for all other waveguides, was constructed of aluminum. An air blower was positioned at the rear of the magnetron to provide cooling, with the heat being removed from the anode fins.

The microwave launcher was connected to a 4 port directional coupler which is used for measuring the forward and reflected power levels. Microwave energy in both forward and reverse directions was picked up by coaxial transducers situated in the top of the waveguide caps. A coaxial cable connected the transducers to terminating power meters, (Thruline® Bird Electronics), where the relative power levels were indicated.

Resonance matching was executed by a 4 stub tuner. Tuning was achieved by using the brass stubs to perturb the microwave field. The stubs could be adjusted to project into the waveguide to a maximum of 28 mm, and recessed by 4 mm.

The design of the applicator is such that it is relatively insensitive to frequency drift, the Q factor of the cavity varying little with small changes in frequency. This effect diminishes further when the cavity is loaded. The applicator for the custom built oven was a stainless steel multimode cavity. The dimensions of the main body of the cavity were 300 mm in diameter by 316 mm in depth. A conical lid was held down by a quick release system. The internal surface of the cavity and the lid was finished to a high polish to reduce skin effects and to allow for easier cleaning. A copper shim between the flanges of the lid and the main body acted as an R.F choke to prevent microwave leakage.

Four ports in the main body of the cavity and the lid, allowed for viewing, insertion of temperature measurement devices and feeding of microwaves. Microwaves could be fed into the cavity via two rectangular ports, 86 mm x 43 mm. The rectangular ports were orientated at 90° to each other and positioned on opposite sides of the cavity. Preliminary investigations in a similar oven indicated that propagating microwaves through the horizontally orientated rectangular port produced more uniform heating compared to the vertically orientated port. Based on this evidence and advice from personnel in the Microwave Applications Research Centre (Illawarra Technology Corporation), the horizontal port was used for all trial work. The other two circular ports, 38 mm in diameter, were located between the rectangular ports on the main body and on the lid, these being primarily for viewing and temperature measurement. The length of the circular ports (100 mm), is sufficient to inhibit microwave leakage. However, the rectangular ports required a blocking plate bolted to the flange.

The system was not equipped for atmosphere control, such as processing under a vacuum or with an inert gas, nor does the cavity have a mode stirrer.

"*Biggles* - I'm not much for betting, sir, but I'd risk a small wager that what you're going to tell me isn't funny."

Captain W.E.Johns
Biggles in Australia.

Chapter 5 System Development.

5.1 Background.

The initial aim of the research was to develop a microwave system to the point whereby controlled uniform heating could be attained. The objectives were to attain a uniform heating zone, and be able to measure and control temperature up to 1500°C, whilst maintaining safe operating conditions. It was envisaged that this would facilitate an investigation of the microwave effect for the sintering of zirconia using the constant rate heating method.[13,94]

This part of the thesis describes the research and development work which was undertaken to meet the initial objectives.

5.2 Trial of Commercial Microwave Oven.

A commercial microwave oven, described in 4.3.1, was used for initial trials to establish the feasibility of temperature measurement and control. The oven had been used successfully for earlier work,[22,23] however, temperature measurement and control were very limited. Heating rates were controlled by altering the "power" levels in 10% increments. It was ascertained that, although it would have been possible to install a temperature to power control loop in the commercial oven, it was more feasible to construct a purpose built oven with a dedicated power supply. Simultaneous control of 2 magnetrons in the commercial oven created the biggest problem. The custom built oven is described in 4.3.2.

5.3 Development of Temperature Measurement and Control.

The temperature control system itself required no development, other than commissioning work. A commercial controller, Eurotherm 818P, was used in a control loop between the temperature measuring device and the power supply. Output power from the magnetron being a variable parameter contolled by the heating schedule programmed in the controller and the measured sample temperature.

The characteristics of microwave energy, cold wall heating and the generated temperatures being very responsive to the power levels meant that the controller had to be tuned differently compared to a conventional oven. Considerable time was spent adjusting the proportional (P), the integral (I), and the derivative (D) parameters within the controller. Retuning of the controller was required with each load/insulation configuration that was used. In general once the controller had been tuned, the entire control system worked to an acceptable level. Heating ramp rates were tracked closely and dwell temperatures were maintained to ±2°C.

The two main techniques investigated for temperature measurement were the thermocouple and the infrared optical pyrometer. These were readily available and initially considered to require minimal development. Other temperature measurement techniques, including fibre optic probes and gas thermometers, were discounted, due to either prohibitive cost or extensive development that would be required.

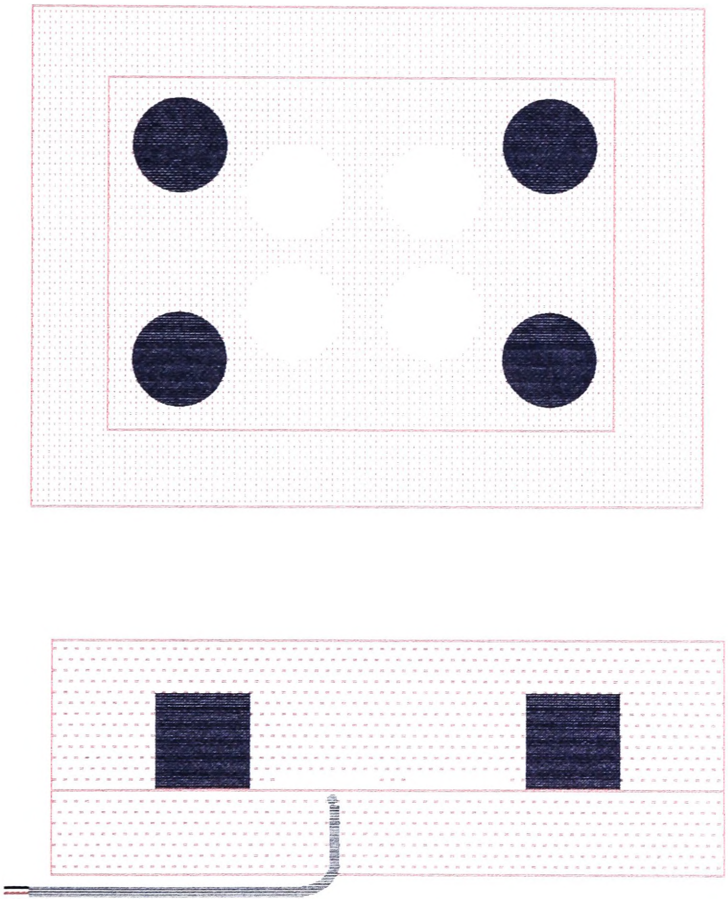
5.3.1 Thermocouple.

Temperature measurement trials with the commercial oven showed that, under normal sintering conditions, temperatures in excess of the operating capability of K-type thermocouples were generated.

Without shielding, the temperature could only be measured when the chopped time cycle was in the power "off" mode. During the power "on" mode the unshielded thermocouple was receptive to the microwaves. The thermocouple acted as an antenna, leaking microwaves to the outside environment to such an extent that the temperature reading on the controller was severely distorted.

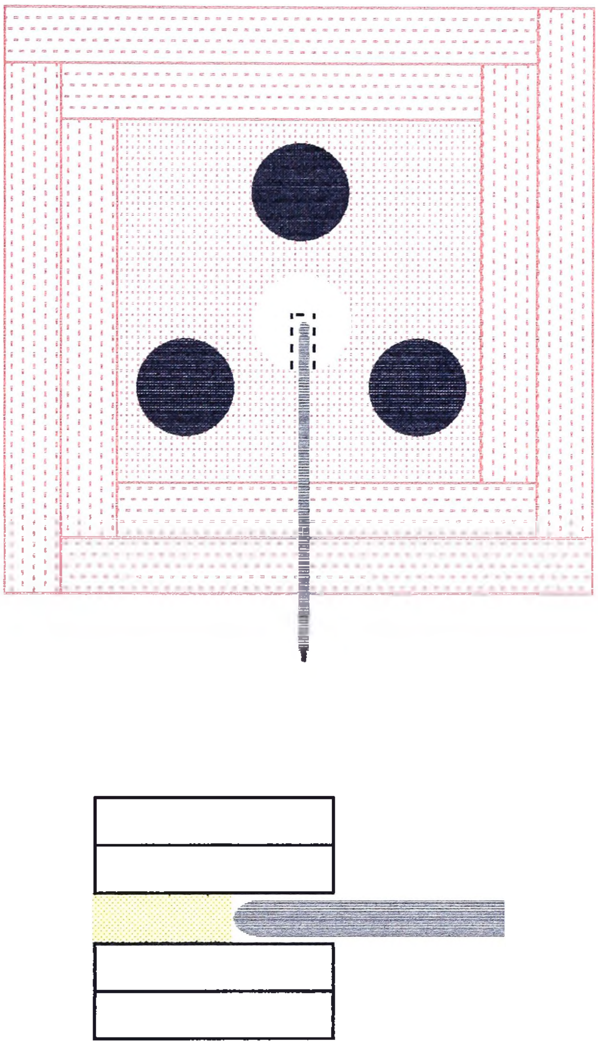
The sample/susceptor configuration used for the commercial oven was 4 x 25g susceptors surrounding 4 x 3g zirconia samples, figure 35. The thermocouple was positioned beneath one of the samples, such that the bead of the thermocouple was touching the surface of the sample.

Figure 35, thermocouple and sample/susceptor configuration, commercial microwave oven.



The remainder of the development work concerning temperature measurement was carried out with the custom built oven. The sample/susceptor configuration used with the thermocouples in the custom built oven was 3 x 25g susceptors in a triangular arrangement around a single stack of 4 x 3g zirconia samples. The thermocouple, positioned in a cap of sintered zirconia, was placed between the 4 zirconia samples, as shown in figure 36.

Figure 36, thermocouple and sample/susceptor configuration, custom built microwave oven.



Work with the commercial oven established the need for shielding and a thermocouple with higher operating limits than a K-type thermocouple provided. Two shielding techniques were trialed in conjunction with an R-type thermocouple: a molybdenum sheath and a wire wrap. The wire wrap was as proposed and used by Meek et al.[28] A platinum/palladium wire was wrapped around the thermocouple and earthed to the cavity of the microwave oven. Initially the pitch of the wire was a 1/4 of a wavelength. However, this arrangement did not protect the thermocouple from electromagnetic interference. The pitch of the wrapping was decreased in an effort to provide a more comprehensive shielding effect. Over numerous trials the pitch was unsuccessfully decreased from a 1/4 to a 1/40 of a wavelength, at which stage the trials were discontinued.

Shielding the thermocouple in a molybdenum sheath, which was earthed to the cavity, was found to be immediately successful. Temperatures up to the normal operating limits of the thermocouple could be measured without interference effects from the microwave field.

The molybdenum sheath, while shielding the thermocouple from electromagnetic effects, was highly susceptible to oxidation, especially at temperatures above 1000°C. The sheath was oxidised to such an extent that large sections had to be discarded after trials above 1200°C. This was found to have detrimental effects on sintering of the zirconia and the insulation. The sintered zirconia was a "straw-yellow" colour, as shown in figure 37, most likely due to vapour deposition of the oxidised molybdenum, (figure 38).

Crystalline precipitates were formed on and in the insulation, when the temperatures were high enough to oxidise the molybdenum sheath. Although precipitates on the surface of the insulation could be easily removed between trials, nothing could be done with those formed internally. Repeated use of the insulation resulted in a buildup of precipitates to such an extent that higher power levels were required for heating. After several high temperature trials the insulation had to be discarded.

Figure 37, Y-TZP microwave sintered "yellow."

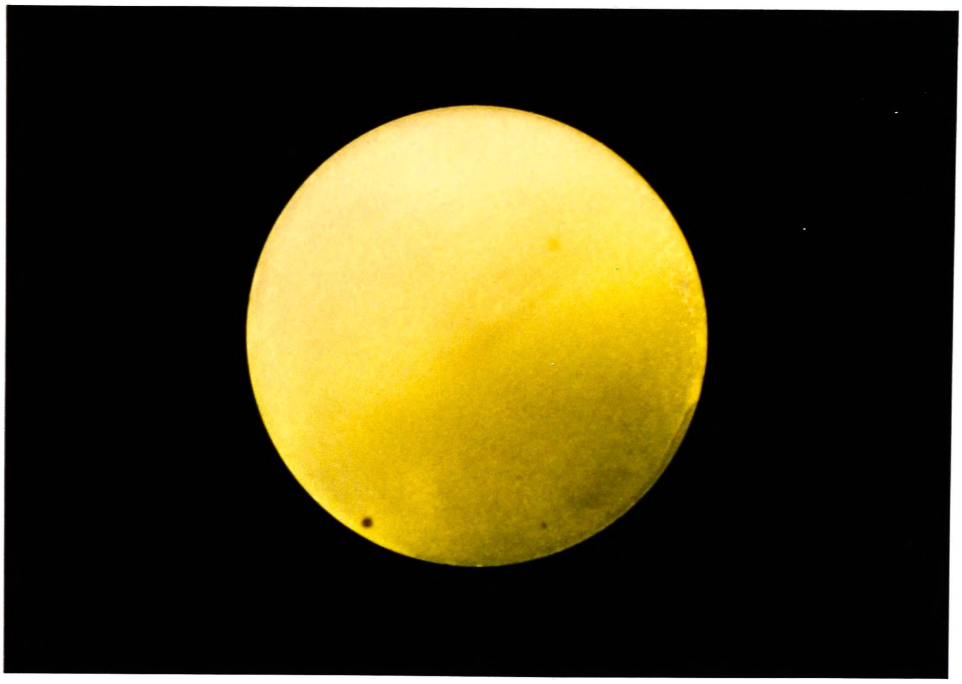
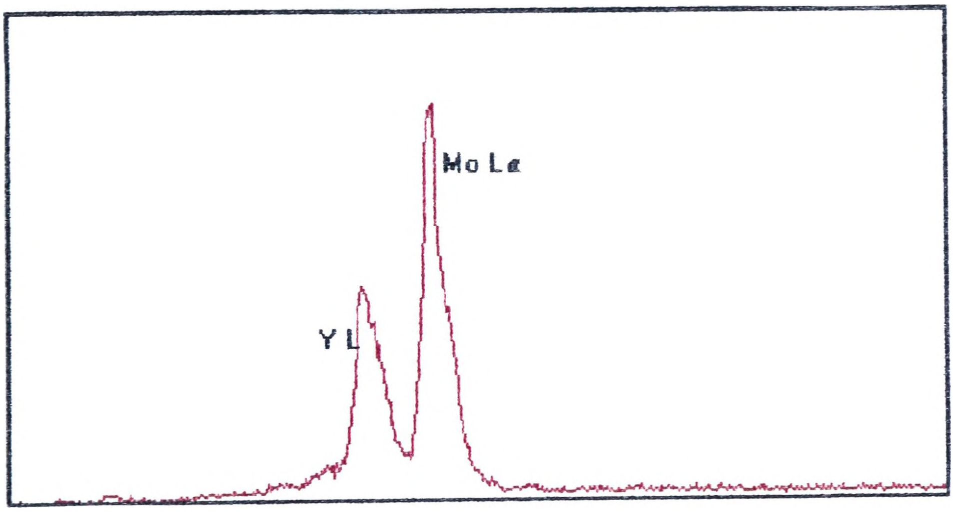


Figure 38, EDS spectrum showing the presence of Mo on surface of Y-TZP.



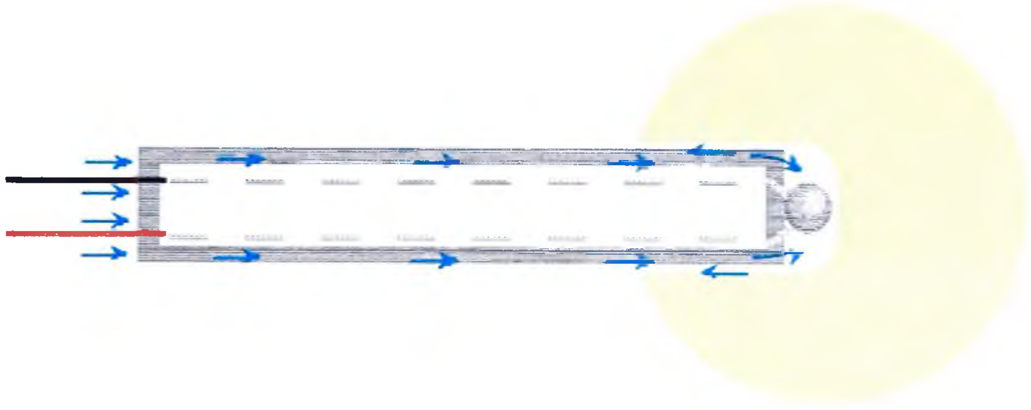
Two techniques were identified to overcome the problem of the molybdenum sheath oxidising. These were either i) coating of the molybdenum sheath or, ii) providing an inert operating atmosphere.

A sol-gel coating was applied to the sheath. However, after several trials the coating, for a number of reasons, was found to be unsuitable. Exact composition of the sol-gel was unknown, but it is likely that priority components of the gel were susceptible to the microwaves. This lead to the sheath itself heating up. The coating was successful in protecting the sheath from oxidation, however, it was not conductive, which created difficulties for earthing of the sheath to the cavity. The greatest problem of the sol-gel coating was in its application, in that a uniform coating being difficult to achieve. The non-uniform coating allowed for oxidation to occur, but in a varied pattern.

Coating of the sheath with a high temperature inert metal, such as platinum or palladium, may have been theoretically feasible but the cost of such an exercise was found to be prohibitive.

The second means of overcoming the oxidation problem was to create an inert atmosphere within the chamber. Two gases were trialed, argon and nitrogen. A very low flow of the gases was bled down the molybdenum sheath, in order to create an inert atmosphere in the immediate area around the sheath, figure 39.

Figure 39, gas flow for protecting Mo sheath from oxidising.



The flow rate of the gases was kept low so as to minimise any cooling effects on the thermocouple bead. By maintaining the low flow rate, it was envisaged that the gas would approach the bead temperature from heating whilst passing through the sheath. This was found to be the situation for both of the gases, with little or no cooling observed.

Argon was found to be successful in protecting the sheath from oxidation. However, the presence of the argon within the cavity created another problem, plasma formation. With no control over the plasma, high temperatures in excess of 1700°C, were quickly generated, causing severe damage to the insulation and samples. The damage is shown in figures 40 and 41.

Figure 40, plasma damage.

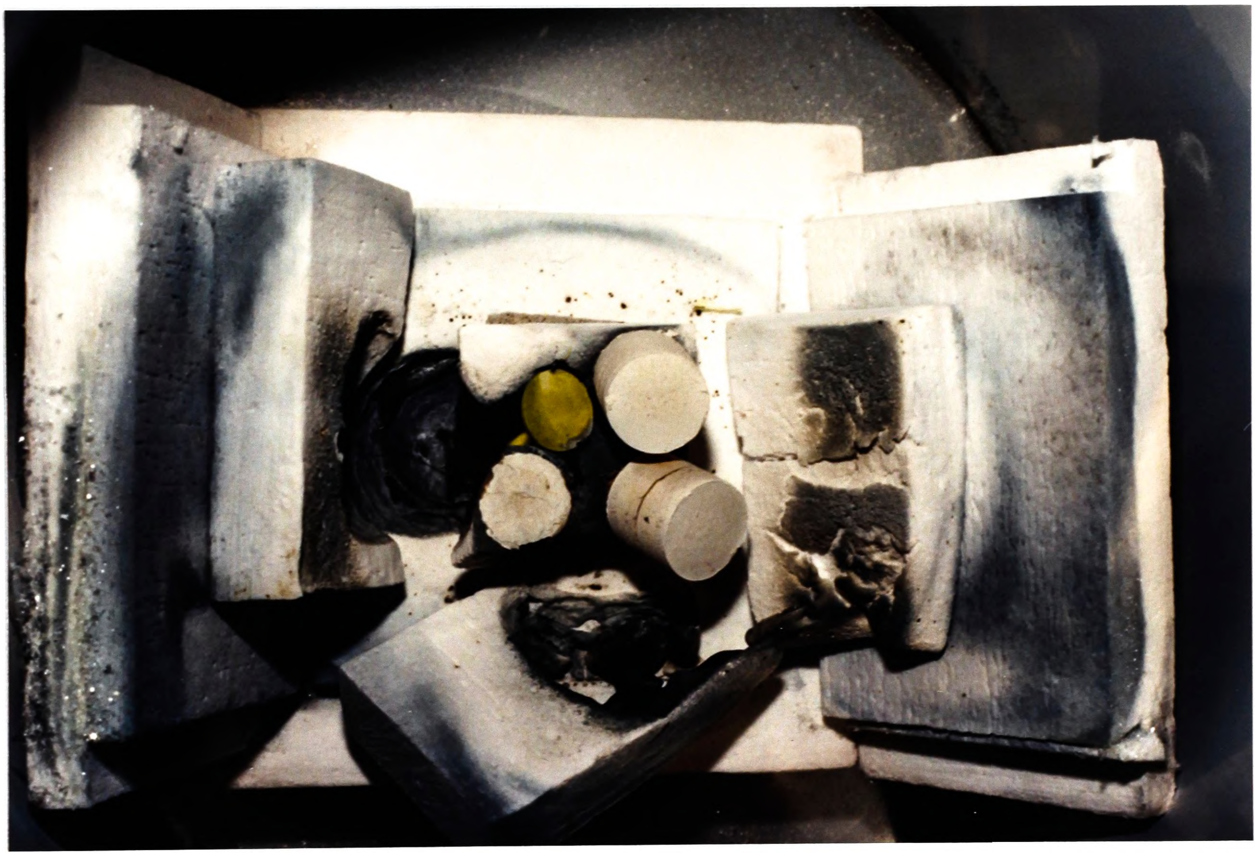
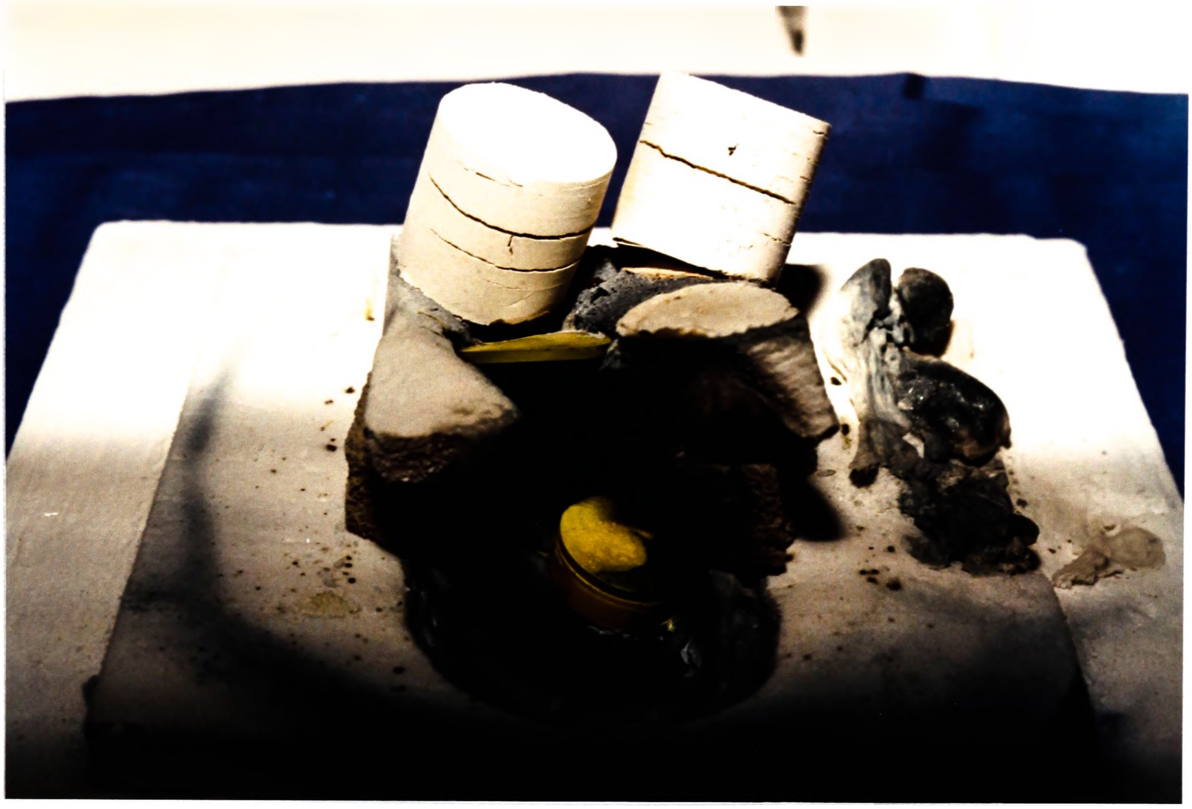


Figure 41, plasma damage.

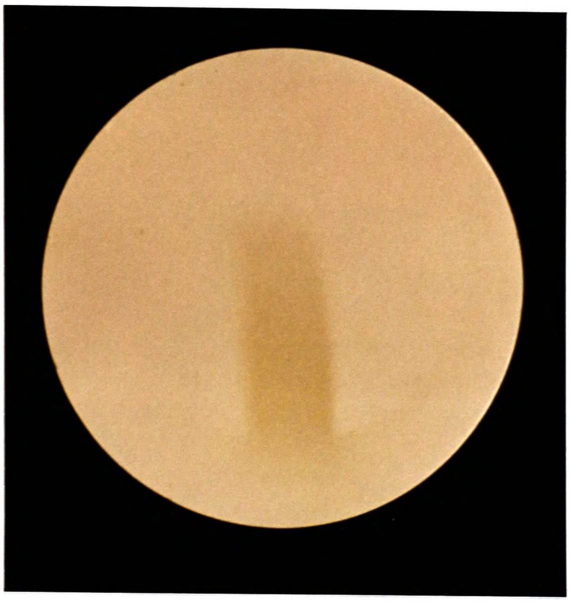


Nitrogen gas produced similar results. The molybdenum sheath was protected with low gas flows, however, a plasma was still formed. The resulting damage was less severe, either due to a shorter exposure time to the plasma or lower plasma temperatures. This is not surprising since greater energy is required to produce a plasma with nitrogen compared to argon.

At this stage, due to the unavailability of a suitable sheathing material for use at high temperature, it was decided to trial a K-type stainless steel shielded thermocouple. Although its operating temperatures were lower it allowed for development and evaluation of the temperature control system.

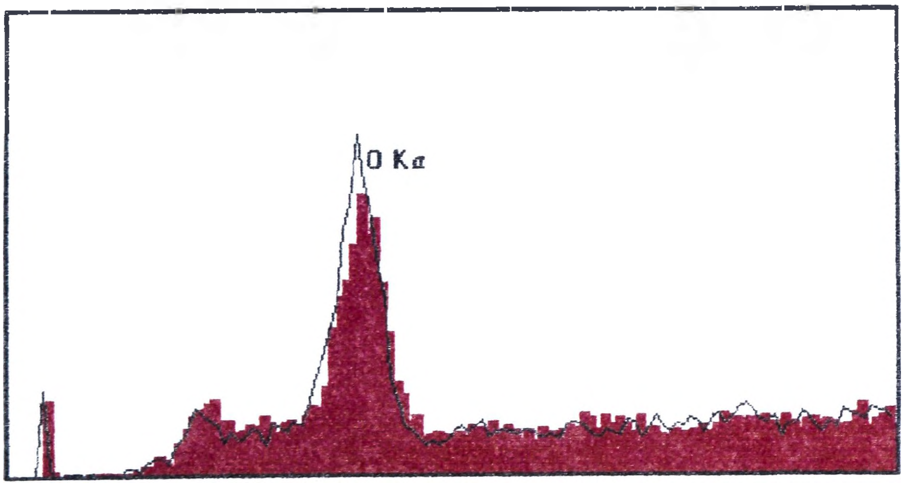
The K-type thermocouple, up to its working limits, was found to operate satisfactorily. Earthing of the shield to the cavity ensured no eddy currents were generated in the thermocouple and no leakage of microwaves occurred. The only operating fault of the K-type thermocouple, apart from its limited working range, was that it often produced darkening of the zirconia. Darkening occurred on the surface of the zirconia, where there was immediate contact with the thermocouple and higher temperatures (greater than 1275°C), this is shown in figure 42.

Figure 42, darkening of Y-TZP due to thermocouple.



The darkening was surmised to be due to the shielding material acting as an oxygen scavenger. The zirconia readily gave up oxygen as the sheath material oxidised. Oxygen depletion of the zirconia was verified by EDS analysis. Figure 43 shows the reduced oxygen content in the zirconia.

Figure 43, EDS spectrum showing regional oxygen levels.



Although the K-type thermocouple was successfully used to measure temperature, its working range meant that the usefulness of the system was limited. To facilitate high temperature measurement, an infrared optical pyrometer was trialed.

5.3.2 Optical Pyrometer.

The optical pyrometer is a non-evasive temperature measuring technique. However, it presented different problems than those that had been encountered with the thermocouple. The optical pyrometer (Agema Thermopoint 5000), operating at a single wavelength, meant that either an accurate emissivity value for the zirconia was required, or a black hole cavity would have to constructed in the samples. A clear optical path was also required, necessitating a hole through the insulation casket. The minimum focus spot size of the pyrometer was 5mm at a distance of 50cm.

Early work with the zirconia in a conventional oven highlighted that the pyrometer system was very susceptible to background radiation. The best approach therefore was to calibrate the pyrometer against a thermocouple, under normal microwave operating conditions. Provided the operating conditions remained similar, background radiation and other system effects could be taken into account by the calibration.

Calibration involved heating the zirconia samples at a controlled rate with the thermocouple, whilst simultaneously measuring the temperature with the pyrometer. The pyrometer was sighted on the zirconia samples and the thermocouple cap through a side port in the oven chamber, as shown in figure 44. The temperature reading on the pyrometer could be varied by adjusting the emissivity setting. Calibration was then simply a matter of setting the emissivity value so as temperature readings from the pyrometer and thermocouple matched. In this way an emissivity value was generated for given temperature and operating conditions.

The sample/susceptor configuration was initially the same as for the thermocouple trials, figure 36, except a hole was cut in the insulation to provide the optical path. The hole in the insulation is shown schematically in figures 45 and 46. With this configuration background radiation was quickly found to be a problem and at low temperatures (<700°C) it was difficult to calibrate the system at all. Stray radiation from the susceptors lying in the optical path, behind the zirconia samples, masked the true temperature. During the initial stages of heating, the susceptors were at a much higher temperature than the samples and emitted a greater amount of radiation.

Figure 44, optical pyrometer sighted into custom built oven.

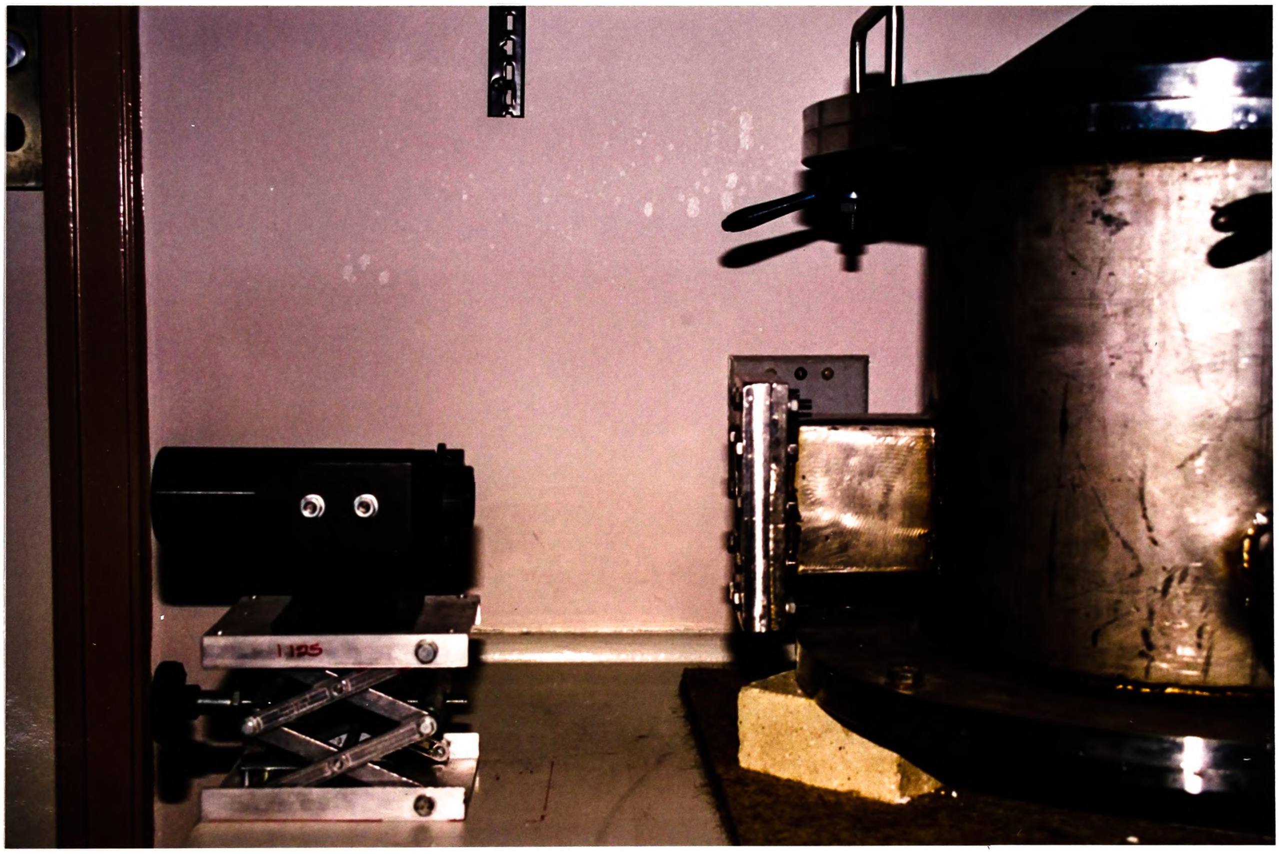


Figure 45, sight hole for optical pyrometer.

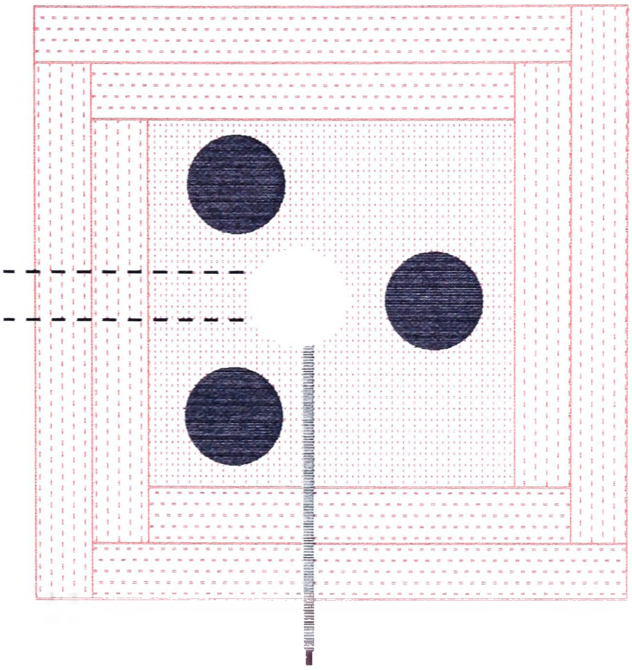
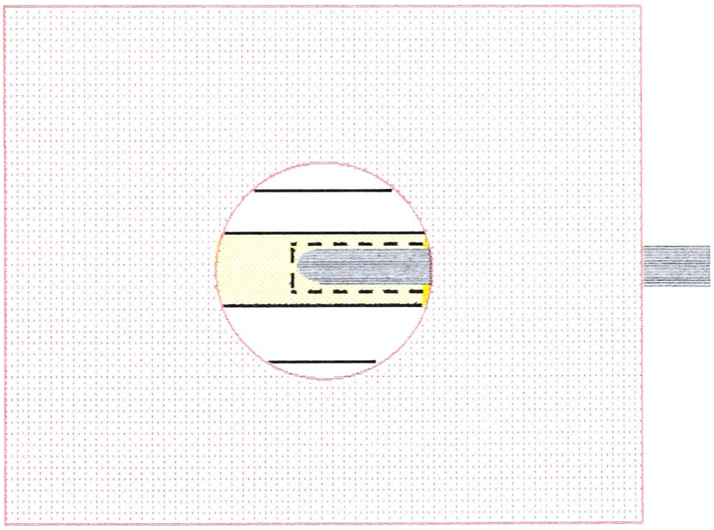
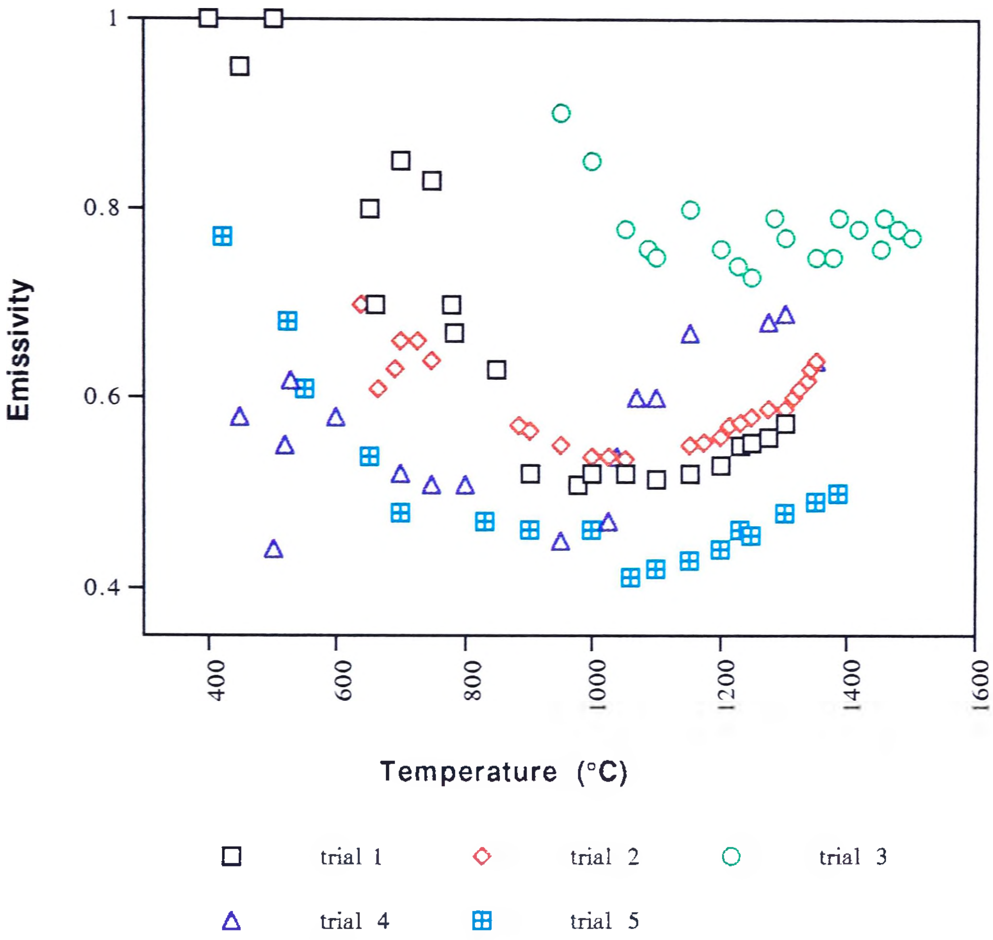


Figure 46, sight hole as seen from optical pyrometers viewpoint.



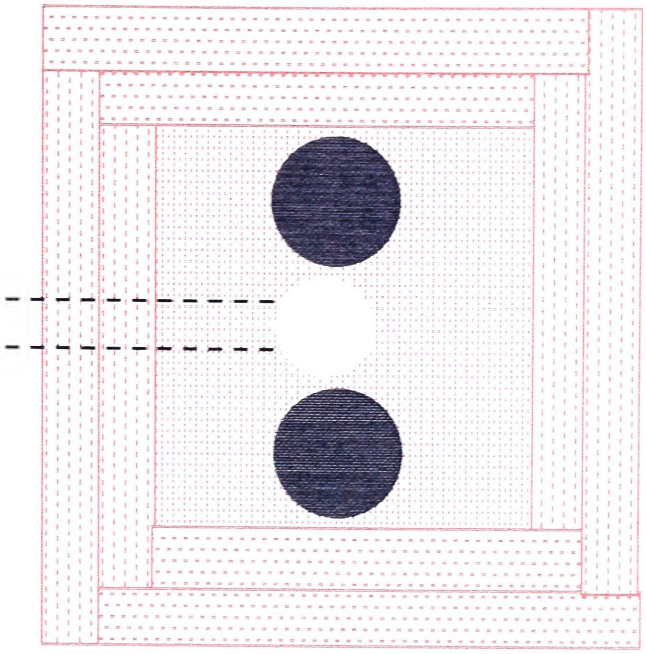
Determining the most suitable arrangement of susceptors, became the main focus of the developing the optical pyrometer as a means of measuring temperature in the microwave oven. Different susceptors configurations were trialed in an effort to reduce background radiation. The emissivity values generated during this stage were very scattered (figure 47).

Figure 47, scattered emissivity values from calibration trials.



Stray radiation was dramatically reduced when a susceptor from a previous trial was reused, even though it was in line with the optical path of the pyrometer. The old susceptor had a considerably lower graphite content than the other susceptors. The configuration was then changed to prevent the susceptor from being in the optical path. Two larger than normal susceptors (1 $^1/_4$" diameter with a total weight of 75g) were successfully used (figure 48). Slightly greater power was required for heating since the larger susceptors provided less surface area for microwave absorption, even though the total weight was the same as the other configurations.

Figure 48, two susceptor configuration.



The number of susceptors was then increased to four (20g each), increasing the total surface area in an effort to reduce the power requirements and give a more even heating profile within the chamber (figure 49). This configuration of susceptors enabled emissivity values to be determined with reasonable reproducibility (figure 50).

Figure 49, final sample/susceptor configuration.

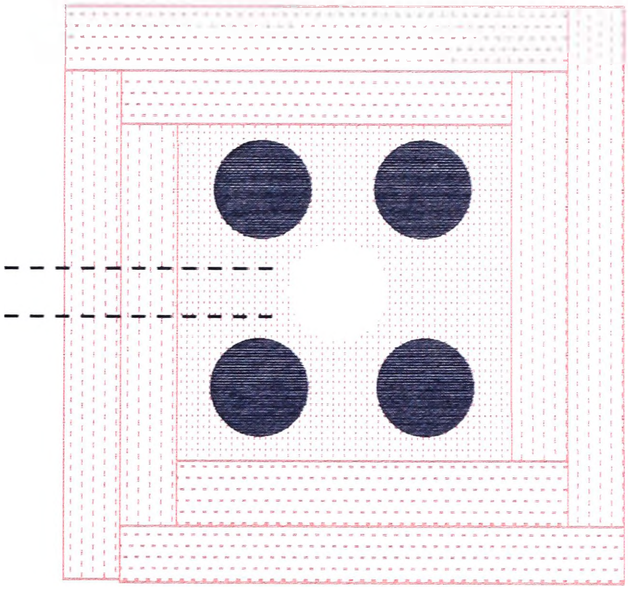
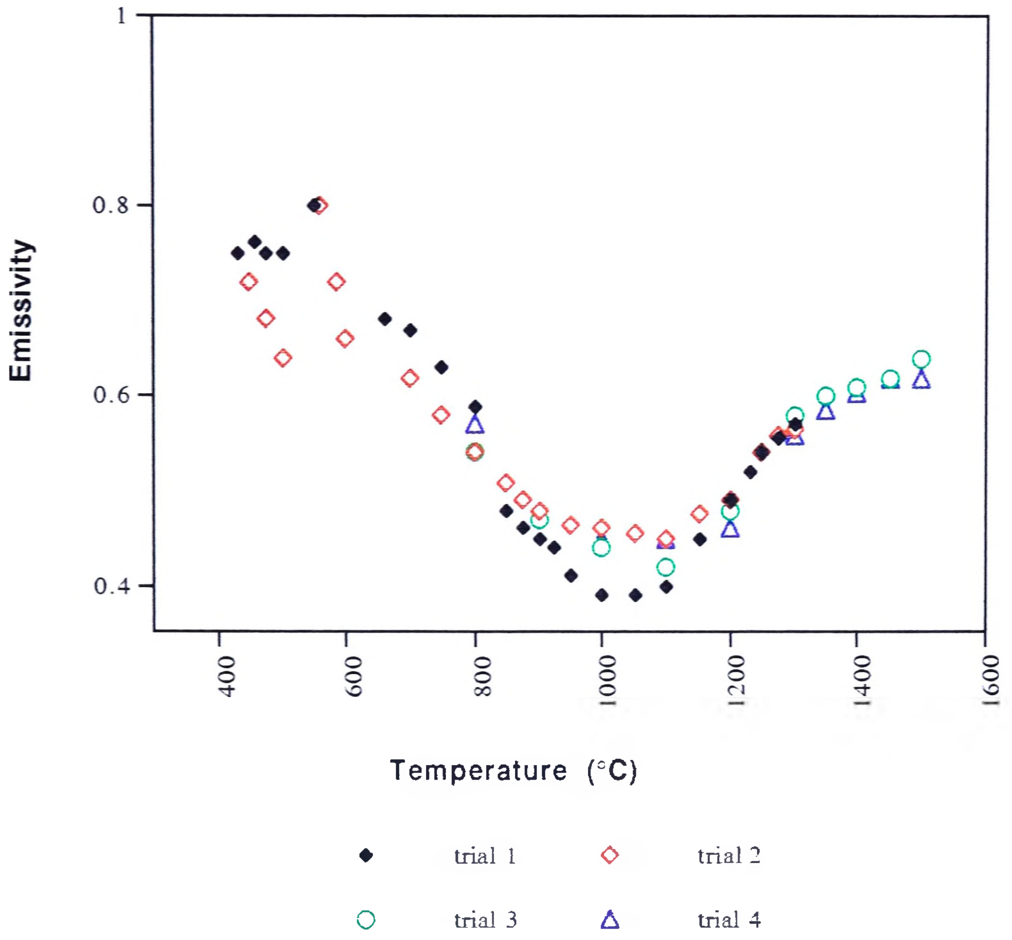


Figure 50, calibrated emissivity values from four susceptor configuration.



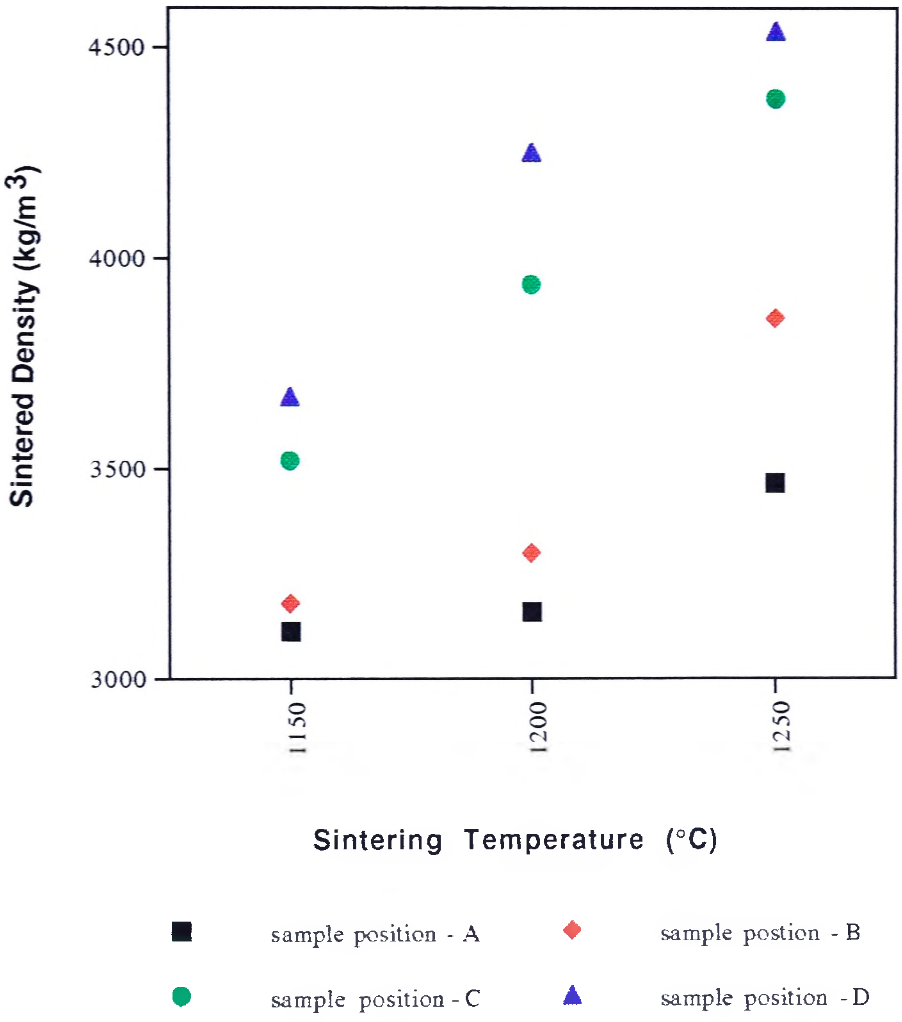
The emissivity values used for evaluation work was the average value determined from final calibration trials for the zirconia, sintered under the given conditions (Appendix C).

5.4 Temperature Uniformity.

Densities of zirconia, sintered in the custom built oven for the initial trials, indicated that temperature uniformity of the heating zone was poor. Although heating was controlled accurately, it was apparent that the temperature was only correct in the immediate vicinity of the thermocouple and its cap.

Temperatures were cooler above the thermocouple and hotter below the thermocouple. Supporting evidence for this is the fact that sintered densities were lowest for the top zirconia sample and highest for the bottom sample, shown in figure 51.

Figure 51, variation of sintered densities for Y-TZP.



Additionally variation of temperature across the heating zone was evident by tapering of the sintered samples. The bottom side of the samples, being at a higher temperature, always had a smaller diameter than the top, figure 52.

Figure 52, tapered zirconia samples.

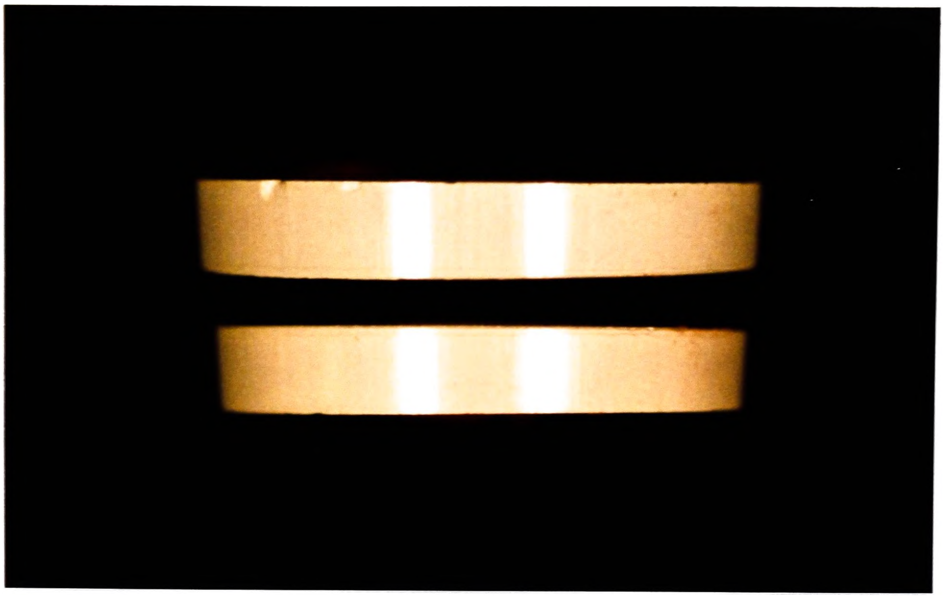
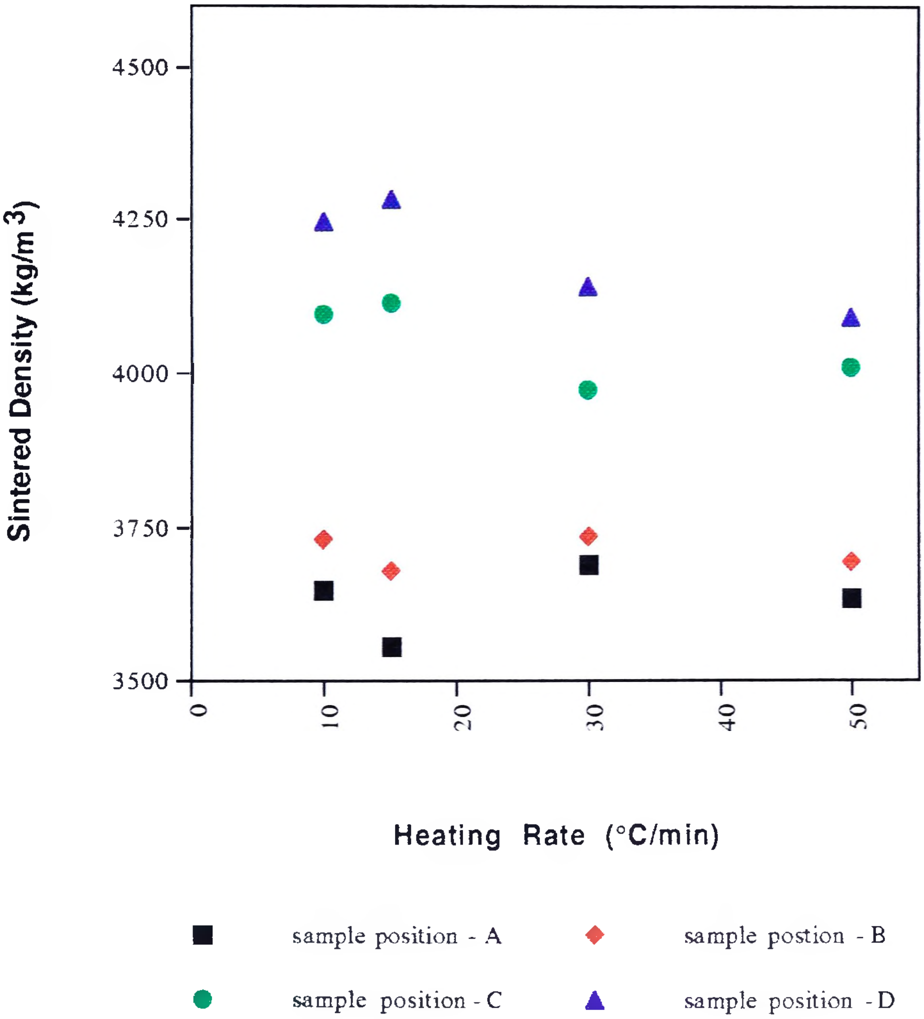


Figure 53, effect of heating rate on sintered densities of Y-TZP.



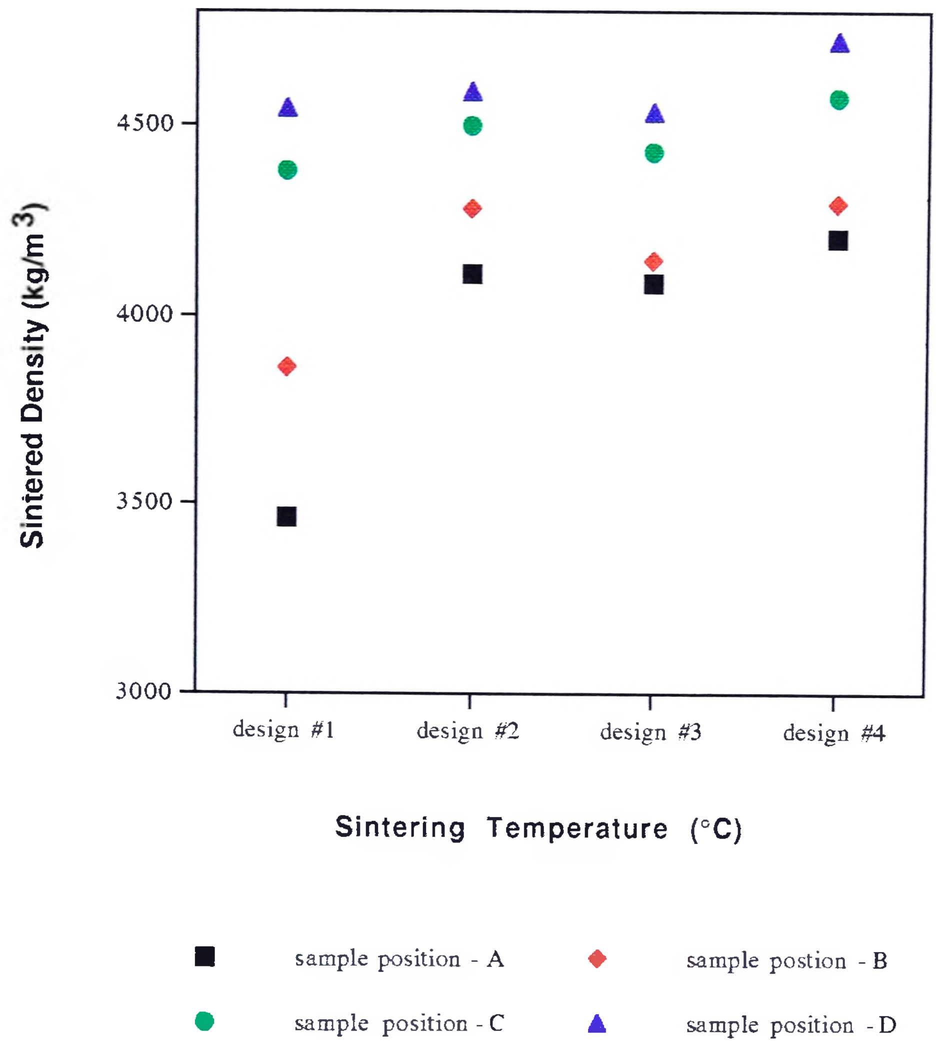
Heating rate was found to have no effect on temperature uniformity (figure 53). Poor uniformity was surmised to be due to insulation and/or field distribution within the chamber.

Work with the insulation was focussed on reducing heat loss through the top of the insulation casket, as well as improving the overall efficiency. The effect of changing the insulation casket was indicated qualitatively by power requirements and densities of the sintered zirconia. The majority of trials were carried out at 1250°C thermocouple temperature, since at this stage of sintering, small differences in temperature across the heating zone could be readily seen by changes in density.

Heat loss was reduced by slightly changing the casket design. The heat locks were increased and the air gaps between the layers of the fibre board were decreased. Other design changes trialed included extra layers of fibre board on top of the casket and the use of different insulative materials. Layers of zirconia-alumina fibre (Zircar) were used in conjunction with the alumina-silica (Kaowool) fibre board. The use of loose chopped fibre was also adopted, and found to be the most effective means of tightly packing the samples with insulation.

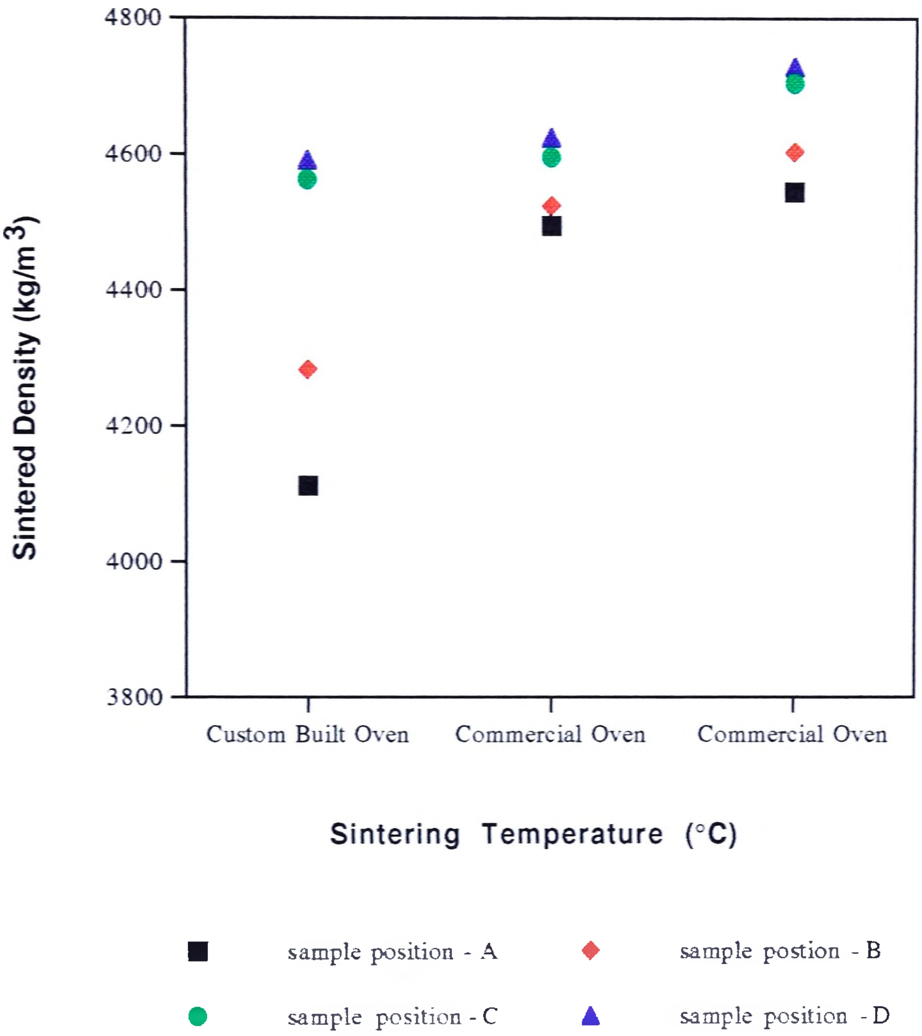
The insulative efficiency of the various casket configurations were found to be similar, indicated by the systems power requirement. However, the variation in the sintered densities did improve slightly (figure 54), although temperature profiles remained similar, with the highest temperatures being generated at the bottom sample.

Figure 54, effect of casket design on sintered densities.



A series of trials in the commercial oven resulted in densities greater than that achieved in any single trial varying the insulation. The exact same casket and sample/susceptor configuration was used in the commercial oven, however, without the thermocouple. Sintering times and power levels were chosen in an attempt to duplicate the heating rates and temperatures of in the custom built oven. The main difference between the two ovens is a mode stirrer in the commercial oven, which creates a more uniform field. It is therefore postulated that the improved heating profile, as seen by the relative similarity in sintered densities (figure 55), was due to a change in the microwave field. The field was more uniform in the commercial oven either due to the presence of the mode stirrer or the absence of the thermocouple. It is well documented that the presence of a thermocouple can perturb a microwave field.[4,19]

Figure 55, Comparison of Microwave Ovens.



Measuring temperature with the pyrometer eliminated the possibility of the thermocouple interfering with the field, however, it created two further problems related to the temperature uniformity. The nature of the pyrometer and the positioning of the ports in the chamber meant that the samples could only be positioned along limited axes, this was further limited by the overall bulk of the insulation casket. These spacial limitations prevented the possibility of achieving uniform heating, by means of relocating samples in the custom built oven to a region with greater field uniformity.

The second problem the pyrometer presented was that a hole in the insulation was required, making the temperature profile was now made more complex due to heat loss through the hole. The size of the hole was relatively large compared to the samples. Heat loss was clearly evident by tapering of the individual samples, the samples being wedged shaped with the thicker edge towards the hole, (figure 56).

Figure 56, tapered zirconia sample.

More power was required for heating with the pyrometer, a clear indication that the hole in the insulation greatly affected the overall insulative efficiency of the casket.

The problem of attaining a uniform heating zone within the custom built oven as it stood remained unresolved.

5.5 Discussion.

The initial aims of the research were to develop a microwave system which could provide controlled uniform heating. This required that the system had a uniform heating zone and that temperature could be measured and controlled. A processing system in general can only be developed to the limits of its support hardware. The custom built oven was developed to the stage where improvements in processing would only come from design modifications and upgrading the support hardware.

Development of the custom built oven allowed for observation of many fundamentals of microwave heating and processing. Most of these fundamentals are already widely recognised, however, the work done for this project was still useful as each microwave system is unique. Not withstanding design limitations and hardware availability, temperature measurement and control were successfully attained with the custom built oven. However, it soon became apparent that a uniform heating zone was not achievable.

The feasibility of measuring temperature was shown with the two most common techniques, the thermocouple and the infrared optical pyrometer. Temperature could be measured with both techniques each having its advantages and disadvantages.

It was found that using the thermocouple technique, shielding was necessary to prevent the inducement of eddy currents in the thermocouple. In the absence of shielding, measurements could only be taken whilst the electromagnetic field was off. For the shield to be effective it needed to be earthed sufficiently to the microwave cavity and be able to withstand the operating temperatures and atmosphere.

Wire wrapping the thermocouple to provide a shield was found to be unsuccessful. The description of this technique given by Meek et al[19] is insufficient and it is unlikely that their setup was exactly duplicated in the trials. This approach eventually would have worked if the pitch of the wire wrapping was reduced even further than the 1/40 of a wavelength which was reached. In this event, the pitch would provide as much coverage to the thermocouple as a solid sheath.

Thermocouples are known to perturb microwave fields, in some cases to an extent where sintering has been affected.[19] Trial results indicated that the thermocouple did perturb the field, but it is impossible to state whether the effect was great enough to interfere with sintering since power was only measured qualitatively. For exact duplication of trials to determine the effect of thermocouples, forward and reflected power would need to be measured and controlled accurately. Repositioning the thermocouple may have resulted in either less, or more interference. It has been shown[46] that the orientation of a dielectric material to a microwave field affects the rate of heating. It is likely that this also applies to a shielded thermocouple. Different orientations and shield configurations would perturb the field to varying extents. No research is known to have been published covering this notion.

Positioning of the thermocouple relative to the sample can effect the temperature that is measured.[19] The two approaches of positioning are to use the thermocouple in direct contact[7,11,19,60] with the sample, or in contact with a mediating material.[16,19,54,57,62] Direct contact relies on the thermocouple having constant contact with the surface. A well is commonly provided in the sample allowing insertion of the thermocouple. The second approach relies on heat conduction from the sample through the mediating material to the thermocouple. The dielectric properties of the mediating material should be similar to that of the sample to stop differential heating. Ideally the mediating material should be the same as the sample itself. Both approaches have merits, although the suitability depends, not only on the microwave system, but the sample itself.

The zirconia cap (figure 36) provided the easiest means to measure temperature with a thermocouple in the custom built oven. The ports in the oven limited the thermocouple positions to the side and the top. Shrinkage during sintering would have resulted in a loss of contact between the thermocouple tip and the samples had the direct contact approach been used.

Non-evasive temperature measuring techniques overcome the majority of problems that are encountered with thermocouples. This was found to be true with the use of the infrared optical pyrometer. Field perturbation was not a problem nor was shielding required. The need for a clear optical path and emissivity values, ensured that the pyrometer operation of the was still complicated.

The hole in the insulation was a contributing factor towards non-uniform heating. Heat loss from the samples was significant, causing a discernible difference in power requirements when the pyrometer was used. Of all the literature reviewed, there was little or no comment made about the problems of heat loss when using pyrometers. One explanation could be that a more suitable insulation casket reduces heat loss through the optical path to a negligible amount. The heat loss problem could be minimised if it were possible to process larger samples in the custom built oven. The percentage of heat lost from a larger sample would be less, since the hole in the insulation remains the same.

The greatest problem of the single wavelength pyrometer is emissivity. The emissivity of a material is dependant on factors such as temperature and surface conditions. As a result, a single emissivity value could not be used, however, it was difficult to determine emissivity values with any accuracy.

Additionally, stray background radiation is known to interfere with the measuring capability of single wavelength pyrometers.[55,95] In this work, background radiation altered the measured sample temperature. This was found during the initial trials, particularly at the lower temperatures. A blackbody cavity eliminates the need for knowledge of the emissivity, as does a two wavelength pyrometer, since it always has a value of 1.00. However, due to the sample and focal spot size, it was not possible to construct such a cavity. Calibration of the pyrometer against a thermocouple was therefore the best available means to account for the background radiation. However, the calibration raises the question of accuracy, not only for the pyrometer but for temperature measurement in general for the microwave system.

Apart from selection problems with the shielding material and the possibility of field perturbation, the thermocouple appeared to provide an accurate means of determining temperature. Concerns citied in literature over the use of thermocouples to measure temperature, are mainly regarding arcing and field interference problems, rather than accuracy. However, inaccuracy is likely to arise when using a mediating material between the thermocouple and the sample, especially when the mediating material has different dielectric properties.

It is doubtful that the pyrometer used in this research provided temperature readings to the same degree of accuracy as the thermocouple. Even small changes in operating conditions after calibration may have been sufficient to alter the emissivity of the sample and/or background radiation. A small change in the emissivity setting on the pyrometer was found to shift temperature readings considerably. Depending on the temperature and the sample/susceptor configuration, a shift of 0.05 in the emissivity setting varied the temperature by up to 50°C. A pyrometer can only measure surface temperature, hence heat loss through the hole in the insulation, means that the temperature measured by the pyrometer is unlikely to be representative of the entire sample. However, calibration against the thermocouple may have provided some correction. It is likely that the difficulty experienced in developing temperature measurement and control, is mostly a reflection on the level of the technology being used. Clark[3] argues that recent advances in equipment has enabled temperature to be measured and controlled accurately. Despite the disadvantages of the pyrometer it was still the method adopted for further evaluation work in the custom built oven. The pyrometer offered the capability of measurement and control at higher temperatures for extended periods, which was not possible with the thermocouple and shields that were available. A more suitable arrangement may have been to use a combination of both techniques, especially since the pyrometer did not work below 400°C. However, this was not possible due to the limited programming capabilities of the controller.

The ability to measure temperature accurately still does not indicate heating uniformity, since temperature measurement tends to be localised. Densities of the sintered zirconia samples verified that the temperatures generated were not uniform and that it was due, at least in part, to the field distribution. It is recognised that an operating limitation of mulitmode cavities is that they can exhibit spatial resonant behaviour.[3,4] For uniform and controlled processing, the field distribution has been found to be important. This often requires that the field is modified within the multimode cavity to improve its distribution.[6,11,17,47,55,56] A poor field distribution can result in non uniform heating. The effect of this on processing can be the generation of "hot spots" leading to thermal runaway,[11] sample cracking,[6] and variable densification. Trials in the custom built oven exhibited only the varied densification, of the numerous samples that were sintered in this oven, none were cracked nor was any thermal runaway observed.

It was evident from trials that the field in the custom built oven was not uniform, however mapping of the field distribution was not carried out for several reasons. In essence current measurement techniques are only qualitative, it is widely recognised that both material volume and dielectric properties greatly influence the field patterns and hence heating profiles.[6,67] The measurement techniques tend to alter the field themselves and hence can only be said to be representative of the field pattern associated with that particular load, rather than of the cavity itself. The most common field mapping technique is to use water, however the dielectric properties of water would be expected to be completely different to the zirconia/susceptor loads, particularly given the large difference in the temperatures. Temperatures during field mapping are generally low, in the case of water less than 100°C, while temperatures of up to 1500°C were attained in the heating trials. The qualitative nature of the mapping techniques also creates uncertainty when applied to small samples and loads such as used in the trials. Overall, characterising the heating profile using current mapping techniques would in no way reflect or indicate heating profiles of the zirconia/susceptor loads. The only reliable indication was the uniformity of sintering of the zirconia samples. Even if a more uniform field position was located it is unlikely that the samples could have been positioned there without modifying the oven. The insulation casket was relatively bulky and temperature measurement fixed to 2 axes. If the samples were placed in a position off the axis of the cavity ports, then temperature could not have been measured.

The field distribution within the custom built oven could have been improved by using one of several common techniques. The most common being the use of a mode stirrer. Similarly, a wave splitter, or an increase in the frequency of the microwaves, can improve the field. A mode stirrer creates a statistically uniform field by perturbing the microwaves. The advantage of sintering in an oven that has a mode stirrer was clearly shown by comparative trials between the custom built and the commercial oven. The commercial oven, with the mode stirrer, had a more uniform heating zone. This was indicated by the closeness of sintered densities of the zirconia samples. Wave splitters have also been shown to be successful,[56] and would be suitable for use with the custom built oven since it already has two opposing rectangular ports, orientated 90° to each other. Wave splitters improve field uniformity since microwaves enter the cavity with opposite polarisation.

Temperature gradients in the heating zone of the custom built oven may have been reduced by changing the sample position and/or orientation. Non uniform fields have been shown to create orientational effects on the temperature and temperature profiles within samples being microwave heated.[46] Similarly, one advantage of using susceptors for hybrid heating is that they alter the field distribution,[60] therefore a different susceptor configuration or even susceptor material may have been more suitable.

Resonance tuning is another means of altering the field distribution. Tuning is useful as it can overcome the mismatching between system components. The system is tuned when the forward power is maximised and the reflected power minimised, so that power is concentrated in the cavity. A four stub tuner, described in 4.3.2, was successfully used for resonance tuning with the custom built oven. In general, it was found that one stub had the greatest effect on tuning whilst resonance varied little by the other three. The state of tuning varied little between comparative trials. Once the temperature was above 500-700°C, minimal tuning was required. Generally, retuning was required after the system had been disassembled, the reassembly most likely changing the mismatching between the flanges of the individual components. Resonance was found to vary with load and sample/susceptor configuration. It was often possible to tell that something had gone astray during a trial by the fact that the system was suddenly out of tune. When the system was considerably out of tune arcing occurred in the waveguides, the reflected power being high as a result of field disturbance. The most noticeable feature of the tuning was the small manipulation required to affect the overall power necessary to maintain heating.

The volumetric nature of microwave heating means that insulation is required for efficient heating. This operates by minimising energy lost through radiant heat. The importance of insulation for microwave heating is now well recognised,[57] there being two main uses. Firstly, it can be used to control the extent of radiant heat loss from a body being heated, and secondly, in the case of hybrid heating, can act as a susceptor[13] if the insulative material is sufficiently lossy. Trials in the two microwave ovens to determine the best insulation arrangement addressed the basic requirements of the insulation and its effect on the heating.

Ideally, a suitable insulation material should be transparent to the microwaves, except where the insulation is to be used as a susceptor for hybrid heating. Contamination of the insulation during trials was found to interfere with heating. Contaminates within and on the insulation can either absorb the microwaves, requiring more power to maintain heating, or reflect the microwaves, altering the field distribution. The contaminates that were found to effect insulation during the development trials were: residual binder leftover in the insulation, and the crystalline precipitate from oxidation of the molybdenum sheath. Both these required greater power for heating.

Temperatures generated during the trials in the custom built oven, appeared to be dependant on insulation rather than power availability. As more efficient insulation configurations were developed, less power was required to maintain the heating rates. Heating was affected by changes in the radiant heat loss. Poor casket designs limited the temperatures that were attained, as did the degradation of the insulation after repeated use. This agrees with the findings of Holcombe et al[96] who found that the "effectiveness of sintering is directly dependant on the casket design." The highest temperatures reached during the trials were well in excess of the operating capability of the insulation, yet the magnetron was only being driven at approximately 50% capacity.

Multimode ovens are more suitable for processing large irregular objects. Uniform heating has been found to be difficult for small samples, whose size approaches that of the microwaves wavelength.[46] As load decreases, so too does the amount of microwave energy which can be absorbed. Processing small samples often requires the addition of ballast material, to increase the overall load in the oven. Janney et al[61] found that it was difficult to control the sintering of small samples (<5g alumina). The problem was successfully overcome by using a ballast crucible of ~150g weight to increase the load in the multimode oven. The ballast material in hybrid heating is often the susceptors, with the relative weight of the susceptors being much greater than the samples.[11,54] For trials in the two microwave ovens, the ratio of the weight of the susceptors to the zirconia samples, varied from between 6:1 to 12:1. Another means of increasing the load, is to increase the lossiness of the sample being heated. This can be achieved by simple preheating[13] or by increasing the content of lossy additives[7] and/or phases.[15]

The effect of load was not directly investigated. In general, observations were qualitative, due in part to the inability to accurately determine the power levels. Preliminary trials with the commercial oven, however, showed that the oven was capable of sintering a wide range of loads. Comparative trials, sintering zirconia, were carried out using 100g of susceptors and 5 to 100g of zirconia. Density decreased slightly from 6.07 g/cm^3 to 6.02 g/cm^3 as the load was increased. This was most likely due to insufficient power availability to drive densification at the same rate for higher loads.

Increasing load in the custom built oven required more power for heating, with the susceptors having a greater effect than the zirconia samples due to their lossiness. As load increased, the reflected power decreased, as did the leakage of microwaves from the system. Small loads were found to be difficult to process in the custom built oven. The system was harder to tune, due to the increased ratio of reflected to forward power, and the low thermal mass which caused problems with the controller. Small loads resulted in the temperature fluctuating around the set points during heating. The addition of extra zirconia samples, from 6 to 12g, was sufficient to overcome these problems. The trials found that for the custom built oven, the minimum load for controllable sintering was 75g of susceptors and 12g of zirconia. This would vary slightly for different grades of zirconia and different susceptor sizes, since a larger surface area can absorb more microwave energy. The final load used for further evaluation work was 80g of susceptors and 20g of zirconia.

The susceptors were found to be an integral part of the load, without which it was not possible to heat the zirconia samples in the multimode ovens. Zirconia is not susceptable enough at low temperatures to be heated at 2.45GHz in a multimode oven. Susceptors such as SiC rods[11] are one means of providing hybrid heating, where the others commonly used are receptive insulation[57] and pre-heating.[13] Graphite-alumina susceptors allowed the zirconia to be heated, however, some problems were associated with their use. Oxidation of graphite in the susceptors produced slight darkening of the zirconia. The darkening was observed to a greater extent in the commercial oven, which is more of a reflection of the insulation casket and the temperatures generated, than differences between oven designs. Darkening was greatest at high temperatures and when the susceptors were openly exposed to the zirconia samples, as in some of the commercial oven trials. The darkening was most likely due to the graphite scavenging oxygen from the zirconia according to;

$$ZrO_2 + C \Rightarrow CO/CO_2 + ZrO_{2-x}.$$

The susceptors were also the cause of stray background radiation which interfered with the use of the pyrometer. This problem has been observed for other hybrid heating systems,[55] and considerable effort was required to minimise interference. The radiation problem showed that different susceptor designs, shape and size, affected the load in the oven. Improved heating could be achieved by choosing a more suitable susceptor design and susceptor/sample configuration. Ideally, the susceptor should have a maximum surface area to volume ratio for microwave absorbance, as well as a shape conducive to concentrating the heat on the zirconia samples.

The graphite-alumina susceptors used in the trials are a consumable item, being only of use for a single trial after which they must be discarded. The oxidation of graphite reduced the lossiness of the used susceptors to an extent where they could not be heated up from room temperature. A better alternative would be to use a re-usable material for the susceptors or use a different susceptor approach such as microwave receptive insulation.

Although it is cited[60] that susceptors can alter the Q factor of a microwave cavity, it was not possible in the trials to distinguish whether this did occur or to what extent. It was only possible to say that the susceptors affected the cavity load. Trials to measure the temperature of the susceptors were unsuccessful. By measuring the temperature of the susceptors and the zirconia samples during heating, it was hoped that it would be possible to determine at what stage the zirconia became more susceptible to the microwaves. Thermocouples were unsuitable for measuring the susceptor temperature even at low power levels. The susceptors were found to rapidly heat to temperatures beyond the limits of the thermocouples. The pyrometer was also unsuccessful since it could only measure surface temperature, with the hole in the insulation allowing the surface to cool to an extent that it was several hundred degrees lower than the insulated surfaces.

Had the temperature been successfully measured, it would have given an indication of the dielectric properties of the graphite-alumina susceptors. It has been reported that for SiC susceptors heating zirconia, once the zirconia becomes sufficiently heated the SiC susceptors begin to cool. The zirconia absorbs a greater amount of the microwave energy due to its higher dielectric loss factor.[11] The behaviour of the graphite-alumina susceptors, however, is likely to be more complex than this. The dielectric properties of two components must be considered, which is further complicated during processing as the graphite is oxidised. The dielectric loss factor varies with both temperature and graphite content in the susceptor. Without being able to measure the susceptor temperature, the amount of microwave energy absorbed by the zirconia during processing is unclear. It could be argued that since the susceptors reach high temperatures (>1500°C) in a relatively short time, the dielectric loss factor of the alumina remains greater than the zirconia for the majority of processing, and the zirconia undergoes little pure microwave heating.

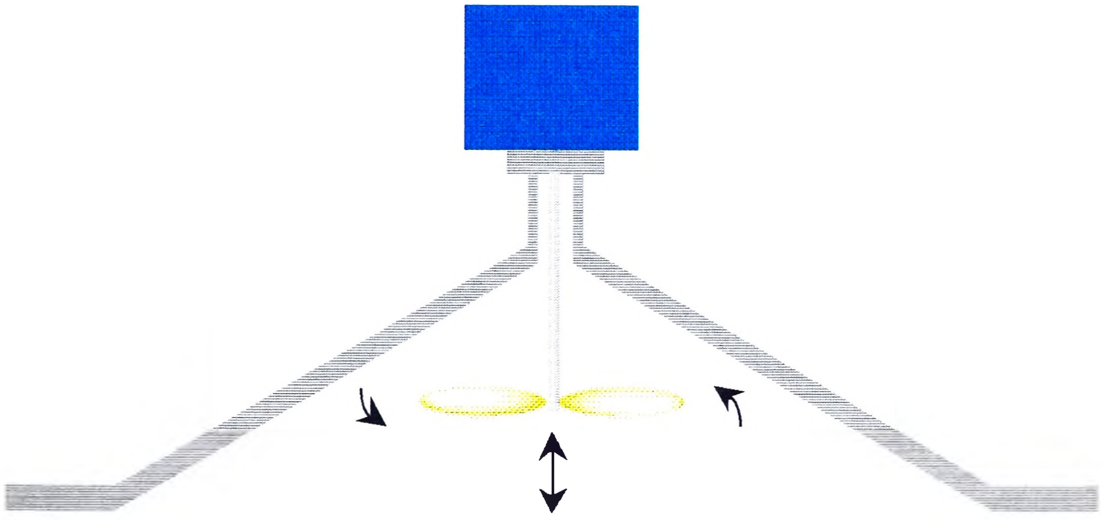
5.6 Recommendations.

Development work addressed the fundamentals of microwave heating in the multimode ovens. It was found that although zirconia could be heated with reasonable control, the custom built system had been developed and commissioned to the limits of its design, therefore improvements in processing would be best achieved with design modifications and upgrading the support hardware. To investigate microwave/matter interactions in depth it is felt that the following recommendations are essential.

The non-uniform heating zone that was generated was in part due to the poor field distribution that is common in multimode ovens, hence improving the field distribution may alleviate this problem to a great extent. The most feasible means of achieving this would be through one or a combination of the following: i) adding a mode stirrer, ii) adding a moving wall, or iii) feeding the microwaves into the cavity out of phase. The recommended alteration to the system is to adopt all of these modifications.

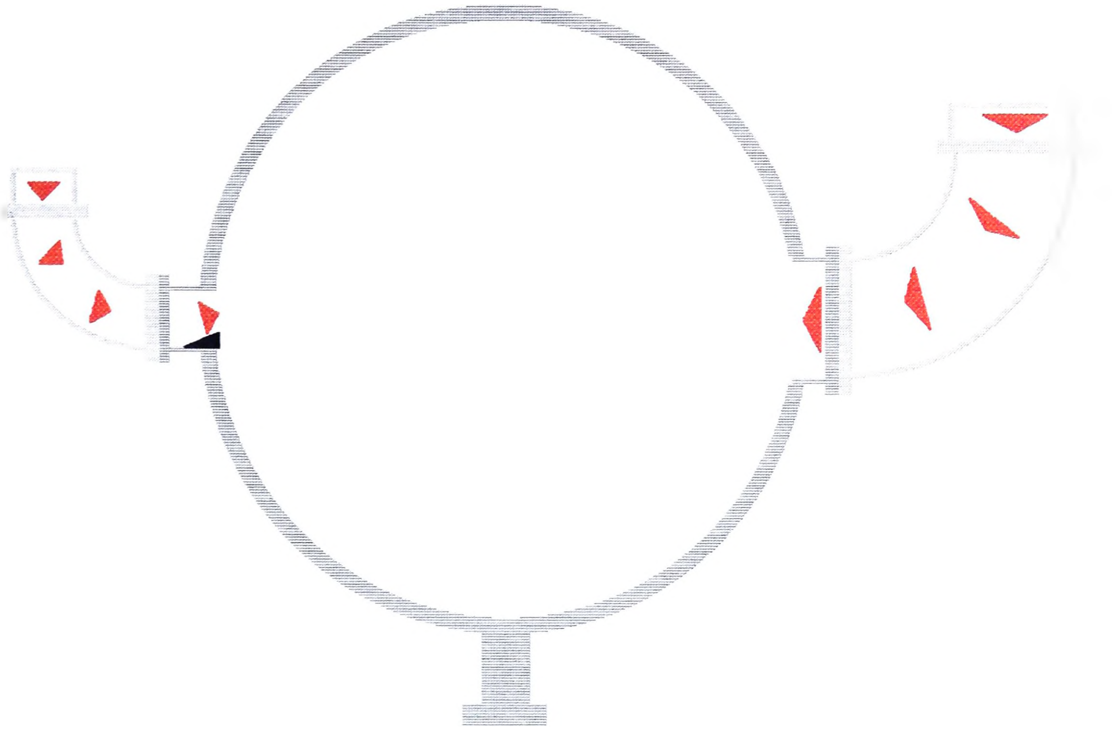
A statistically average field would be created by using either the mode stirrer or the moving wall, shown to be successful by Schu et al,[6] both of these improve the field by perturbation. It may be possible to combine both these by designing a mode stirrer which not only rotates but oscillates along a fixed axis. The most suitable position for this would be in the lid of the oven, shown in figure 57. Since the oven chamber already has two rectangular ports, at 90° to each other, a wave splitter should also be used to feed the microwaves into the cavity out of phase.

Figure 57, proposed mode stirrer in cavity lid.



The two microwave feed ports of the cavity are directly opposite each other, (figures 58 and 59). The field distribution may be improved by directing the incident waves away from the opposite port, using a small deflection plate. The deflection plates should be aimed in opposite directions to maximise the effect.

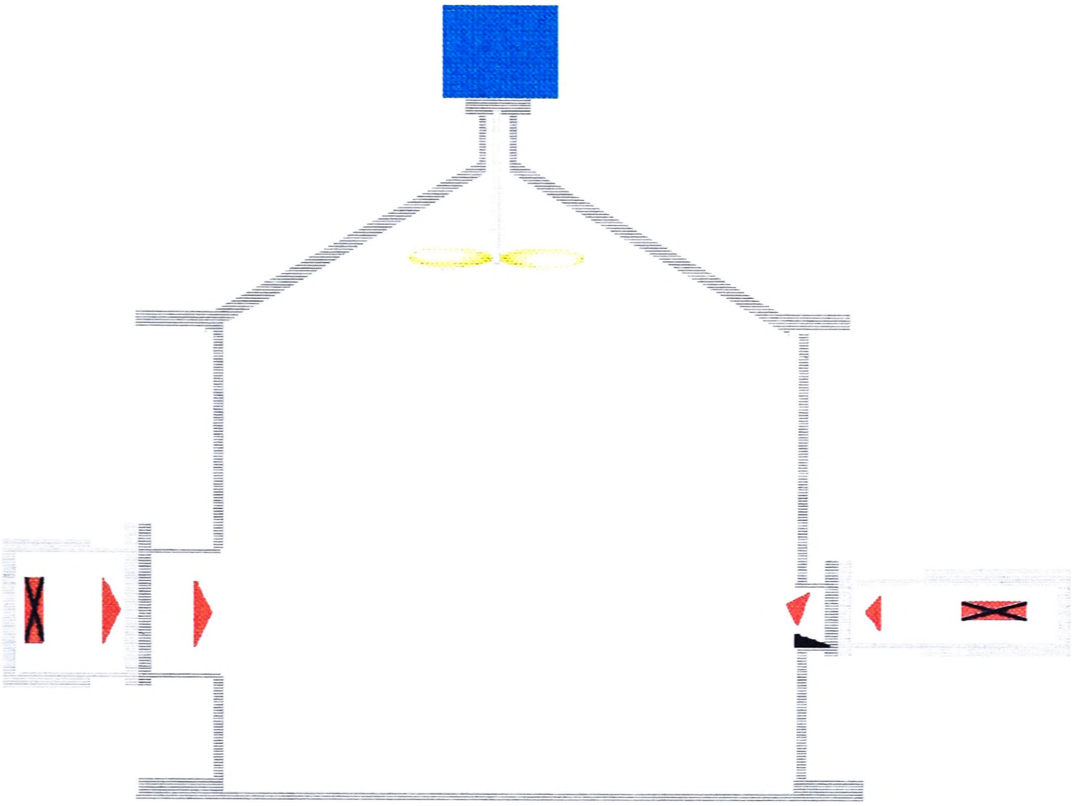
Figure 58, microwaves being fed into the cavity out of phase.



Further improvements should be made to the general area of measuring the systems parameters, namely temperature and power. Since no single technique is ideal for measuring the temperature in a microwave field, a dual arrangement may be more suitable. A platinum/rhodium sheathed R type thermocouple would be adequate for processing at temperatures up to 1650°C in a wide range of atmospheres. A non-evasive technique would provide a good comparison to the thermocouple. The problems of the emissivity values with the single wavelength pyrometer dictate that a dual wavelength pyrometer is essential.

An accurate means of measuring power should also be installed. The current arrangement of terminating power meters provides only a qualitative measurement. Interpretation of the heating is limited by the inability to determine forward and reflected power levels.

Figure 59, proposed modifications to improve field uniformity.



To take advantage of improved temperature and power measurements the system should be interfaced with a computer to allow for constant data logging. A suitable lab management software package could also provide control, replacing the Eurotherm controller. Automated tuning should be installed for further progress of computer control, and facilitated by connecting the tuning stubs to servo drives.

Atmosphere control should also be set up, since many materials require processing under vacuum or in an inert atmosphere. Currently the system is limited to those materials which can be heated in air. By having atmosphere control the operating latitude is greatly increased.

The development work highlighted the need for further investigation of the susceptors. Although the graphite-alumina susceptors used were able to heat the zirconia, a more suitable susceptor shape and material may exist.

However, if the graphite-alumina susceptors are to be retained, it is felt that simultaneous temperature measurement of the samples and the susceptors is required, to address the uncertainty concerning the extent of microwave heating.

5.7 Conclusions.

A custom built multimode microwave oven, operating at 2.45GHz was developed to the stage where controlled hybrid heating of zirconia could be achieved. Development and commissioning of the equipment allowed for the fundamentals of microwave heating to be addressed, in particular temperature measurement and control, insulation and field uniformity.

Sheathed thermocouples worked satisfactorily in the microwave fields, however, due to the unavailability of a suitable sheathing material, high temperatures could not be measured. Although a single wavelength optical pyrometer allowed for high temperatures to be measured, there is some doubt over the accuracy of the readings due to variable emissivity.

During the trials it was not possible to generate uniform heating zones. This was due to the field distribution, and to a much lesser extent, the insulation. It was found that the insulation casket design affected heating characteristics, the temperature which could be generated being dependant on the thermal efficiency. It was also evident that the field distribution in the custom built multimode cavity was not uniform.

Several recommendations were made to improve the system. It is felt that these are warranted if an in depth study of microwave/matter interactions is to be undertaken.

"For a moment, I thought he was joking, and then I realised that he was serious, that the worst of the journey which I had thought was behind us was still ahead."

Wilfred Thesiger
Arabian Sands.

Chapter 6 Evaluation of Microwave System for Processing of Zirconia.

6.1 Background.

Although the initial aims of the development had not been fully realised, it was felt that sufficient work had been undertaken for those aims which still had not been achieved to be done so confidently with system modifications and upgrades. This is the basis of the recommendations of section 5.6.

Time constraints dictated that it was more prudent to conduct limited evaluation research than pursue the recommendations in section 5.6, even though it was apparent that the custom built microwave system had been developed to the limits of its current configuration.

It was envisaged that the evaluation work could be useful for several reasons. Evaluation would provide further insight into the operating capabilities of the system. This may have defined problems that had not been fully addressed with earlier development and it would also allow for a critical comparison with other hybrid heating systems cited in literature.

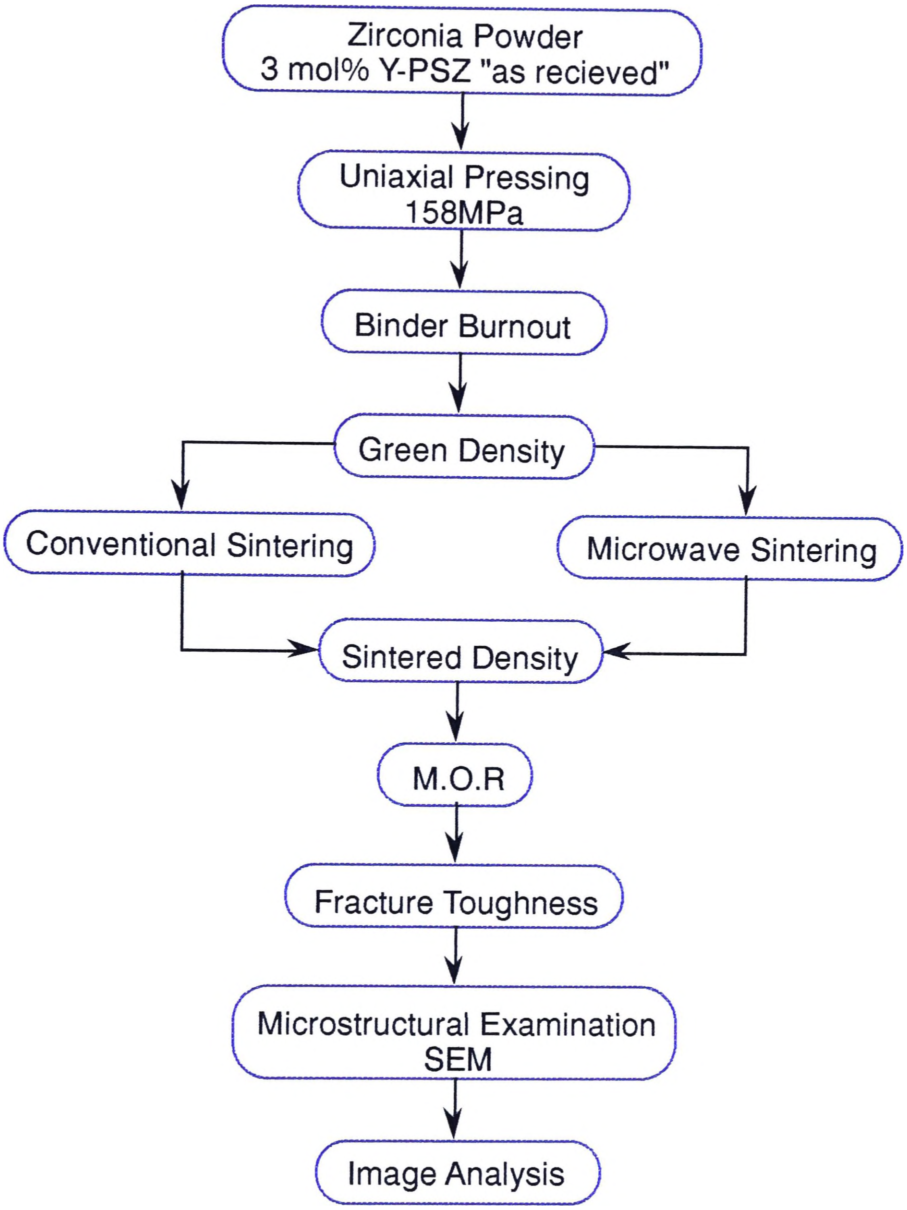
This chapter of the thesis describes research undertaken to evaluate the custom built microwave oven for processing of zirconia. In particular, sintering and ageing were studied in an attempt to qualify enhanced transport properties.

6.2 Sintering.

6.2.1 Experimental.

A series of comparitive sintering trials were performed with a 3mol% yttria partially stabilised zirconia utilising both conventional and microwave heating. A flow chart depicting the experimental work is shown in figure 60. The objective of the work was to determine whether heating in a microwave field resulted in enhanced densification.

Figure 60, Experimental Flowchart.



Zirconia samples were produced for sintering in the same manner as for those for the development work. Characteristics of the "as recieved" zirconia powder are given in Appendix B, whilst sample preparation is described in section 4.2.

Microwave sintering trials were carried out in the custom built oven using hybrid heating, provided by four graphite-alumina susceptors, descibed in 4.1. The sample/susceptor configuration used was that described in 5.3.2 (see figure 50). Sample temperatures were measured with the optical pyrometer using predetermined emissivity values, (Appendix C).

Heating profiles of 10, 15 & 50°C/min were followed to maximum sintering temperatures, where the samples were then left to oven cool. A comparison was provided by sintering in a conventional electric resistance furnace using heating profiles of 4, 10 & 15°C/min. Sintering temperatures ranged, in 50°C steps, between 1100°C and 1500°C.

Densities of the sintered samples were determined using the Archimedes method with distilled water as the immersion fluid, AS 1774.5 1989. The strength of the sintered discs (Modulus of Rupture, M.O.R) was determined using the biaxial flexure strength test, ASTM F394-78. The test rig was used in an Instron 4302 unit with a crosshead travel rate of 0.3mm/min. Fracture toughness was determined by the indentation method, where indents were made with a Vickers diamond indentor using a 30kg load.

After mechanical testing, selected samples were polished to a 1 micron finish for microstructural investigation on a scanning electron microscope, (Leica S440). The samples were thermally etched for 5 minutes at 1500°C. Grain size was measured from the photomicrographs using an image analysis system, (MD20 Flinders Imaging).

6.2.2 Results

A total of 108 zirconia samples were sintered in the custom built oven using controlled heating profiles. None of the samples cracked, nor did any observably warp. However, many of the samples had tapered profiles as during the development work.

Densities achieved at the sintering temperatures for both microwave and conventional heating are shown in figures 61 and 62. Figure 63 shows a direct comparison between the two techniques using the same heating profiles. Sintering produced maximum densities of 6072 kg/m^3 in the conventional oven and 6025 kg/m^3 in the microwave oven.

At the lower sintering temperatures microwave heating clearly resulted in higher densities. However, at sintering temperatures above 1400°C conventional heating was slightly superior.

Profiles of the conventional sintering density-temperature diagrams follow classical Arrhenius behaviour, that is, a smooth transition of density with temperature. The conventionally sintered samples exhibited little variation in density, (Appendix D), the standard deviation being too small for sufficient representation on the figures.

The standard deviation of densities for the microwave sintered samples were much wider. Profiles of the density-temperature diagrams only roughly follow Arrhenius behaviour, the transition of density with temperature not being less as well defined in comparison to the conventionally sintered samples.

Figure 61, Comparison of Heating Rates, Density vs Temperature.

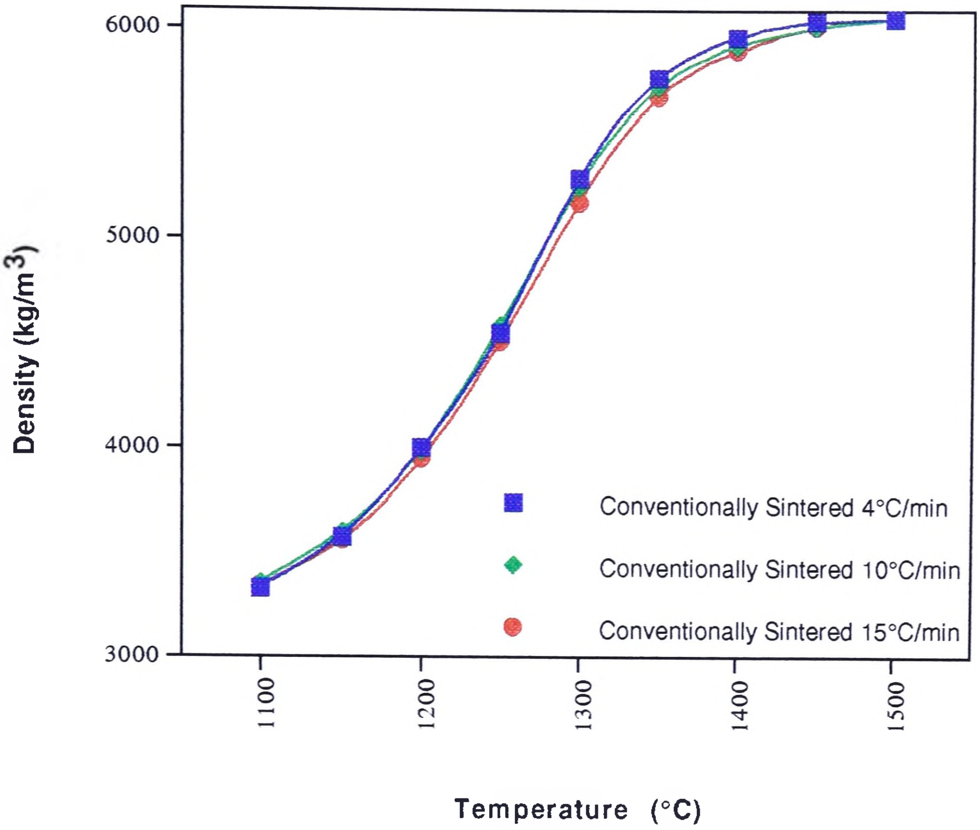


Figure 62, Comparison of Heating Rates, Density vs Temperature.

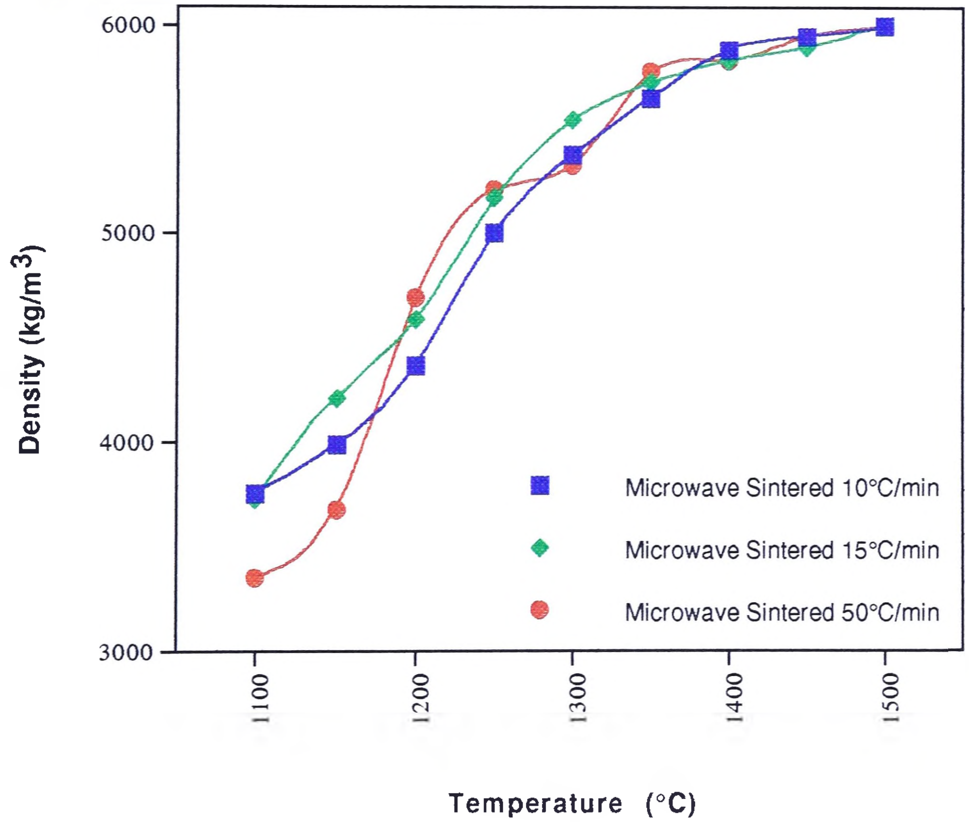
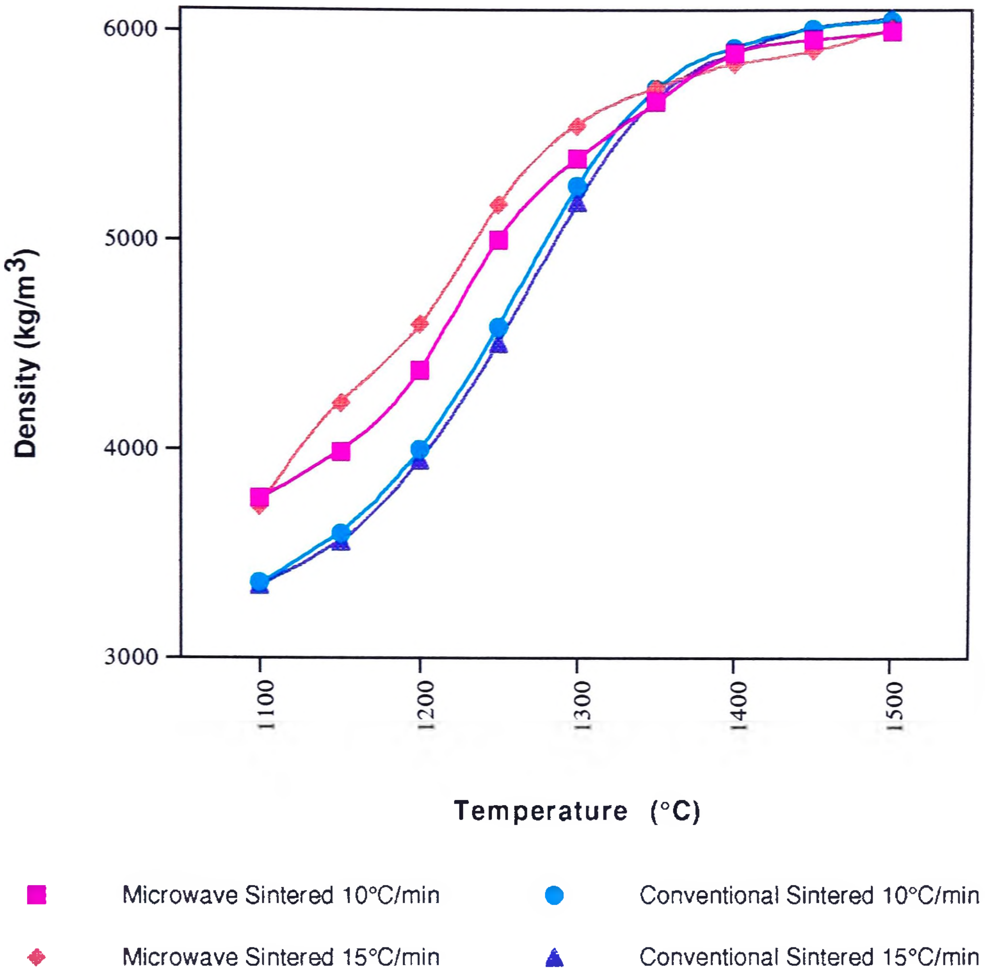


Figure 63, Comparison of Microwave to Conventional Sintering.



The biaxial flexural strength (M.O.R) of the sintered zirconia samples is shown in figures 64 and 65. Figure 66 shows a direct comparison between the two heating techniques using the same heating profiles. The general trend observed, as expected, was a strength increase with density. It was not possible to distinguish whether the conventional or microwave sintered samples had greater strength, since the limited number of samples resulted in considerable scatter in the M.O.R values obtained, especially for the more densified samples. The highest strength values measured for the zirconia were 1036MPa for conventional sintering and 1056MPa for microwave sintering, (Appendix E).

Figure 64, Comparison of Heating Rates, M.O.R vs Density.

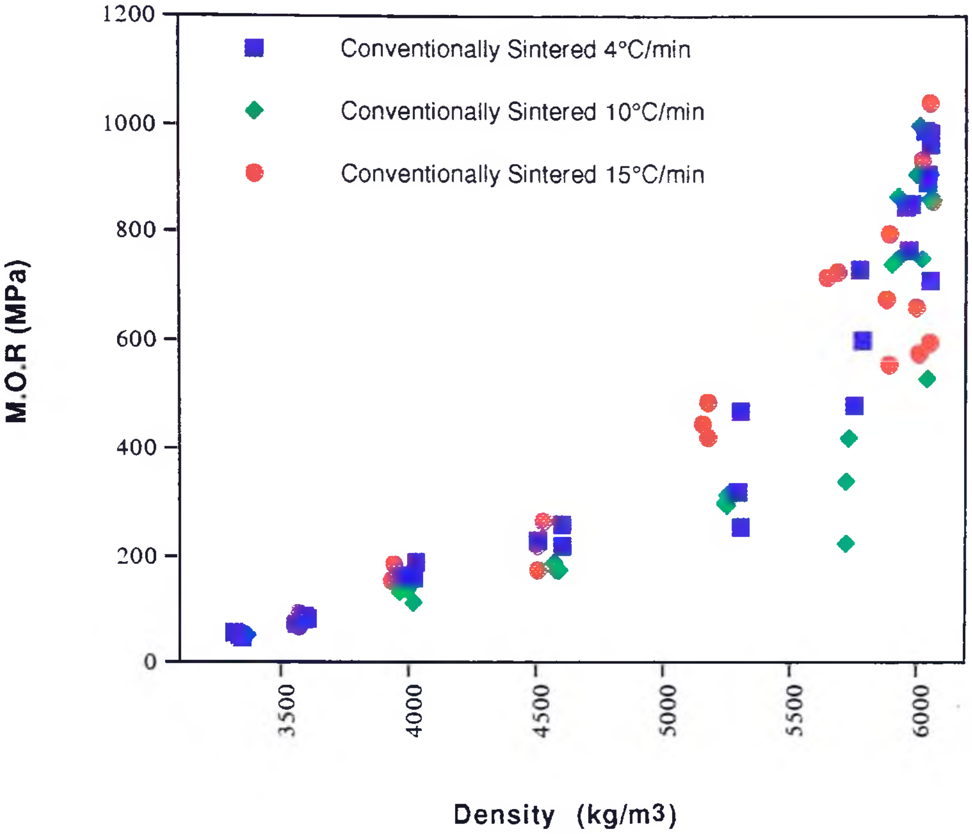


Figure 65, Comparison of Heating Rates, M.O.R vs Density.

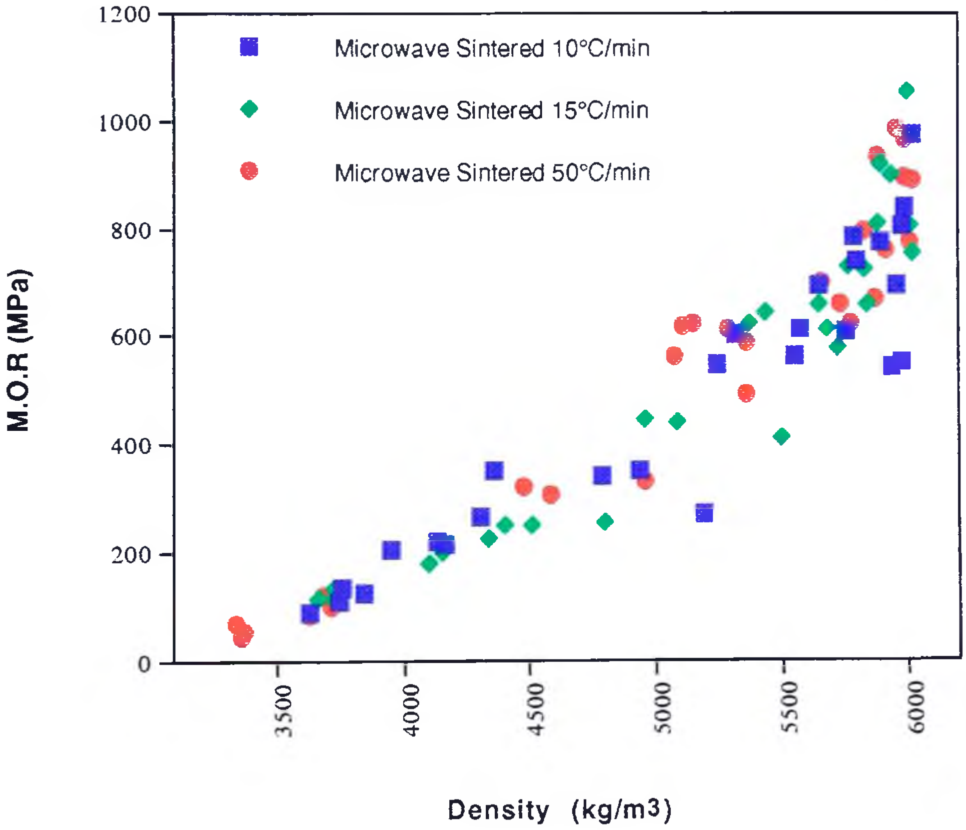
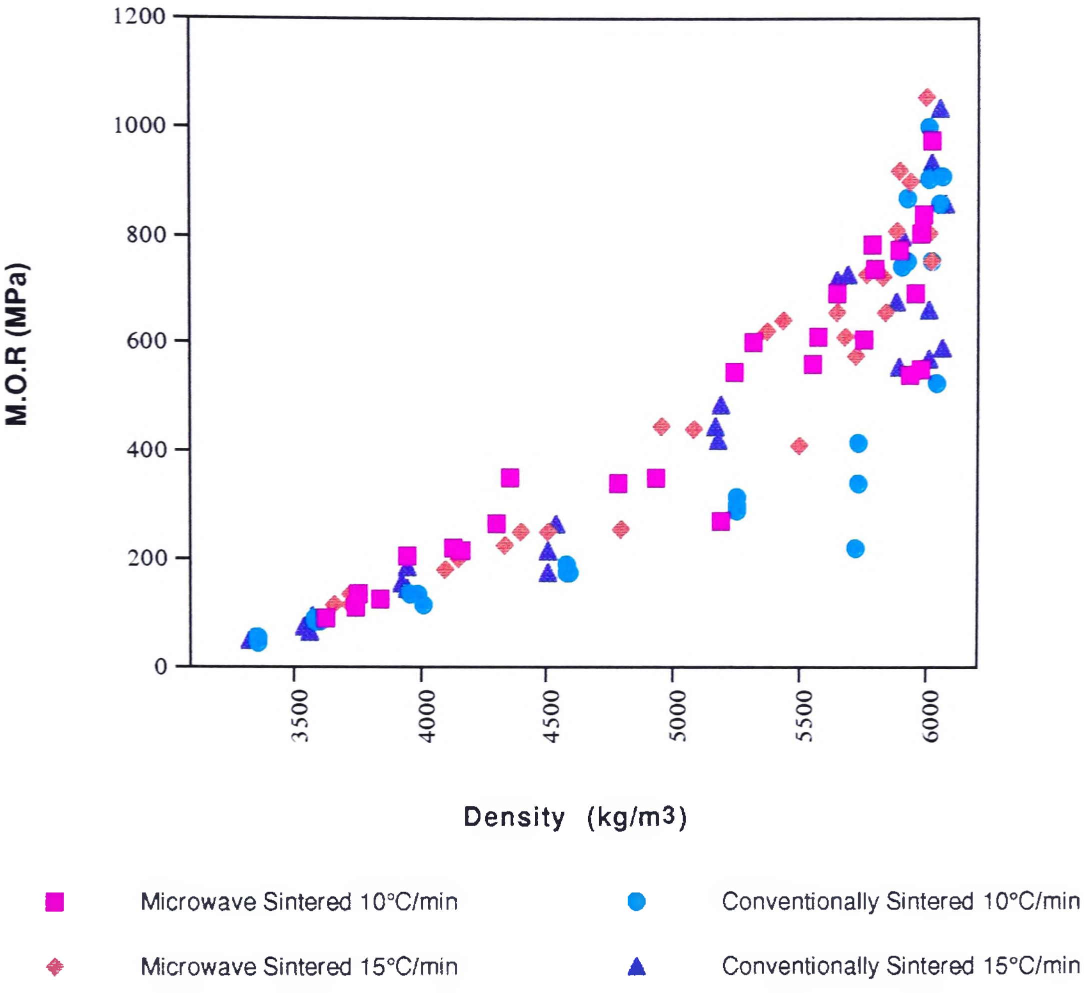


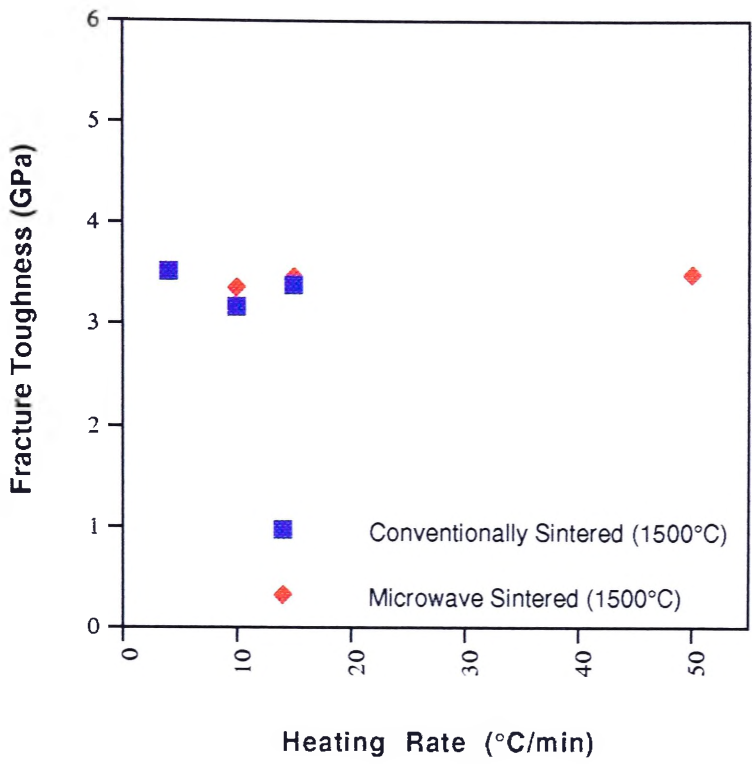
Figure 66, Comparison of Microwave to Conventional Sintering.



A limited number of samples were used to determine fracture toughness. Samples sintered at 1500°C from each of the heating rates were chosen for testing since these were likely to have the largest grain size and exhibit transformation toughening. Figure 67 shows fracture toughness results for both conventional and microwave sintered samples. The fracture toughness for all samples was approximately 3.5MPa√m (Appendix F). Transformation toughening was not observed. No further samples were tested since similar results were attained for all samples, independent of the heating route.

Microstructural evaluation of the zirconia sintered at 10°C/min showed little difference between conventional and microwave heating in terms of structure.

Figure 67, Fracture Toughness of Sintered Y-TZP.



The average grain size of conventionally sintered samples varied between 0.20 and 0.25µm, whilst for microwave sintered samples the variation was between 0.20 and 0.21µm, (Appendix G). Figure 68 shows a comparison of grain sizes for the two heating techniques. Increasing the sintering temperature had little effect on the grain size for microwave heating, compared to conventional heating which showed a slight increase in the grain size from 1450°C onwards. Cross sectional examination also showed that the grain size was relatively constant throughout the sample thickness. Figure 69 clearly shows that neither heating technique resulted in samples with grain sizes which were appreciably larger at the surface or the interior.

Evolution of the microstructures during sintering was similar for both microwave and conventional heating. As shown in figures 70 to 74, it is difficult to discern an observable difference between the structures produced by the two heating techniques.

Figure 68, Grain Size of Sintered Y-TZP.

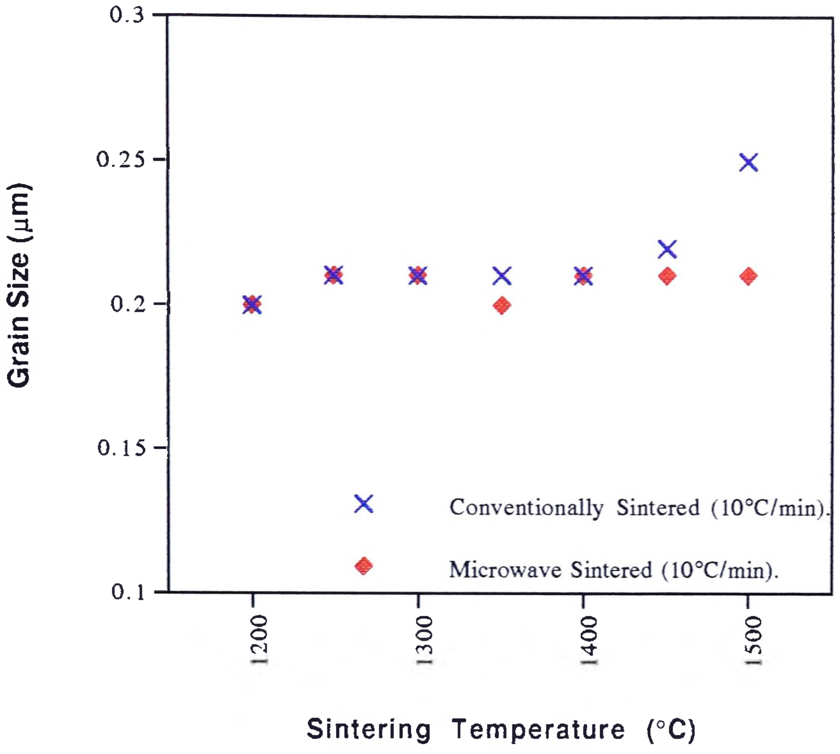


Figure 69, Variation of Grain Size Through Cross Section.

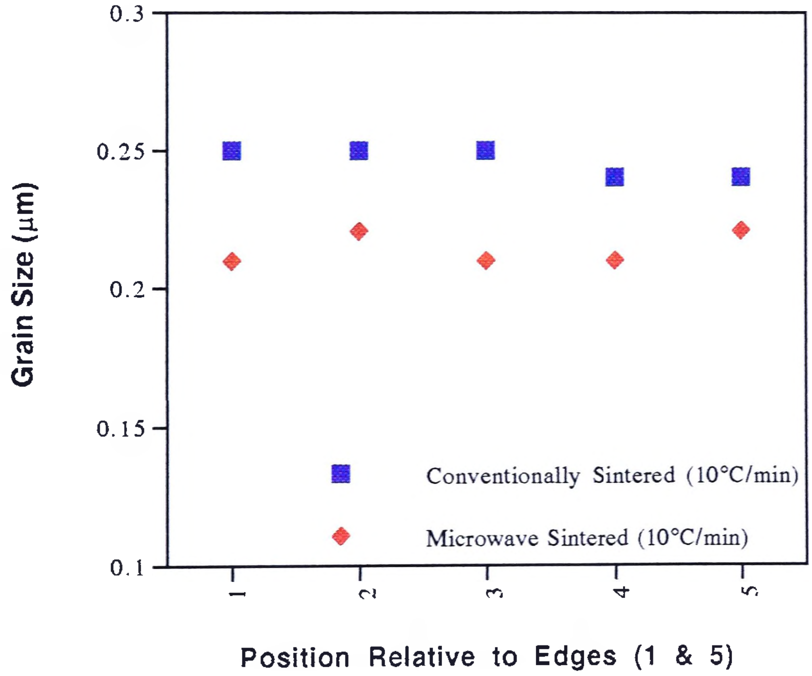


Figure 70A, Y-TZP Conventionally Sintered at 1100°C.

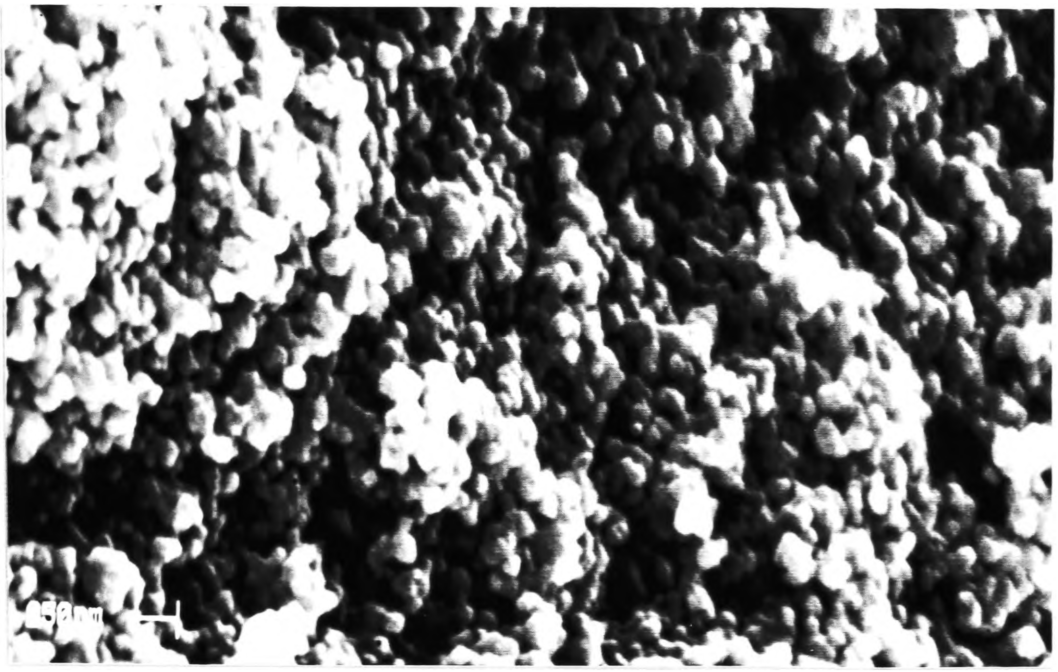


Figure 70A, Y-TZP Microwave Sintered at 1100°C.

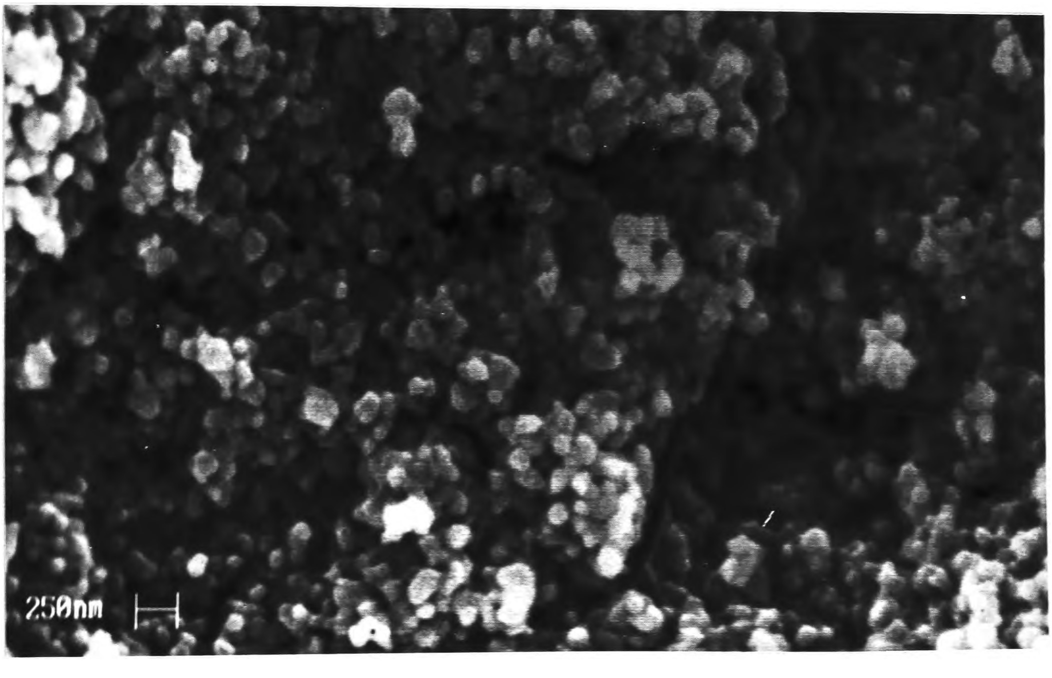


Figure 71A, Y-TZP Conventionally Sintered at 1200°C.

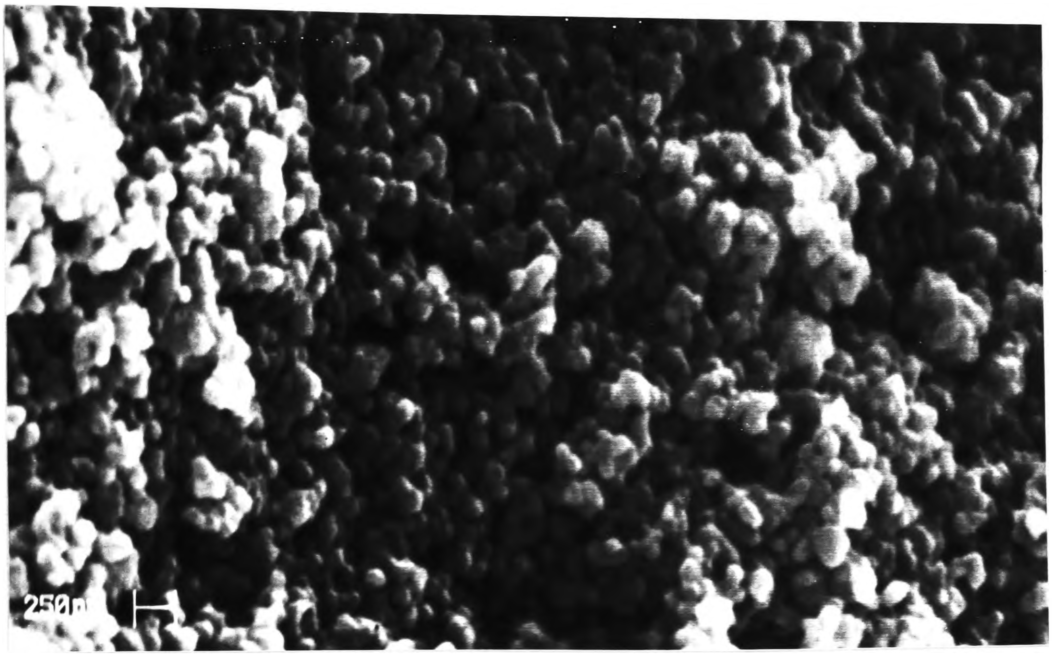


Figure 71A, Y-TZP Microwave Sintered at 1200°C.

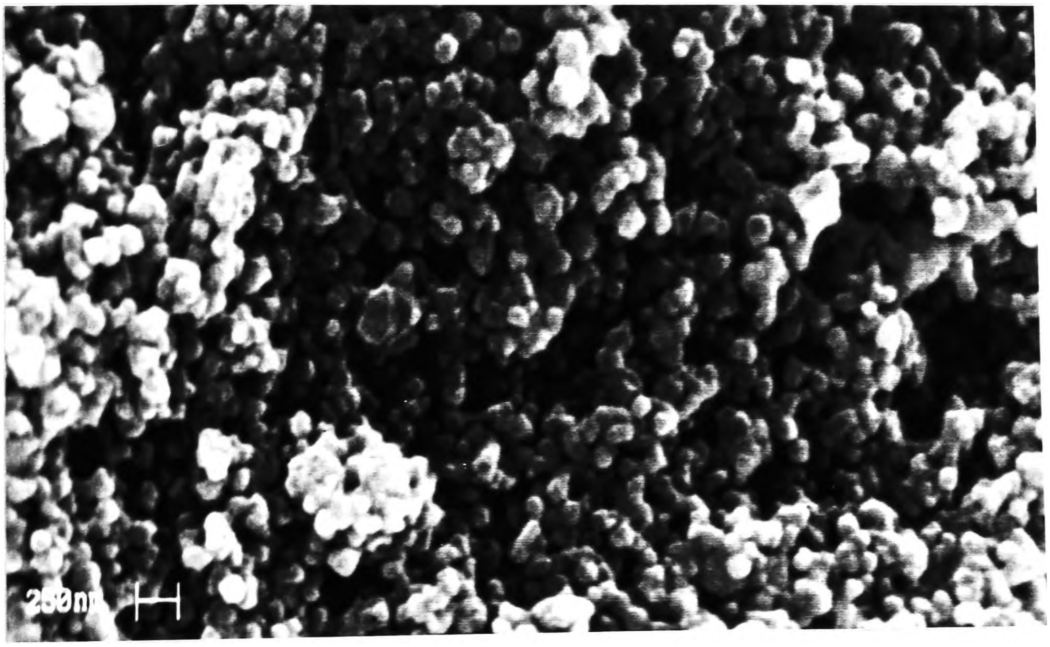


Figure 72A, Y-TZP Conventionally Sintered at 1300°C.

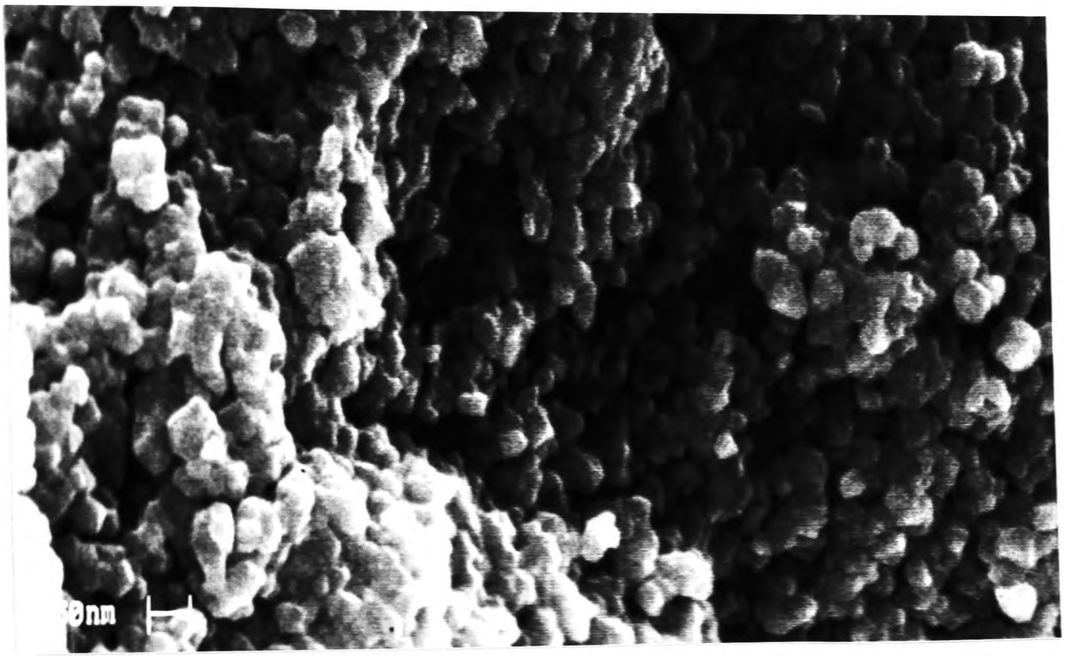


Figure 72A, Y-TZP Microwave Sintered at 1300°C.

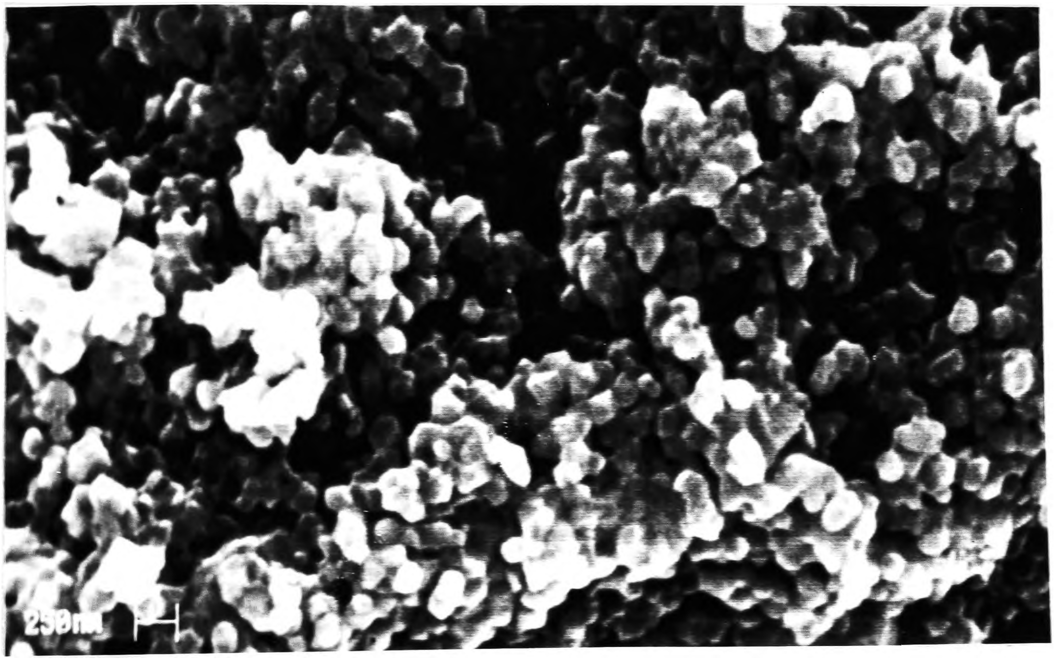


Figure 73A, Y-TZP Conventionally Sintered at 1400°C.

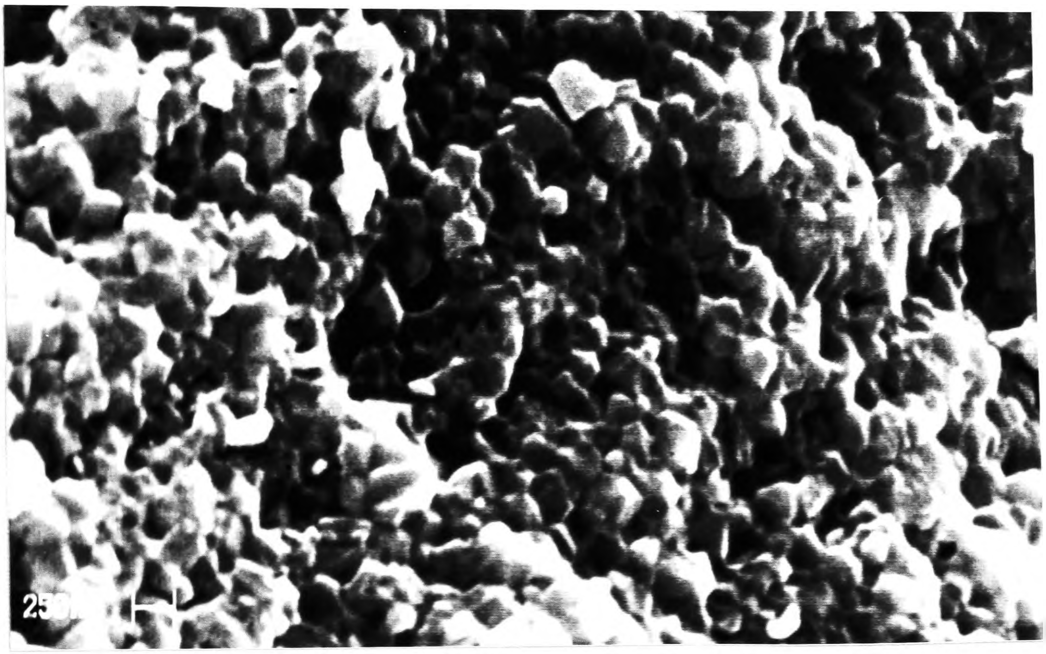


Figure 73A, Y-TZP Microwave Sintered at 1400°C.

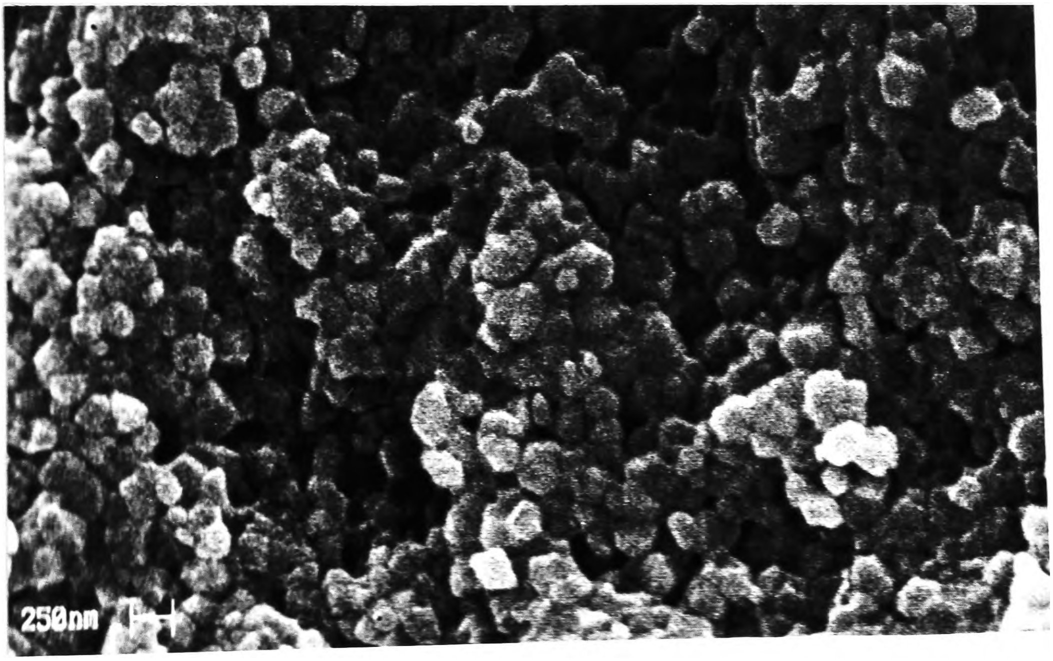


Figure 74A, Y-TZP Conventionally Sintered at 1500°C.

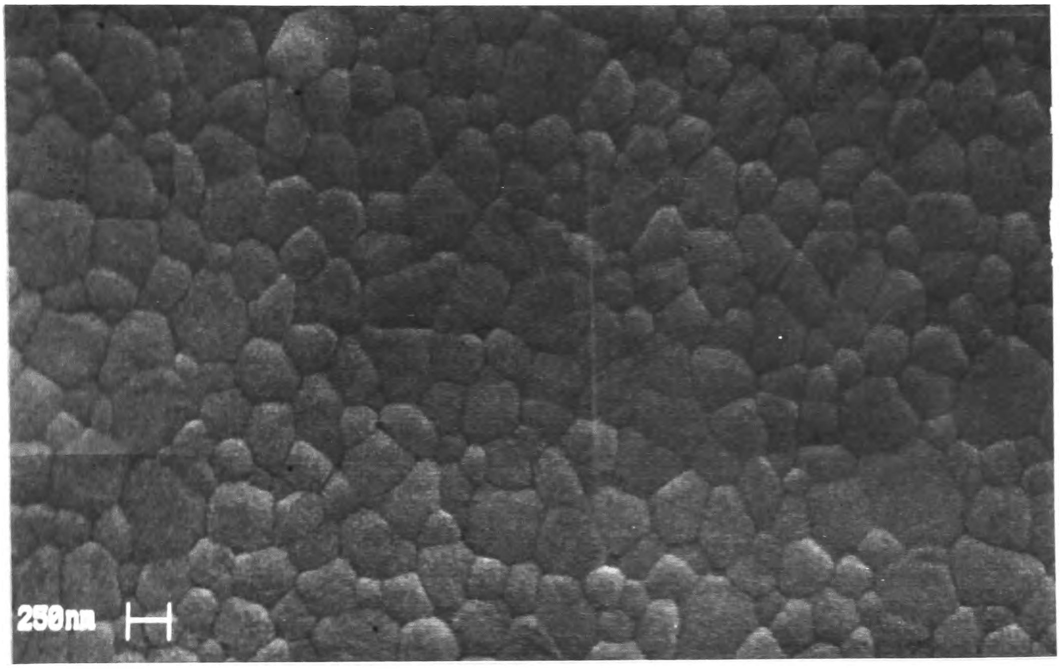


Figure 74A, Y-TZP Microwave Sintered at 1500°C.

6.3 Ageing.

6.3.1 Experimental Procedure.

Comparative ageing trials were undertaken with the microwave and conventional ovens to observe whether grain growth was enhanced by heating with microwave energy.

Green zirconia compacts were produced in the same manner and from the same powder as for sintering, described in 6.2.1. The green compacts were conventionally sintered using a slow heating schedule: 1°C/min from room temperature to 500°C, then 2°C/min from 500°C to 1500°C, a 2 hour dwell at 1500°C and then left to oven cool. This schedule enabled the zirconia samples to reach their theoretical density.

Ageing was carried out at 1500°C for dwell times of 1, 2, 5, and 10 hours. The samples were initially heated at 15°C/min and then left to oven cool after ageing.

Ageing trials in the microwave oven were conducted in the same manner as for sintering trials. The load and sample/susceptor configurations were maintained and temperature was measured with the optical pyrometer.

Evaluation of the aged zirconia samples was limited to microstructural examination. No mechanical testing was carried out. Polished and etched samples were examined with the SEM, and photomicrographs were analysed to determine the grain size, as described in 6.2.1. These were compared to the starting grain size to determine the extent of ageing.

6.3.2 Results.

Grain growth was achieved with both heating, techniques, however the conventional oven was found to be superior. Ageing in the microwave oven was not as effective and resulted in considerably less grain growth.

The zirconia aged by conventional heating showed an appreciable increase in grain size. After 10 hours of ageing the grains had grown from the initial diameter of 0.31µm up to 0.55µm. Overall grain growth was relatively constant, increasing almost linearly for the ageing times trialed.

Grain growth in the samples aged by microwave heating was not as constant as the growth for conventional heating. After 10 hours of ageing the average grain size had only grown to 0.39µm. Slower grain growth in the microwave heated samples is clearly shown in figure 75, (and Appendix H). The microstructural difference between the zirconia aged in the conventional and microwave ovens is best illustrated by comparing photomicrographs of samples aged for 10 hours, see figure 76.

Figure 75, Grain Size of Aged (1500°C) Y-TZP.

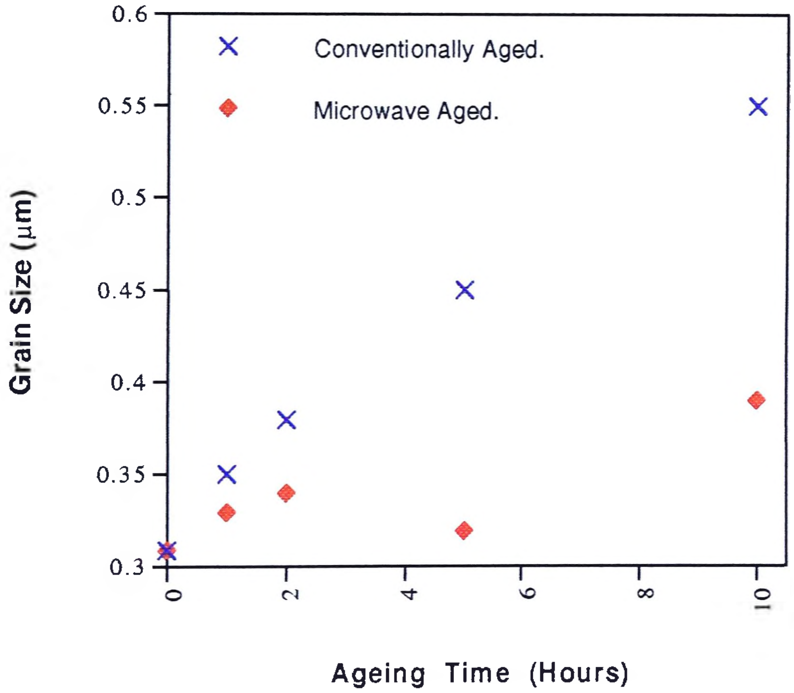


Figure 76A, Y-TZP Conventionally Aged for 10 hours at 1500°C.

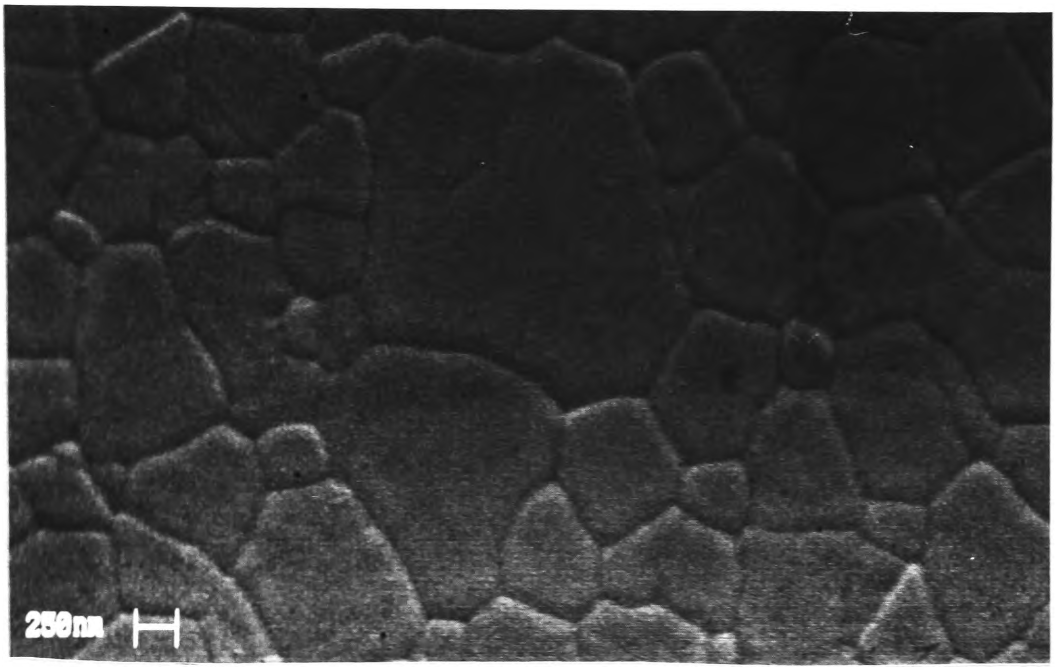
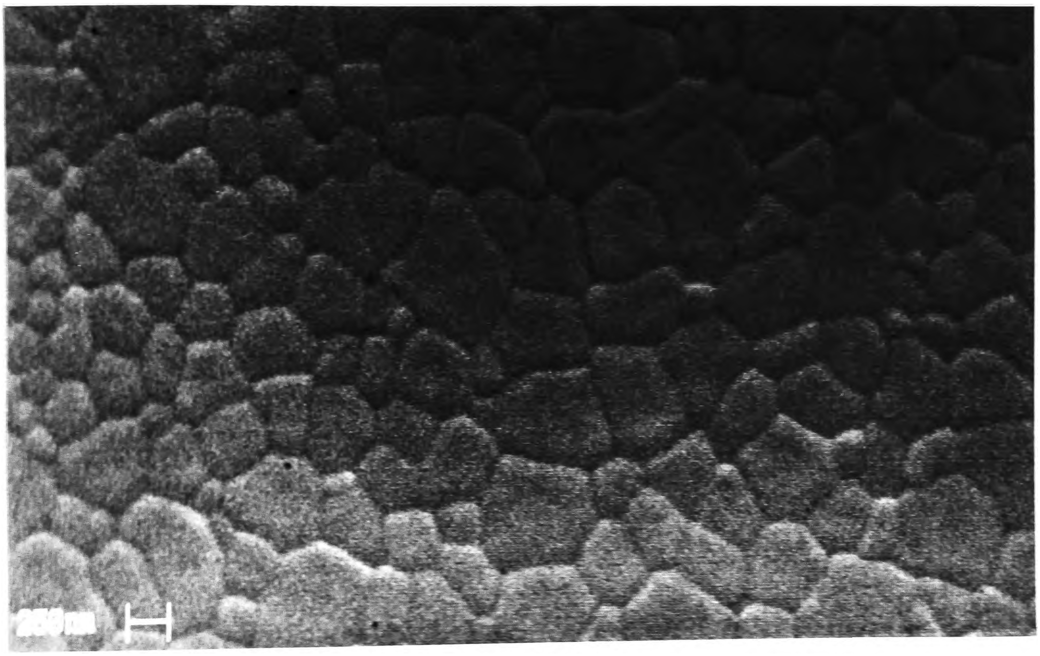


Figure 76A, Y-TZP Microwave Aged for 10 hours at 1500°C.



6.4 Binder Burnout.

Apart from the sintering and ageing trials, a minor investigation of binder burnout was undertaken. A series of comparative trials were carried out using conventional and hybrid microwave heating. The sample/susceptor arrangement was the same as that used in the sintering and ageing trials, described in section 5.3.2. Temperature was measured using a K-type thermocouple.

Green compacts of the zirconia powder were heated at 1°C/min to temperatures of 150, 200, 300, 450, and 600°C and were then left to oven cool. Weight loss was simply determined by weighing the samples before and after heating.

Binder was successfully removed from the compacts using hybrid microwave heating. Figure 77 shows the comparison of weight loss for the two heating techniques. The rates of binder removal for both heating techniques were similar, according to the results obtained, (Appendix I). Therefore it is not possible to say that the use of microwave energy enhanced the binder burnout process.

It was also found that the binder could be removed in the microwave oven without the use of the susceptors. A heating rate of 1°C/min was used, however, no set temperature was chosen as it was of more interest with this trial to determine the upper temperature to which the zirconia could be heated. A maximum temperature of approximately 650°C was attained at which stage the magnetron was operating at full power. The weight loss (3.55wt%) from the "pure" microwave heating was comparable to that due to hybrid microwave and conventional heating at 600°C.

A single trial was also carried out to determine the feasibility of using the custom built oven for thermal etching. Hybrid heating was used to etch a polished sample of sintered zirconia. The zirconia was heated at the fastest rate the system could be driven at (at times up to 200°C/min) and the temperature was held at 1500°C for a 10 minute dwell, after which the sample was removed from the oven. The microwave etched surface of the zirconia is shown in figure 78.

Figure 77, Weight Loss in Y-TZP due to Binder Burnout.

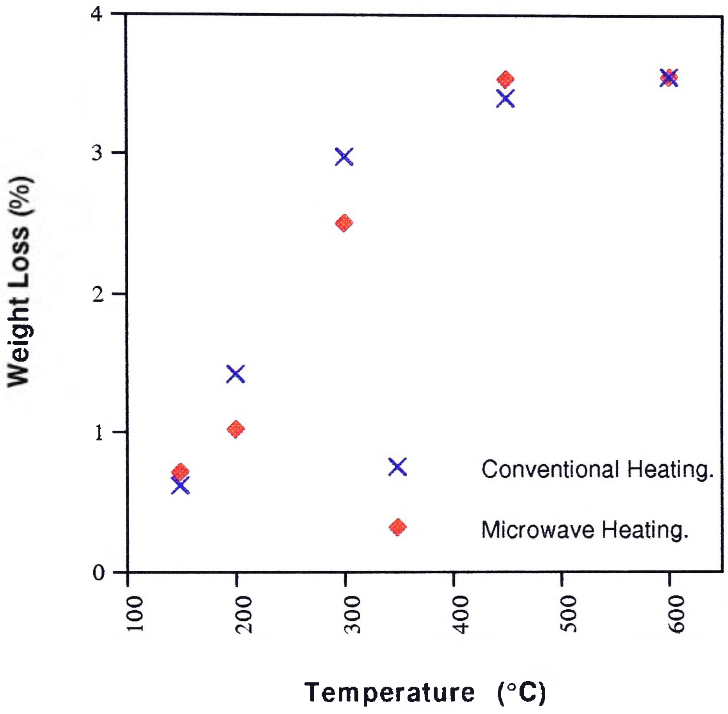
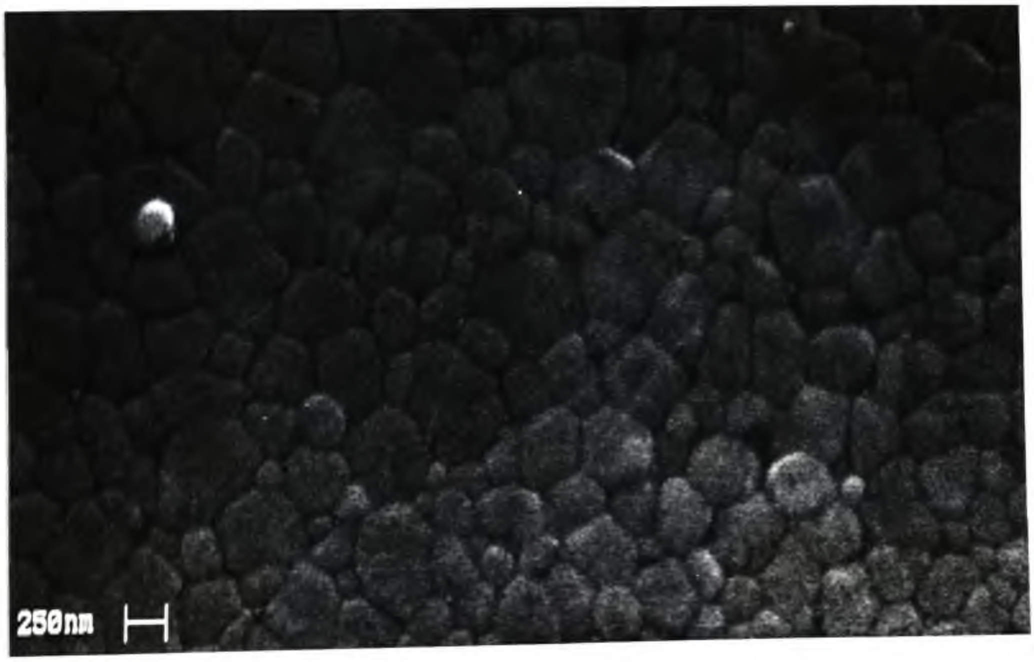


Figure 78, Microwave Thermally Etched Y-TZP.



6.5 Discussion.

Evaluation of the custom built microwave system indicated that the accuracy of the temperature measurement was questionable. This is based on the findings of the sintering and ageing trials.

Sintering in the microwave oven resulted in enhanced densification at the lower sintering temperatures (figure 63), however, at higher temperatures greater densities were achieved in the conventional oven.

Lower densities in the microwave sintered zirconia may have been due to: i) microwaves retarding the sintering process, ii) oversintering of the zirconia, or iii) the indicated temperature being incorrect.

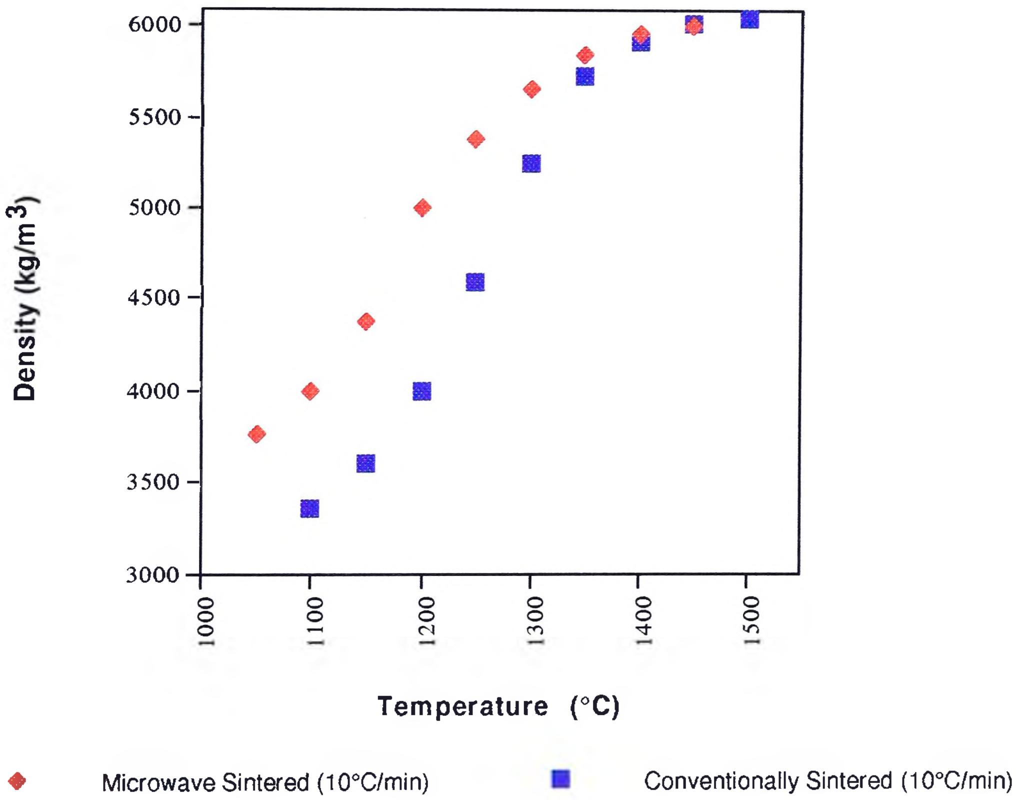
It is unlikely that the microwaves retarded the sintering process. This contradicts all findings cited in literature about the capabilities of microwave energy to enhance densification, including those observed during the trials at the lower sintering temperatures. Oversintering of zirconia can result in reduced densities. Shi et al[15] found for Y-TZP, maximum densities were produced at 1450°C, after which the densities sharply decreased, due to pore entrapment. During the sintering trials increasing temperature was at no stage found to decrease the sintered density, shown by the absence of a peak in the density-temperature curve. Additionally, it is expected that oversintering would be accompanied by grain growth, as seen from figure 68, where the grain size for the microwave sintered samples remained constant. The most plausible explanation for the lower densities at the higher sintering temperatures is that readings from the optical pyrometer were not indicative of the true sample temperatures.

Grain sizes of the conventional and microwave sintered samples were similar up until approximately 1400°C, see figure 68. The grain growth, which is usually associated with the final stages of sintering, was absent in the microwave sintered samples, however, the conventionally sintered samples exhibited some growth from 1450°C onwards. Enhanced grain growth was also absent in the zirconia samples aged by microwave heating. The temperature the microwave samples were heated to, provided less growth than that experienced by conventionally heated samples.

It is felt that based on the grain size analysis and the sintered densities, the temperature reading may have been as much as 50°C too high at 1500°C.

Erroneously high temperature readings explain lower sintered densities, as well as slower grain growth, in the aged samples. If the temperature was in error by as much as 50°C then the true density-temperature curve would appear different to that shown in figure 63. Assuming a constant 50°C error then the appearance of the density-temperature curve would more closely approach that shown in figure 79 (however, it is worth noting that it is unlikely that the error was constant).

Figure 79, Density of Sintered Y-TZP.



Temperature readings from the optical pyrometer were probably incorrect due to the emissivity value settings used. Either, the original calibration was misleading and generated false emissivity values, or there was a change in the system conditions between calibration and the evaluation work which sufficiently altered the emissivity, such as increased radiant heat from susceptors.

Uncertainty in temperature measurements makes it difficult to investigate the kinetics of sintering with any confidence. However, if the original data is assumed to be correct, the technique used by Wang and Raj[74] may indicate the relative activation energies for sintering. Wang and Raj[74] suggest that a higher peak temperature and rate for sintering implies a greater activation energy.

Figure 80, Sintering Rate versus Temperature.

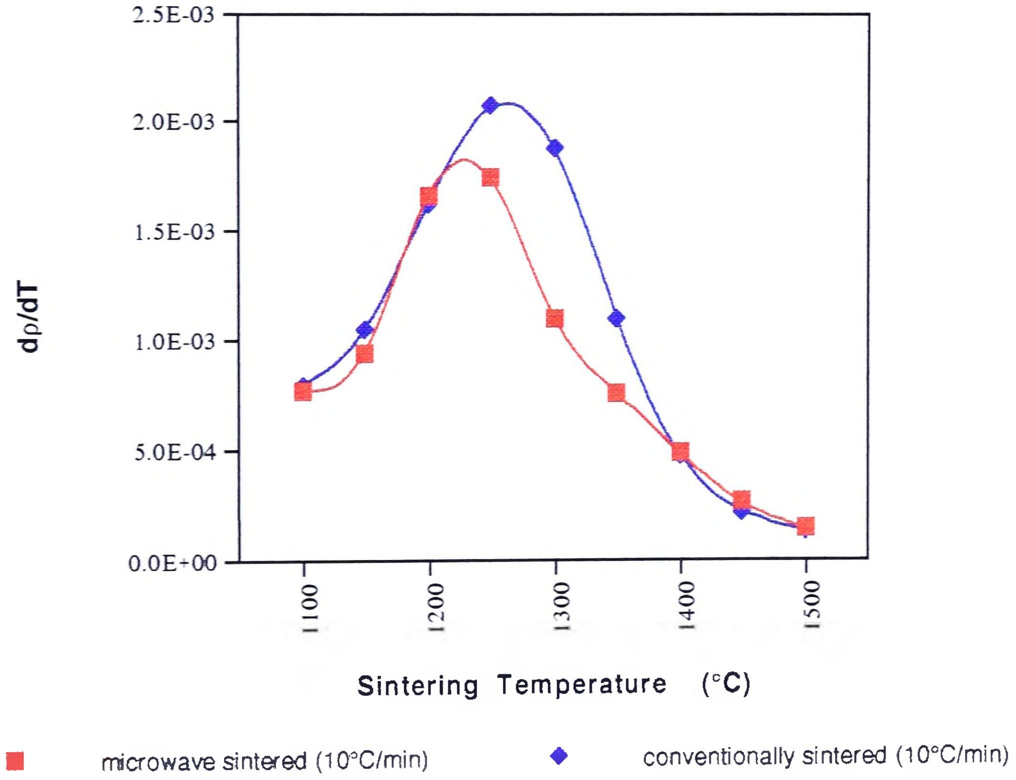


Figure 80 shows an approximation of $^{d\rho}/_{dT}$ for both microwave and conventionally sintered samples heated at 10°C/min. From the graph it is clear that the peak sintering rate for conventional heating is greater and occurs at a higher temperature than for microwave heating. Following the arguments of Wang and Raj[74] this would suggest that microwave sintering has a lower activation energy.

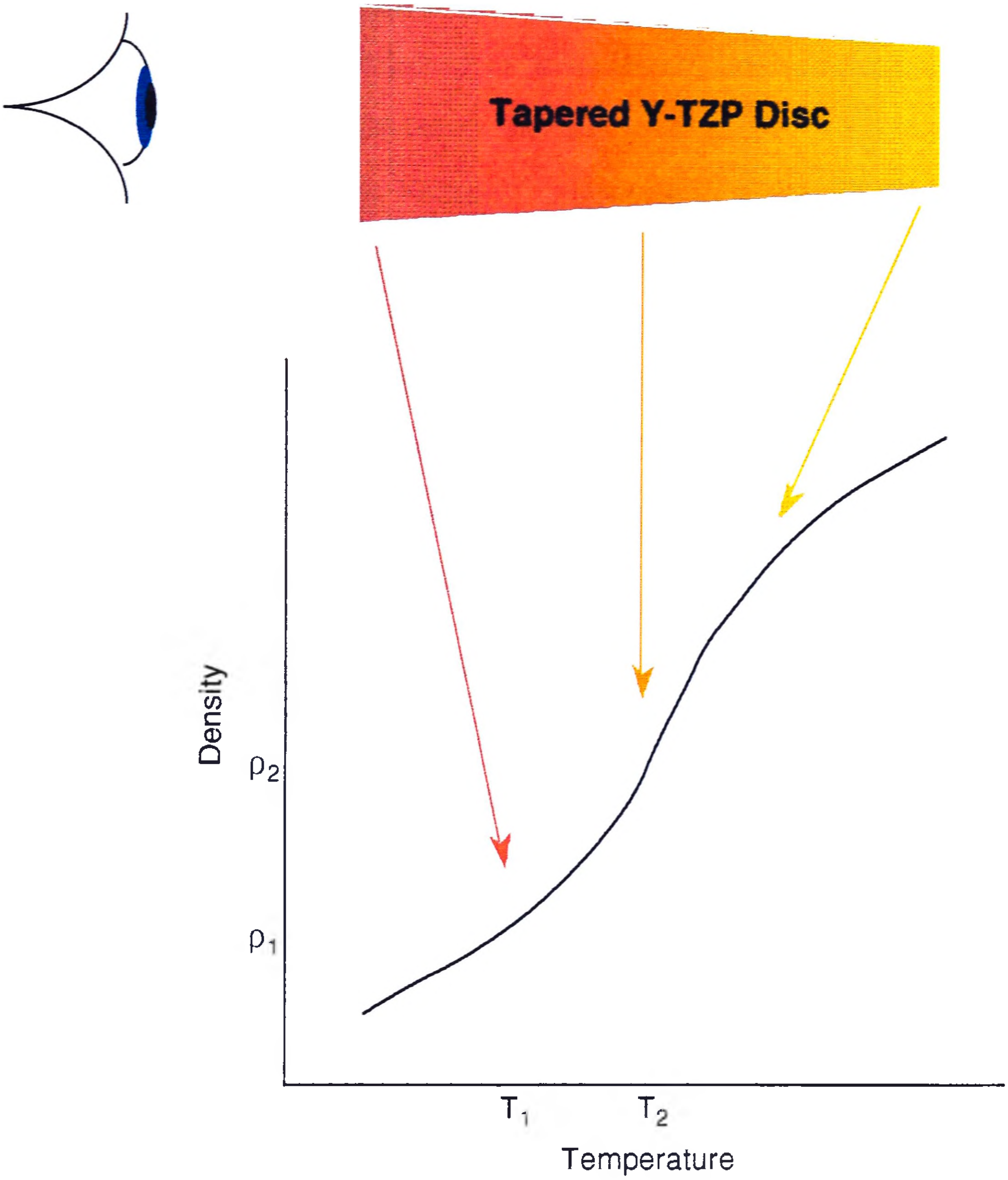
The analysis of the sintering kinetics was taken no further due to temperature inaccuracy, as well as differences in thermal gradients between the two heating techniques which may have complicated the interpretation. Thomas et al[75] question the validity of comparing sintering kinetics when there are large differences between thermal gradients, arguing that interpretation in such cases is impractical.

The existence of thermal gradients in the microwave heated samples, readily observed by the sintered samples being tapered, further confuses the interpretation of the sintering data.

Thermal gradients created in the samples during heating were a result of the hole required in the insulation for the optical pyrometer, which allowed for non uniform heat loss. The gradients meant that the surface temperature was not indicative of the average bulk temperature, but was actually lower. This has the effect of shifting the density-temperature curve artificially to the left. This is best illustrated in figure 81 (where T_1 is the measured surface temperature and T_2 is the average bulk temperature, ρ_1 and ρ_2 are the respective densities for samples sintered at temperatures T_1 and T_2).

Contradictions arise in interpretation of lower densities at higher sintering temperatures, and slower grain growth for microwave ageing, given that thermal gradients are argued to result in lower temperatures being measured. However, it is felt that the error in temperature readings from the pyrometer, due to incorrect emissivity settings, was far greater than that due to thermal gradients and measurement of the surface temperature.

Figure 81, Effect of Thermal Gradients on Density.



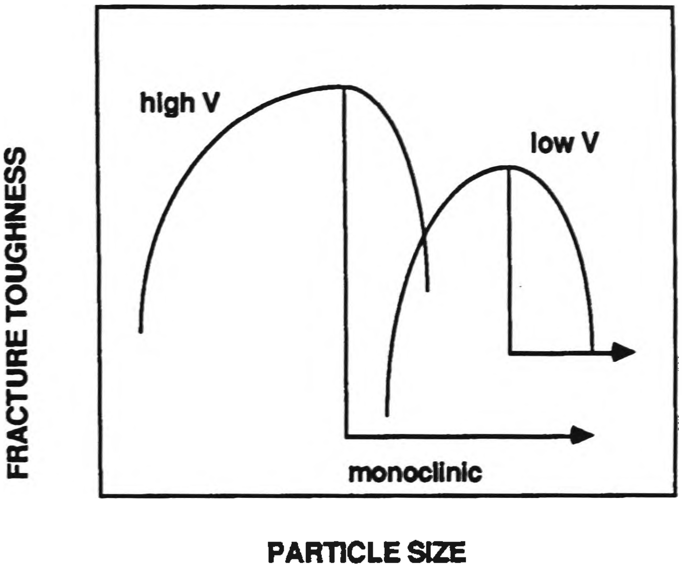
Sintered densities achieved with the microwave heating were comparable to that produced by Shi et al[15] and Plovnick and Kiggans,[62] who were also investigating 3mol% Y-TZP. Shi et al[15] were able to sinter zirconia to a density of 98.5% at 1500°C, while Plovnick and Kiggans[62] sintering at 1300°C achieved a density of 99%. Similar densities were also achieved by Samuels and

Brandon,[13] 98.5%, and Janney et al,[11] 99%. This compares with the maximum density of 99.2% achieved during sintering trials in this work.

Measured mechanical properties of the zirconia were as expected, given the grain size and limited number of samples tested. The grain sizes were similar, up until 1400°C, where the conventionally sintered samples underwent limited grain growth. Janney and Kimrey[14] suggest that smaller grain size is due to microwave energy enhancing the transport properties governing densification, rather than coarsening. Similarly microwave energy enhanced diffusion during ageing of the fully dense samples which resulted in greater grain growth. Although the predicted small grain size was observed for sintering, enhanced ageing was not. It is felt that inaccurate temperature measurement can explain these two contradicting observations.

Mechanical testing gave no indication that the property values were process dependent. It is more likely that they were simply structure dependent, since mechanical properties for both samples within the accuracy of the tests were similar. The flexural strengths for the fully dense samples were in the range reported in literature[97] (700-1000MPa), however, the fracture toughness values were somewhat lower (approximately 3.5MPa√m). Fracture toughness for 3mol% Y-TZP is typically 5.8-9.0MPa√m.[97] The indentation test produced indents and cracks that were well defined and developed, and no lateral cracking was observed, indicating that the results obtained were reasonably accurate. The low fracture toughness is a direct result of the grain size being too small for significant toughening to occur. Increasing grain size increases the extent of transformation toughening up to a critical size, where the tetragonal to monoclinic transformation becomes spontaneous, resulting in a decrease in fracture toughness. This is shown schematically in figure 82. It is likely that the fracture toughness of the aged samples was significantly higher, in particular the conventionally aged samples, due to their larger grain size.

Figure 82, Effect of Increasing Tetragonal Particle Size on Fracture Toughness. From Green, Hannink and Swain.[97]



Microwave heating was shown to be successful in removing the organic binder from the zirconia compacts, at a rate of removal which was similar for both conventional and microwave heating. Disagreeing with this, Moore and Clark[73] found that conventional heating was superior in all cases, while Harrison et al[16] found microwave heating removed the binder faster and at a lower temperature.

The load in the cavity was also found to effect power requirements during heating. Harrison et al[16] observed that, as sample weight decreased, so did the coupling efficiency. Although pure microwave heating required more power than hybrid heating, the binder was still removed. The reduced load in the cavity meant that to maintain the heating rate, the system was operating at full power towards the end of the cycle. The maximum temperature of 650°C that was reached, indicated that for the existing power capabilities of the system, susceptors are essential for heating to high temperatures.

The success of the binder removal trials suggests that it is feasible to combine binder burnout and sintering into a single microwave heating schedule. However, microwave thermal etching, does not appear to be a practical use of microwave energy. Plovnick and Kiggans[62] argue that microwave etching was worthwhile because it was a faster process and resulted in greater resolution of the microstructure. Even though etching was found to be possible using microwave energy, the microwave oven was more difficult to set up and insulation requirements meant a greater chance of surface contamination. The ease of use of a conventional oven makes microwave thermal etching an impractical option.

A critical comparison of the evaluation work with results cited in literature is at best difficult. A single description of what should be considered fundamental operating parameters was not located. Varying heating systems, power levels, heating schedules, material compositions and powder size, could all be expected to influence the final sintered properties. Similarly, mechanical testing to determine the effects of heating with microwave energy is also rarely reported.

Apart from stating the obvious, that the custom built microwave oven was used successfully for binder removal, sintering, ageing and thermal etching of zirconia, it is difficult to compare the performance of the oven, due to the lack of quantified descriptions. It is reasonable to assume that differences in the operating parameters in some cases may have had a greater effect than the heating technique itself.

6.6 Conclusions.

Evaluation of the custom built microwave oven provided an insight into the systems capabilities for processing zirconia. Hybrid microwave heating was used successfully for binder removal, sintering, ageing and thermal etching of a 3mol% Y-TZP. However, the comparative studies of sintering, ageing and binder removal did not confirm that heating with microwave energy enhances processing.

A large number of zirconia samples were sintered, to near theoretical densities for heating rates of 10, 15 and 50°C/min. Microwave heating resulted in higher densities at lower sintering temperatures, however, above 1400°C conventional heating was superior.

Microstructural analysis showed that the grain size of the microwave and conventionally sintered samples were similar. The mechanical properties were determined to be typical for Y-TZP, although the small grain size ensured that transformation toughening did not occur and as a result fracture toughness values were low. Although limited, the mechanical testing and microstructural analysis indicated that the properties may simply be structure rather than process dependent.

The grain growth for the microwave aged samples was considerably less than the conventionally aged samples. The most plausible explanation for the ageing and sintering behaviour is that the temperature readings were inaccurate. Temperature measurement was recognised as a potential problem during development of the microwave system, and verified by the evaluation work.

The inaccuracy of temperature readings meant that interpretation of the experimental data, in particular the sintering kinetics, was carried out with little confidence. Before any further work is undertaken, it is felt that the recommendations of section 5.6 should be acted upon, in particular the problem of temperature measurement.

"It was as if I had burst through the bottom of my plans and was falling through darkness..............This was not the time or place to reflect on the futility of the trip."

Paul Theroux
Worst Journeys
Picador Book of Travels

Chapter 7 Conclusions.

A custom built multimode 2.45GHz microwave oven was developed, commissioned and evaluated for thermal processing of a commercial grade of zirconia.

The fundamentals of microwave heating and control were addressed during development and controlled hybrid heating of zirconia was achieved. Temperature measurement in the microwave field was achieved with both an optical pyrometer and a thermocouple, however evaluation highlighted problems with both techniques. In particular, the temperature readings indicated by the optical pyrometer appear to have been inaccurate due to variable emissivity. Difficulties were also encountered in trying to attain a uniform heating zone due mainly to non uniform field distribution.

Comparative experiments using conventional and hybrid microwave heating were used to evaluate the suitability of the custom built microwave oven for thermal processing of a 3mol% Y-TZP. It was successfully demonstrated that the custom built oven was suitable for sintering, ageing, thermal etching and binder burnout of zirconia. However, interpretation of experimental data to investigate enhanced processing due to interactions with the microwave field was carried out with little confidence. In particular it was unresolved whether material properties were process or merely microstructurally dependant.

As a result of the development and evaluation work several recommendations were made to improve the overall heating and control characteristics of the custom built microwave oven. Subsequent trial work has seen many of these recommendations incorporated into the system, specifically in the areas of temperature measurement, computer control, data logging, and field uniformity.

As recommended a Pt/Rh, sheathed R type thermocouple has been obtained, for measuring temperatures. This new thermocouple allows for accurate temperature measurements up to 1650°C without many of the problems encountered during development. The small diameter (1.6mm) of the thermocouple ensures that perturbation of the field is minimal.

Control of the system has been changed from the Eurotherm controller to a PC running the Labview software package. This, as predicted, has resulted in effective management of the system parameters and greater operating flexibility particularly in data logging, with considerable scope for expansion with further development.

The problem of attaining a uniform heating zone in the custom built oven has been overcome by adopting the thermocouple as the technique for measuring temperature. Heat loss through the insulation casket is more uniform with the thermocouple arrangement as compared to the optical pyrometer. A mode stirrer installed in the lid of the oven as recommended, has resulted in statistically more uniform field distributions. This is reflected by the higher and more uniform sintered densities being achieved.

As many of the recommendations of section 5.6 to improve the overall performance have been acted upon, and proven successful, it is reasonable to claim that the custom built microwave oven is now suitable for investigating the fundamental phenomena of microwave heating.

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Appendix A Electromagnetic and Microwave Equations.

1)
$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

2)
$$\mu^* = \mu' - j\mu''$$

3)
$$\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'}$$

4)
$$P_{abs} = 2\,\pi\, f\, \varepsilon_0\, \varepsilon_r''\, E^2$$

5)
$$P_d = \frac{3\lambda_0}{8.686\,\pi\,\tan\delta\left(\frac{\varepsilon_r}{\varepsilon_0}\right)^{\frac{1}{2}}}$$

6)
$$\frac{\partial T}{\partial t} = P[k_a + k_m f(T)] - \sigma T^4$$

7)
$$\frac{\partial T}{\partial t} = \frac{0.556 \times 10^{-10}\, \varepsilon''\, f\, E^2}{\rho\, C_p}$$

8)
$$P = \frac{C_p\, k\, \Delta T\, m}{t}$$

Appendix A List of Symbols.

ε^*	- complex permittivity
ε'	- dielectric constant
j	- $\sqrt{-1}$
ε''	- dielectric loss factor
μ^*	- complex permeability
μ'	- magnetic permeability
μ''	- magnetic loss factor
$\tan \delta$	- loss tangent
ε''_r	- relative dielectric loss factor
ε'_r	- relative dielectric constant
P_d	- penetration depth
λ_0	- incident wavelength
E	- electric field strength
f	- frequency
P	- power
$k_{a \& m}$	- coefficients related to absorption
σ	- Stephen Boltzman Constant
T	- temperature
t	- time
C_p	- heat capacity
m	- mass
ρ	- density
ε_0	- permittivity of free space.

Appendix B Zirconia Powder Characteristics.

The zirconia samples used during this research were made from a 3 mol% yttria partially stabilised zirconia powder specifically SY-P Ultra 5.2 from Z tech, ICI.

Chemical Analysis	
Y_2O_3	5.1 wt%
SiO_2	70ppm
Al_2O_3	50ppm
Fe_2O_3	60ppm
TiO_2	100ppm
CaO	50ppm
S	60ppm
HfO_2	1.8 wt%

Particle Size Distribution	
- 0.1μm	10%
- 0.3μm	50%
- 0.6μm	90%

Surface Area	14m^2/g (BET)
Loss on Ignition (@ 1100°C)	4.0% (includes binders)

Appendix C Emissivity Values of Zirconia.

400°C	0.74	450°C	0.74
500°C	0.73	550°C	0.71
600°C	0.69	650°C	0.66
700°C	0.64	750°C	0.60
800°C	0.56	850°C	0.50
900°C	0.47	950°C	0.44
1000°C	0.43	1050°C	0.43
1100°C	0.43	1150°C	0.45
1200°C	0.48	1250°C	0.54
1300°C	0.57	1350°C	0.59
1400°C	0.61	1450°C	0.62
1500°C	0.63		

Appendix D Sintered Densities.

Conventionally Sintered Y-TZP

Density (kg/m^3)			
Sintering Temperature (°C)	Heating Rates		
	4°C/min	10°C/min	15°C/min
1100	3334	3361	3333
	3343	3363	3355
	3336	3353	3352
	3320	3365	3342
1150	3606	3594	3546
	3595	3594	3568
	3554	3607	3543
	3565	3607	3575
1200	4030	3964	3948
	4019	3999	3931
	3974	3998	3959
	3973	4017	3951
1250	4611	4576	4506
	4611	4586	4506
	4496	4595	4489
	4507	4593	4534
1300	5311	5253	5182
	5310	5248	5166
	5240	5263	5166
	5300	5254	5184
1350	5784	5721	5648
	5794	5728	5692
	5759	5728	5681
	5740	5734	5686
1400	5979	5908	5894
	5973	5929	5900
	5946	5923	5902
	5957	5928	5883
1450	6043	6014	6020
	6037	6008	6013
	6048	6014	6021
	6047	6024	6008
1500	6061	6058	6072
	6057	6059	6053
	6059	6050	6041
	6062	6047	6061

Appendix D Sintered Densities.

Microwave Sintered Y-TZP

Density (kg/m^3)			
Sintering Temperature (°C)	Heating Rates		
	10°C/min	15°C/min	50°C/min
1100	3637	3665	3361
	3752	3727	3379
	3809	3801	3364
	3842	3733	3340
1150	3759	4099	3637
	3952	4159	3682
	4116	4277	3695
	4138	4337	3721
1200	4164	4396	4473
	4301	4506	4582
	4487	4661	4776
	4355	4795	4951
1250	4780	4956	5072
	4933	5082	5144
	5102	5259	5296
	5189	5371	5360
1300	5238	5436	5103
	5319	5498	5356
	5410	5587	5581
	5573	5678	5283
1350	5553	5645	5659
	5651	5726	5736
	5697	5782	5843
	5757	5761	5872
1400	5791	5784	5773
	5802	5838	5831
	5876	5861	5874
	5898	5877	5878
1450	5940	5825	5916
	5953	5938	5953
	5965	5956	5955
	5974	5893	5986
1500	5988	6005	5992
	5975	5998	6013
	6015	6025	5987
	6018	6016	6018

Appendix E Modulus of Rupture.

Conventionally Sintered Y-TZP

M.O.R (MPa)			
Sintering Temperature (°C)	Heating Rates		
	4°C/min	10°C/min	15°C/min
1100	52	45	47
	48	54	54
	55	52	55
1150	85	90	74
	88	86	65
	90	86	95
1200	187	133	185
	157	136	152
	162	114	146
1250	259	187	175
	219	174	217
	229	173	264
1300	469	314	421
	253	300	444
	321	292	487
1350	732	222	716
	602	340	728
	482	418	-
1400	852	740	556
	765	753	799
	848	868	678
1450	905	999	933
	988	905	573
	892	751	663
1500	711	860	856
	981	909	1036
	964	528	856

Appendix E Modulus of Rupture.

Microwave Sintered Y-TZP

M.O.R (MPa)			
Sintering Temperature (°C)	Heating Rates		
	10°C/min	15°C/min	50°C/min
1100	87	114	45
	109	136	54
	123	114	70
1150	136	180	84
	203	200	118
	219	226	101
1200	217	251	322
	265	251	306
	350	257	332
1250	338	448	563
	352	439	621
	272	622	492
1300	548	643	615
	603	413	586
	613	613	610
1350	561	657	698
	693	576	655
	609	727	665
1400	785	738	623
	738	658	795
	772	809	932
1450	540	723	757
	693	896	986
	553	920	962
1500	837	803	892
	803	1056	774
	837	751	888

Appendix F Fracture Toughness and Hardness.

Conventionally Sintered (1500°C) Y-TZP.

	4°C/min	10°C/min	15°C/min
Hv (30kg)	1373	1388	1374
True Hardness (GPa)	14.53	14.69	14.54
Fracture Toughness (GPa)	3.52	3.18	3.38

Microwave Sintered (1500°C) Y-TZP.

	10°C/min	15°C/min	50°C/min
Hv (30kg)	1390	1376	1342
True Hardness (GPa)	14.67	14.56	14.20
Fracture Toughness (GPa)	3.37	3.47	3.49

Appendix G Grain Sizes.

Y-TZP Sintered at 10°C/min.

Sintering Temperature (°C)	Conventionally Sintered Grain Size (µm)	Microwave Sintered Grain Size (µm)
1200	0.20	0.20
1250	0.21	0.21
1300	0.21	0.21
1350	0.21	0.20
1400	0.21	0.21
1450	0.22	0.21
1500	0.25	0.21

The grain size values listed above and in Appenidx H are the average spherical grain sizes determined using ASTM E112-88.

Appendix H Grain Sizes.

Y-TZP Aged at 1500°C.

Ageing Time (hours)	Conventionally Aged Grain Size (µm)	Microwave Aged Grain Size (µm)
0	0.31	0.31
1	0.35	0.33
2	0.38	0.34
5	0.45	0.32
10	0.55	0.39

Appendix I Binder Burnout.

Heated at 1°C/min.

Burnout Temperature (°C)	Conventionally Heating Weight Loss (%)	Microwave Heating Size Weight Loss (%)
150	0.63	0.72
200	1.42	1.03
300	2.99	2.50
450	3.40	3.53
600	3.56	3.56