Microwave Sintering of Esthetic Dental Materials

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Contents

List of Figures

List of tables

1. Abstract

Dental materials are routinely used to restore broken, lost or carious (i.e., diseased) tooth structure. Among the esthetic materials that are available, dental ceramics (e.g., zirconia) are popular choices for crown and bridge fabrication. Traditional techniques for sintering/processing dental ceramics include the use of conventional electric heating ovens. The existing sintering process (from a green state to a fully sintered state) for a zirconia dental ceramic takes about 7 to 10 hours to complete. However, alternate techniques including the use of microwave energy has been shown to be beneficial for processing ceramics. A research microwave (operating frequency of 2.45 GHz and maximum power input of 2 kW) was utilized to sinter zirconia (3 mol% yttria-stabilized zirconia) dental materials. Various configurations (i.e., strips, pellets and actual tooth copings) of the zirconia materials were sintered in the microwave furnace. The least time required to sinter the zirconia materials was studied. The sintered materials were characterized for their microstructural and mechanical properties. This included the study of grain size distribution and porosity, three-dimensional shrinkage, hardness, fracture toughness and flexural strength. The results of our study showed that microwave sintering provided an effective alternative to conventional sintering techniques. The overall mechanical and microstructural properties of the microwave sintered zirconia materials were comparable with conventionally sintered equivalents. The specimens sintered with and without hold times showed a linear rise in the hardness values based on their maximum sintering temperatures, with specimens sintered at 1400 °C and 1450 °C with a hold time of 5 minutes showing the highest hardness. The fracture toughness values were highest for specimens sintered at a maximum sintering temperature of

1400 °C with and without a hold time of 5 minutes. The average grain sizes observed for the fully sintered specimens in microwave fields were 0.5 μm to 1 μm, with some specimens showing grain sizes that were smaller than 0.3 μm. All values from the characterization tests were within prescribed guidelines (i.e., ISO standards for dental ceramic materials) for dental applications.

1. Introduction

Esthetic dental materials (e.g., zirconia ceramics and porcelain-fused-to-metal dental restorations) are popular choices for the treatment of patients who require dental rehabilitation due to various reasons (1-4). The most common types of dental crowns include all-ceramic and porcelain-fused-to-metal (PFM) restorations, albeit other variations (e.g., composites and polymer crowns) are indicated for use in some clinical situations. Since the introduction of all-ceramic and PFM dental crowns, several areas of research have been conducted with respect to improvements in the mechanical, optical and microstructural properties of these dental materials. In addition, dental researchers have sought novel techniques in the past and currently to minimize the processing times that are necessary for fabricating these dental materials. There has been a growing demand for esthetic dental materials, which has been fueled by the increase in patient demands along with concurrent improvements in material properties and clinical performance. According to the latest figures available from the Survey Center of the American Dental Association, the use in the number of esthetic dental materials (e.g., dental crowns) has grown exponentially during the last decade (1990-1999) (Figure 1).

Zirconia dental ceramics are currently processed in conventional dental furnaces. However, one of the shortcomings from utilizing conventional dental furnaces includes long processing times (typically 7 to 10 hours to sinter zirconia dental materials from their green state). In addition, some of the other treatment drawbacks from these current processing techniques include the need for temporary dental crowns and multiple patient visits. Authors have proposed that if newer techniques can hasten the processing of esthetic dental ceramics (e.g., zirconia and porcelain-fused-to-metal) while maintaining or improving the material properties, it would significantly improve restorative dentistry by benefiting clinicians and patients.

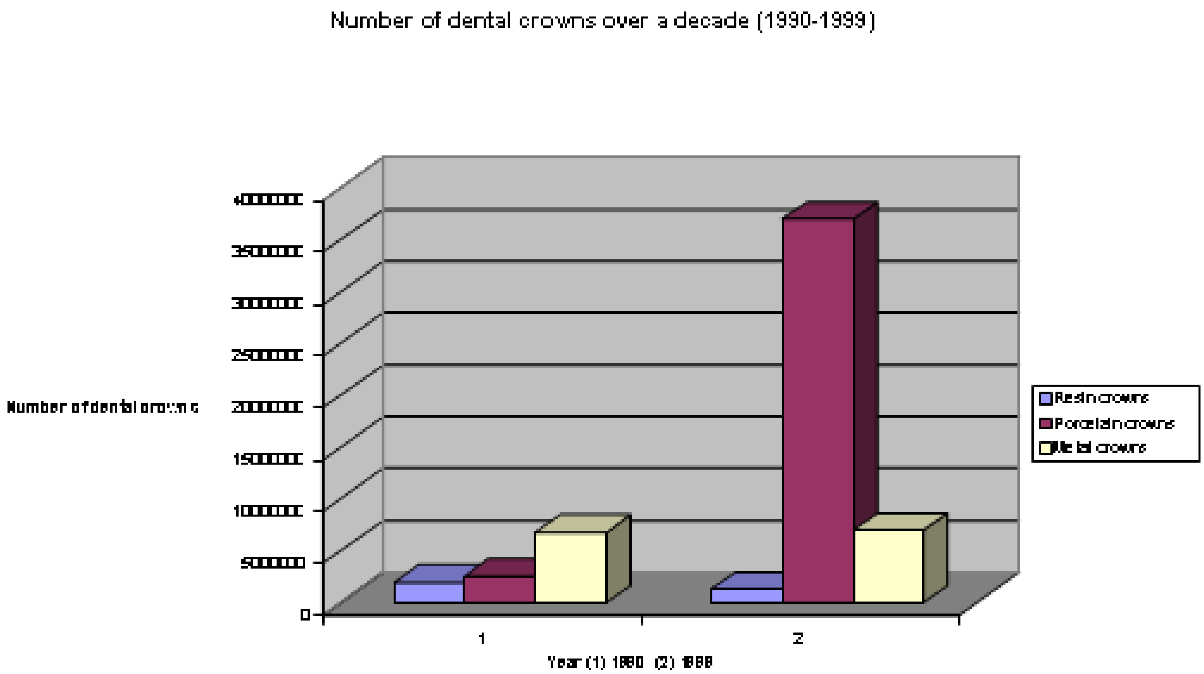


Figure 1. Number of dental crowns utilized in the US (1990-1999)

Microwave sintering technology is an effective means of processing zirconia dental materials when compared to conventional sintering techniques that utilize electric furnaces. Several benefits from utilizing microwaves include shorter processing times (typically 45 minutes to 1 hour for complete sintering of the zirconia dental material, i.e., from its non-sintered or green state to its fully sintered state) and improved mechanical and microstructural properties of the sintered materials. Although microwaves have been used to a much greater extent for industrial applications (for example, drying of paper and wood as well as fabrication of ceramic industrial parts), they have only been used minimally for biomedical applications due to the incomplete knowledge and lack of widespread acceptance of this process. Therefore, a more comprehensive investigation of microwave sintering of zirconia and other dental materials is necessary to understand the underlying processing mechanisms.

It has been shown recently that it is possible to sinter porcelain-metal composite dental structures in the microwave. However, many microwave parameters (e.g., optimum time-temperature profiles, the minimum amount of power needed to achieve complete sintering in the shortest possible time) that are specifically suited for dental applications need to be established. The mechanical and microstructural properties of zirconia dental materials with varying amounts of dopants (e.g., 3%, 4%, 5%...wt% yttria) need to be studied. The mechanical and microstructural properties of the esthetic dental materials in microwave sintered vacuum environments need to be investigated. Apart from these previously mentioned parameters, the marginal fit and three dimensional shrinkage behavior of microwave sintered dental materials that are going to be important for dental applications need to be evaluated. According to the currently available literature, there are no studies that have investigated all these previously mentioned properties for microwave sintered specimens. Critical aspects in dentistry (e.g., optimum marginal fit, shrinkage behavior and the need for uniform sintering) are important when compared to industrial sintering of materials using microwave energy.

We have investigated these previously mentioned parameters as part of this doctoral research work. The Materials and Methods section of this proposal explains in further detail the type and number of specimens that was studied. The characterization of the sintered dental materials was performed jointly at SUNY Downstate Medical Center, Polytechnic Institute of NYU, NYU School of Dentistry, and other external research laboratories (e.g., NIST). All characterization tests were performed according to the American Dental Association (ADA) and International Organization for Standardization (ISO) recommended standards for evaluating dental materials (further description is provided in the section on Characterization of Materials).

2. Specific Aims

a. To use microwaves to sinter all-ceramic (i.e., zirconia core substrate materials) dental materials.

b. To optimize the temperature, time and power input for microwave sintering of the highest quality zirconia dental restorations.

c. To determine the physical and mechanical properties (density, hardness, shrinkage, compressive, tensile and flexural strength) of dental zirconia processed by microwave energy and compare it to conventionally processed equivalents.

d. To propose the sintering parameters and design specifications for a prototype microwave sintering furnace that can be specifically used in a dental laboratory or dental clinic.

3. Significance/Related R & D

The majority of dental crowns/onlays placed in the US are porcelain-fused-to-metal dental crowns (Figure 1). There are many reasons for this, some of which include better mechanical properties (i.e., the presence of flexibility of the porcelain-fused-to-metal dental crowns in certain clinical situations including high load conditions such as posterior restorations when compared to all-ceramic crowns), and cost-effectiveness. However, some of the drawbacks with PFM dental crowns include inferior aesthetic appearance when compared to the all-ceramic (i.e, zirconia based) dental crowns. Reductions in the processing times without compromising the properties (mechanical and physical) of the finished dental restorations would be a significant improvement in restorative dentistry. We hypothesize that with the use of microwave sintering technology, benefits including energy savings and improvements in the quality of the finished product can be achieved.

The enamel and dentin of the natural tooth structure is semi-translucent in appearance which significantly contributes to its appearance. Among the existing dental restorative materials, simulating this appearance in artificial dental crowns can be fulfilled somewhat better with all-ceramic dental crowns when compared to PFM dental crowns. This is due to better optical properties (e.g., better translucency) with all-ceramic materials when compared to PFM crowns. The market potential for the introduction of a microwave system to sinter dental materials, especially dental ceramic crowns are evident from the figures of the number of dental crowns placed in the US as mentioned earlier (Figure 1). Our proposed research studied microwave processing techniques that were capable of sintering zirconia substrates from their green (i.e., non-sintered) state to the fully sintered state in very short times. Furthermore, we believe that our studies have helped to improve the understanding of microwave-materials interactions. Additionally, these experiments can help us to develop the microwave sintering technologies to process other dental materials in the future.

Dental ceramics are generally classified into two types – I and II. Type I dental ceramics are supplied in powder form. Type II ceramics are typically used as substructures including CAD-CAM (computer aided design/computer aided machined) machinable ceramics for fabrication of crowns, inlays, onlays and veneers onto which Type I powders can be applied (ISO Standards for Dental Ceramics 6872:1995)(5). A list of some of the all-ceramic core materials that is routinely used in dentistry is provided in Table 1.

Table 1. Different types of all ceramic core materials for dental applications

Core material	System
Zirconia – 3 mol% Yttria stabilized zirconia or 3 mol% tetragonal zirconia polycrystal (3Y-TZP)	Milled, Green milled and sintered, densely sintered and milled
Aluminum-oxide (Al_2O_3)	Milled, densely sintered, slip-cast and milled
Glass ceramics – e.g., lithium disilicate, leucite, feldspathic	Heat pressed, milled

The zirconia materials utilized in this research project belongs to the group type II. These ceramics are further sub-classified based on the addition of color pigments to identify them (Table 2).

Table 2. Colors for dental ceramic powders – Type 2(5)

Class	Material	Color Coding
1	Core ceramic	Yellow or none
2	Dentine/body ceramic	Pink
3	Enamel ceramic	Blue
4	Neck material	Green
5	Transparent material	None
6	Stains	None
7	Add-on material	None
8	Glaze material	None

3.1. Masticatory or Chewing Loads

The event of chewing or "mastication" subjects the natural dentition to high loads (typically, they are a combination of compressive, tensile and torsional stresses or forces). Researchers have previously reported that the average loads recorded during chewing range between 250 N and 400 N (6, 7). The natural tooth structure is composed of an outer enamel layer that has a three-dimensional crystalline microstructure. The enamel layer is hard but brittle in nature and is capable of absorbing high compressive loads, albeit it is weak in tension. The enamel surrounds an underlying dentin layer that is more compliant and absorbs most of the mechanical insults due to its flexible nature. The combination of this hard outer layer with a relatively compliant or softer inner dentin layer work together to withstand millions of cycles of chewing during a lifetime (8).

Cyclic loading of a material over a time period may render it weak due to the repeated application of stresses and the subsequent generation of microcracks. These microcracks can act as initiation sites for the eventual failure of the structure. This phenomenon is observed in most artificial materials including bioceramics. However, it is important to note that almost the entire human tooth structure is living (i.e., dentin, pulp, and periodontal ligament), with only the outermost enamel layer comprising of dead cells, and is thus considered dead tissue. Dental ceramic materials aim to replace missing or diseased enamel and dentin mostly. In order to design artificial materials that can withstand masticatory stresses, several factors need to be considered. The most important among these include the ability of the material to withstand a combination of compressive, tensile and torsional loads, resistance to cyclic loading, in vivo temperature variations and biocompatibility. Any biomaterial for dental applications needs to be able to address these previously mentioned factors, with microwave sintered dental ceramic prostheses being no exception.

3.2. Dental core materials

Dental crowns are commonly utilized to rehabilitate broken or missing teeth. Zirconia (specifically 3 mol% yttria-stabilized zirconia) is used as a core material that provides mechanical strength and structural stability to dental crowns. They have been very popular clinically for a long time for dental crown fabrication (9). Examples of other core materials that are used for dental crown fabrication include alumina and metals (e.g., nickel, cobalt, gold, cobalt-chromium, palladium). Among the all-ceramic materials, investigators have previously reported that zirconia materials might be more suitable when compared to alumina owing to its more favorable long-term strength (4). There are several benefits and drawbacks of these previously mentioned core materials. For instance, metals are capable of resisting high chewing loads due to their ductility. However, their major drawbacks include its inferior esthetics and allergies in some individuals.

3.3. Fabrication of dental prostheses

Machining of dental ceramic materials, especially zirconia has witnessed the introduction of various techniques, some of which include direct ceramic machining and CAD/CAM machining (10). The fabrication of a dental prosthesis (e.g., dental crown) is a customized process based on the individual patient’s tooth anatomy. In order to build the artificial prosthesis, the tooth is prepared (i.e., it is reduced with a high-speed diamond bur). Following this, a wax impression is built up and three-dimensional measurements are sent to a CAD-CAM computer program. Recent introductions to the field of dentistry allow the recording of the three-dimensional outlines of a tooth by a laser scanning device instead of the traditional wax build up. However, debate exists about the accuracy of this technique compared to the more traditional techniques. Precise machining in order to obtain prosthesis of the correct shape is realized from the automated CAD-CAM process. The machining is generally done on pre-sintered or green zirconia blocks which can be obtained from several ceramics manufacturers. An alternative technique is to machine the ceramics in a fully dense form, which is much harder to accomplish and with a higher probability for the material to produce microcracks. However, this latter technique might offer higher precision and simpler thermal treatments because of the need for a single-step sintering process (11). Most of the currently followed techniques utilize pre-sintered ceramic blocks, which are machined to approximately 20% greater than the final desired dimensions, taking into account shrinkage upon final sintering. Once the zirconia has been fabricated to the shape of a dental crown, veneering porcelains (e.g., fluoro-apatite glass ceramic) is applied in order to produce an esthetically appealing final product.

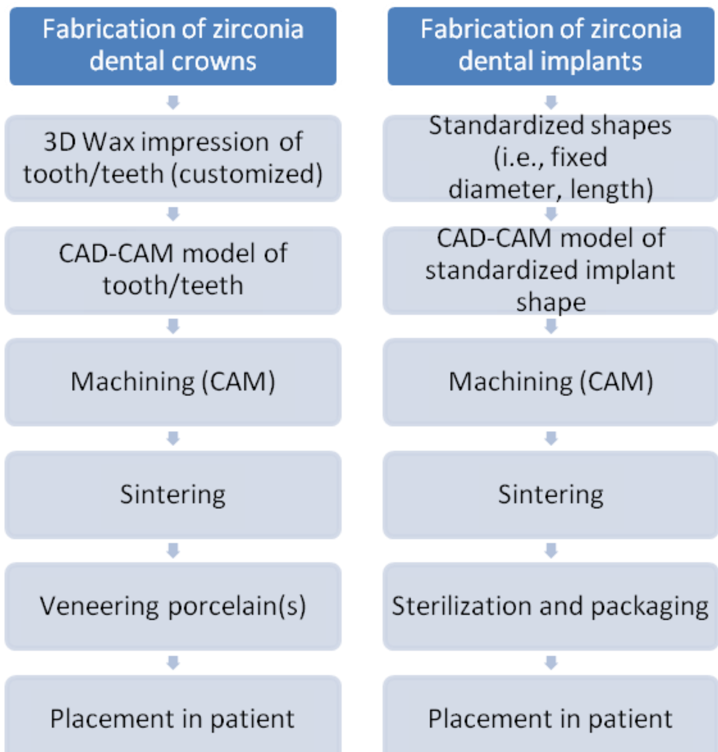


Figure 2. Steps involved in fabrication of zirconia dental crowns and dental implants (11)

In the case of zirconia dental implants, most of the prostheses are not customized as in the case of dental crowns. They are machined to standardized shapes of different diameters and lengths, although customization is a possibility. In addition, zirconia dental implants do not require the final step of additional veneering porcelains as they are embedded in alveolar bone where esthetics is not a major requirement.

4.4. Temperature measurements within microwave cavity

Temperature measurements during microwave sintering are critical to understand the behavior of a material in relation to changes in its processing temperature. The use of thermocouples for temperature measurements during microwave sintering of ceramic materials has been recognized (12). However, this technique has several drawbacks including local thermal runaways, field distortions as well as thermal and density gradients within the material being processed (13, 14). Thermal runaways constitute confined regions that are higher in temperature when compared to the rest of the sample being sintered. The consequences of this phenomenon can include differential densification, formation of cracks within the sample and mechanical stress (13, 15, 16). The main limitations with the use of thermocouples and infrared thermal imaging are that they provide temperature measurements of the surface and not within the bulk or thickness of specimens. Further, the use of thermocouple probes during high temperature sintering sometimes leads to plasma generation at the tip due to the buildup of electrons. This can damage the thermocouple probe, distort the temperature readouts and can even render the instrument unusable for temperature recording.

Alternative techniques to address temperature measurements of dielectric materials such as ceramics during microwave sintering have been proposed previously (15-20). The main benefit with this technique includes temperature measurements deep within a sample, which is typically not possible with other techniques such as the use of thermocouples and optical pyrometers. Microwave radiometry is based on the principle of the Rayleigh-Jeans law, which states that in the microwave frequency range, the thermal noise power (a few pico-watts) emitted by a lossy material (e.g., ceramic) is directly proportional to its temperature, i.e., thermal loss power of a lossy material (e.g., ceramic) is directly proportional to temperature. The radiometric measurement in the microwave range is related to the heat gradient, which is established from the surface to within several centimeters within a material (15-20). Dental ceramic prostheses are only a few millimeters in thickness and are odd shaped structures unlike most of the specimens sintered for industrial applications (which mostly have prescribed dimensions and shapes). This might make the use of microwave radiometry a potentially useful technique for measuring the sintering temperature of dental ceramic specimens. Further research to determine the feasibility of utilizing this previously mentioned temperature measurement technique needs to be investigated.

Another technique proposed to measure the dielectric constant of materials sintered in microwave fields includes the use of infrared thermography. Researchers have carried out preliminary experiments on distilled water to study the feasibility of this technique (17). If this technique can be successfully used for recording high temperature microwave processes, it can eliminate some of the drawbacks associated with other measurement techniques including the use of thermocouple probes.

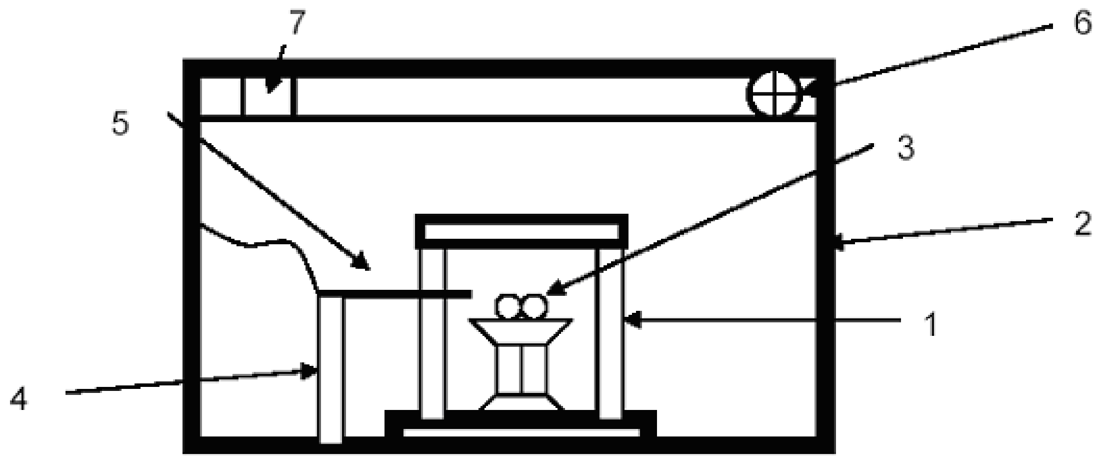
5. Preliminary studies

Existing knowledge pertaining to the research on porcelain-fused-to-metal dental restorations includes the development of dental alloys, and their matching porcelains. However, recently, investigators have reported that microwaves can be successfully utilized to sinter powder metals into fully formed parts, hardmetals, alloys and other composite structures (19, 21-36). With the use of dental alloys as copings, ceramic layers may be sintered onto them with the use of microwaves (21, 25, 26, 31, 37, 38). Only one group of investigators has shown that the same holds true for dental applications (39). In addition, almost no data is available to suggest that microwaves can be successfully used to sinter porcelain-metal composite dental structures. Microwave sintering of metal-ceramic composite structures can produce sintered products with significantly better properties (mechanical and microstructural) when compared to conventionally sintered equivalents (39). We have previously studied/characterized various commercially available dental alloys (both precious and non-precious alloys) and low-fusing dental ceramics in microwave fields. Preliminary research investigating the feasibility of using microwaves to sinter porcelain-metal dental structures was conducted as a part of my Master's thesis. The initial results of the microwave sintering of porcelain-fused-to-metal dental materials were positive, albeit certain problem areas such as build up of electrons at sharp edges of metals and thermal runaways need to be addressed. Material scientists and engineers have utilized microwaves to sinter ceramics, powder metals and solid metal structures for engineering purposes (21, 25, 26, 31, 36-44). Porcelains layered onto metal alloy copings are known as low-fusing dental porcelains, which require them to be sintered at temperatures that reach to about 750 °C to 900 °C for complete sintering, as compared to all-ceramic materials including zirconia which typically require maximum sintering temperatures of about 1450 °C to 1550 °C.

Several studies have been conducted for the industrial applications (e.g., sintering of ceramic tiles) of zirconia and other ceramic materials (21, 38, 40, 45-50). However, there have been very few reports that have investigated the same for biomedical applications (51-54). Further, there are very few studies that have utilized microwave technology for dental applications (55). Bioceramics have been used for a long time in the fields of dentistry and orthopedics. Although there have been several improvements in terms of material properties, for instance, by altering their chemistry, or by introduction of vacuum during their sintering process, the processing techniques have not changed significantly. All-ceramic dental materials generally require high temperatures (typically, greater than 1000 °C) for complete sintering. The microwave time-temperature profiles for sintering of all-ceramic dental materials (e.g., 3 mol% YZP zirconia) need to be refined to produce reliability. Due to shorter sintering times by microwave, smaller grain sizes and superior mechanical properties of the sintered dental materials can be expected when compared to conventionally sintered equivalents (21, 37, 40). In addition, smaller grain sizes of the sintered ceramics might provide a better final product in terms of improved mechanical and microstructural properties. Based on these previous experiments, we plan to make initial proposals for the design of a prototype microwave oven that can be used by dentists and dental technicians for preparing ceramic and PFM crowns as well as other types of dental restorations (e.g., inlays) in the future. We have utilized microwave sintering techniques in preliminary studies to sinter zirconia dental materials in the past. However, these materials were not characterized fully for their suitability toward dental applications.

5.1. Microwave-materials interactions

Microwaves interact with materials at the molecular level. We have successfully sintered porcelain-metal composite structures as part of our preliminary studies (56). Many investigators believe that metals are not microwave “friendly”, but recent scientific evidence has demonstrated that microwaves can be successfully utilized to sinter metal powders into solid forms, and metal solid structures, provided certain principles are followed (57-59). Some of these include the size of the metal powders (usually desirable for them to be in the 1-50 μm range).With solid metal structures, elimination of sharp edges/sharp corners is an important consideration in microwave sintering, in order to prevent the build-up of electrons at these sites and the resultant production of arcing (31, 57). A schematic of the microwave utilized in all the experiments is shown in Figure 3.



Legend to Figure 3:
1. Alumina Thermal Containment Box
2. Stainless Steel Microwave Cavity
3. Dental Ceramic Samples
4. Stainless Steel Pedestals
5. Thermocouple
6. Power Input Control and Adjustment Knob
7. Digital Temperature Indicator

Figure 3. Microwave set-up with sample in place (susceptor not shown)

The microwave furnace that was used for sintering the dental ceramics during the preliminary studies and some of the actual experiments during this doctoral research project is shown in Figure 7. Ceramic materials are normally transparent to microwaves at room temperature (21, 31, 36, 60-62). However, they can be successfully sintered by increasing their initial temperature by incorporating susceptors in their vicinity such that they are capable of transferring heat to the ceramic body. For a better understanding of the microwave interactions with dielectric materials, permittivity (dielectric constant – ε^*) and the loss tangent ($\tan \delta$) need to be explained . The complex relative permittivity is a measure of the ability of a dielectric to absorb and to store electrical potential energy. Further, it is composed of the real permittivity (ε') and the loss factor (ε''). Equation (1) describes this relationship:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{1}$$

where $j = \sqrt{-1}$

The dielectric constant (ε') represents the penetration of the microwaves into the material. It can also be said that this indicates the amount of incoming energy that enters the sample and the energy that is reflected off the sample. Loss factor (ε'') indicates the ability of the material to absorb energy. The dielectric loss tangent ($\tan \delta$) is the ability of the material to convert absorbed energy into heat. It is the ability of a material to absorb and convert the absorbed energy into heat that allows successful microwave sintering, i.e., an ideal combination of moderate ε' (to allow adequate penetration), and high loss (maximum ε'' and $\tan \delta$) is desirable for microwave sintering. The interaction of microwaves with dielectric materials usually leads to a net polarization of the substance.

For this to occur, several polarization mechanisms are involved including electronic, ionic, molecular (dipole) and interfacial (space-charge). For any given material, the sum of the contributions from each of the previously mentioned mechanisms would determine the net polarization, P, of the dielectric material.

Depending on the complex permittivity, microwaves penetrate the material and some of the absorbed energy is converted to heat. This heat generation raises the temperature of the material. Consequently, the surface of the material loses more heat to the surroundings than the interior. Thus, the interior parts of the material become hotter than the exterior. Translational motions of the electrons or the ions rotate charge complexes such as dipoles due to the electrical field generated. This leads to a build-up of inertial, elastic, and frictional forces, leading to losses and weakening of the electric field. Equation (2) describes these losses by tan δ.

$$\tan \delta = \varepsilon''/\varepsilon' \tag{2}$$

Based on the dielectric loss factor (ε''), materials can be classified as shown in Table 3.

Table 3. Materials Classified According to Dielectric Loss Factor(s)

Material	Penetration
Transparent (low-loss insulator)	Total
Opaque (conductor)	None (reflected)
Absorber (lossy insulator)	Partial to Total
Mixed Absorber (matrix + additives)	Partial to Total

The method of sintering employed in all the experiments is known as Microwave Hybrid Heating (MHH), which is described in further detail in the ensuing section.

5.2. Microwave Hybrid Heating

Microwave Hybrid Heating (MHH) is employed to sinter materials, such as SiO_2, Al_2O_3, and ZrO_2 that are electrically transparent (63-67). In other words, MHH is employed to sinter materials that are difficult to heat at room temperature and whose dielectric loss factors rise rapidly with increase in temperature (25). In order for the samples to be sintered in microwave fields, they need to be preheated by another source; usually one which can couple with microwaves at room temperature. A suitable material for this application is silicon carbide, due to its high loss factor (68, 69). The silicon carbide susceptors help in the sintering of the dielectric material(s) by raising the temperature rapidly to their microwave coupling temperature. The low-loss sample and the high-loss susceptors are placed together in the microwave cavity. Since the susceptors are capable of coupling directly with the microwaves at room temperature, they heat up rapidly. Subsequently, this heat is transferred to the surface of the specimen by radiant heating. The heat then is conducted from the surface of the specimen to its interior by radiative and phonon conduction, thus raising the overall temperature of the sample. Once the sample reaches a critical temperature, it begins to couple with the microwaves directly. At this critical temperature, the low-loss material (i.e., zirconia) becomes more absorbent than the preheaters (i.e., silicon carbide) due to an increase in loss tangents.

5.3. Advantages of microwave sintering

The main benefit of MHH is its ability to be applied to a range of ceramic materials, which are virtually transparent to microwaves at room temperature. Further, MHH promotes effective and rapid heating. The transfer of heat in microwave sintering occurs in a volumetric heating manner opposite to that observed in conventional sintering. This leads to uniform heating within the bulk of the material being sintered. Consequently, this results in significant reductions in thermal stresses. Additionally, numerous advantages when compared to conventional sintering include

- Reductions in energy consumption (70)
- Improved microstructure of the sintered material(s)
- Shorter processing times and improved productivity (43, 71)
- Ability to synthesize new materials and microstructure(s)
- Ability to dry materials uniformly with varying moisture content
- Ability to produce stronger structures (26, 38, 72)

The experimental set-up for sintering the zirconia dental materials during the preliminary investigations is shown in Figure 4. A circular high purity alumina box (> 99%) was used as a thermal containment chamber. The box consisted of a 6 inch diameter by 5 inch height cylinder, and two lids (one on top and the other at the bottom) with dimensions of 6 inch diameter by 1 inch height. Within this box, two semi-circular silicon carbide susceptors were placed such that they enclosed the sample materials (i.e., zirconia) to be sintered (Figure 4). The zirconia materials were placed on reticulated zirconia blocks that acted as secondary susceptor materials and as a base for them to rest on. For a second set of specimens, we utilized a double cylinder high purity alumina (> 99%) thermal containment chamber with an opening for the thermocouple from the top (Figures 9 and 10).

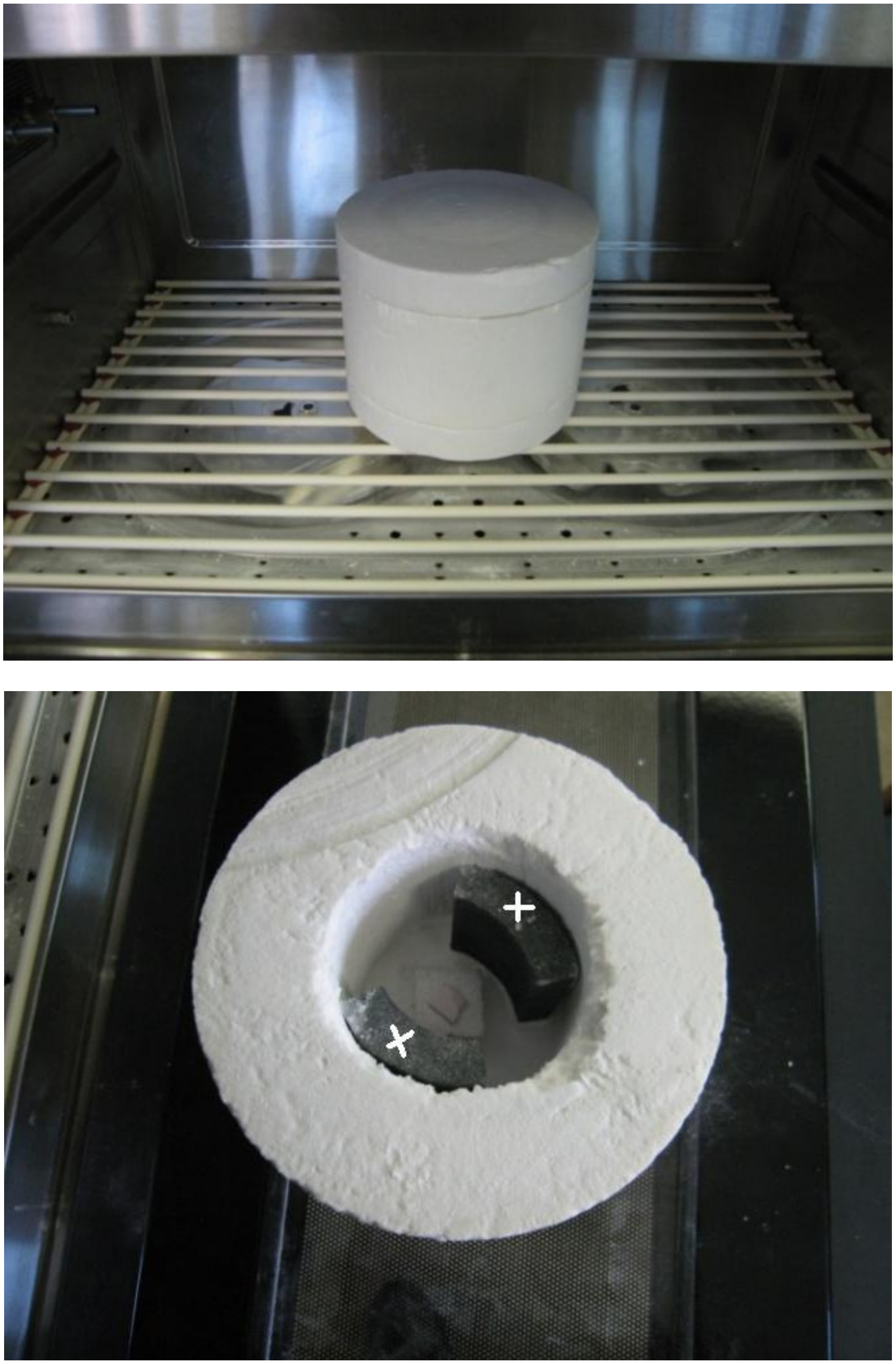


Figure 4. Top – Alumina thermal containment chamber; Bottom – silicon carbide susceptors (white cross in figure), reticulated zirconia block, and zirconia dental material

5.4. Temperature Distribution in the Microwave Cavity

During microwave sintering, the temperature distribution inside the furnace cavity can vary in different locations. Although it is important to determine the temperature distribution within the microwave furnace during sintering, this process can be challenging due to variations in power input, magnetic field interactions and other complex phenomenon. Investigators have previously reported about the redistribution of fields in a microwave furnace during sintering (73). An attempt to determine the temperature distribution inside the microwave cavity before the zirconia dental materials could be sintered was made. We hypothesized that the placement of the alumina thermal containment chamber at the correct position (i.e., the region with the highest and the most consistent temperature) inside the microwave cavity would provide us with the appropriate sintering parameter. In order to determine the temperature distribution inside the microwave cavity, we carried out the following experiment. A template of the base of the microwave cavity was created using a cardboard. The cardboard was then divided into 48 equal blocks using a permanent marker to represent the entire surface of the microwave base. This cardboard template was placed inside the microwave chamber (Figure 5). A Pyrex beaker that was able to fit on the individual blocks on the cardboard base was selected.

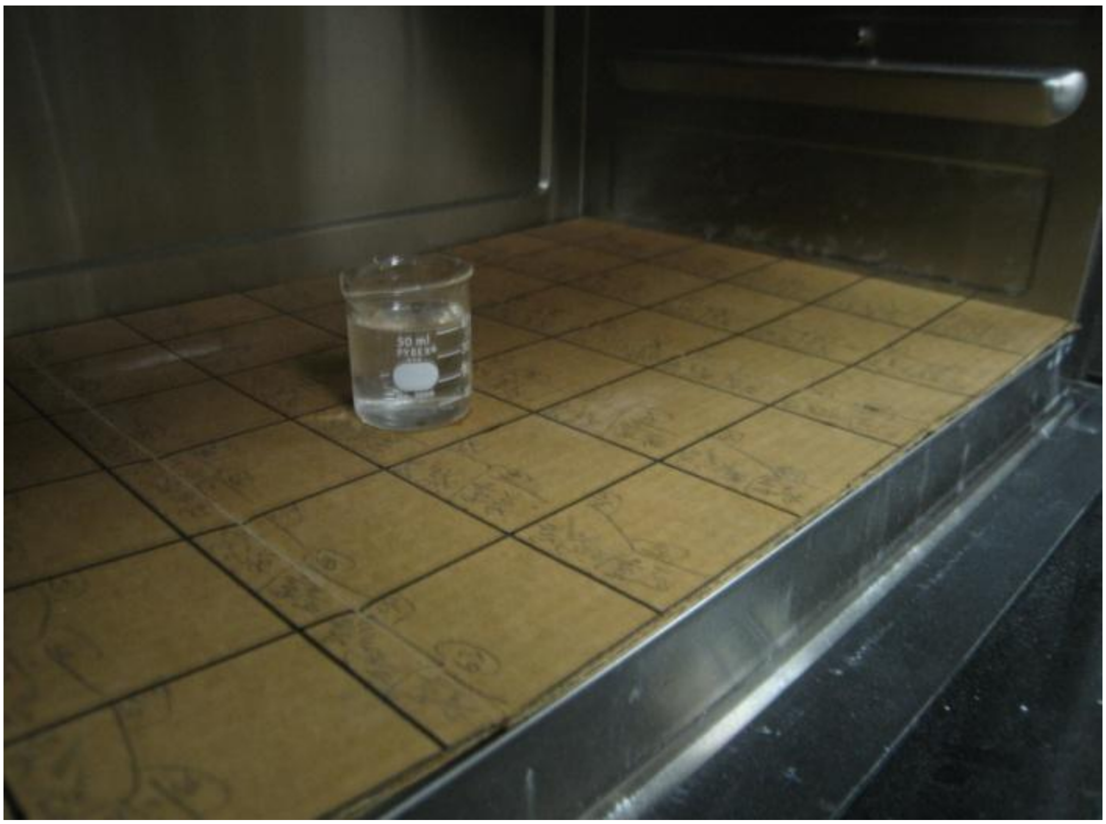


Figure 5. Cardboard template with beaker placed in microwave cavity

The beaker was filled with 40 ml of water and the microwave was turned on for 45 seconds at 45% power input. Following this, the door was quickly opened and the temperature of the water was recorded using a thermometer. A fresh beaker was used to record the temperature in other regions while the hot beaker was allowed to cool down to room temperature before it could be used again. Two sets of temperatures were recorded and their average was taken into consideration. This allowed us to map the entire surface of the microwave cavity and determine the temperature distribution in different regions of the cavity. From our experiment, we were able to show that higher and more consistent temperatures were located toward the middle and interior portions of the cavity while lower temperatures were produced toward the outer regions of the microwave cavity (Table 4, Figure 6).

Table 4. Temperature distribution inside microwave cavity (°C)

	Back								
Left	61	64	66.5	69	63.5	66	67	64.5	Right
	69	71.5	66.5	70	72.5	72.75	73.5	75.5	
	68.5	75	71.5	70.5	72.5	76	79	71.75	
	70.5	73.75	67.75	70.75	67.5	62.75	78.5	71	
	65.5	67.5	64.25	66	69.5	67.5	71	63	
	55	57.75	67.5	58.5	58	59.5	60.5	55.5	
	Door								

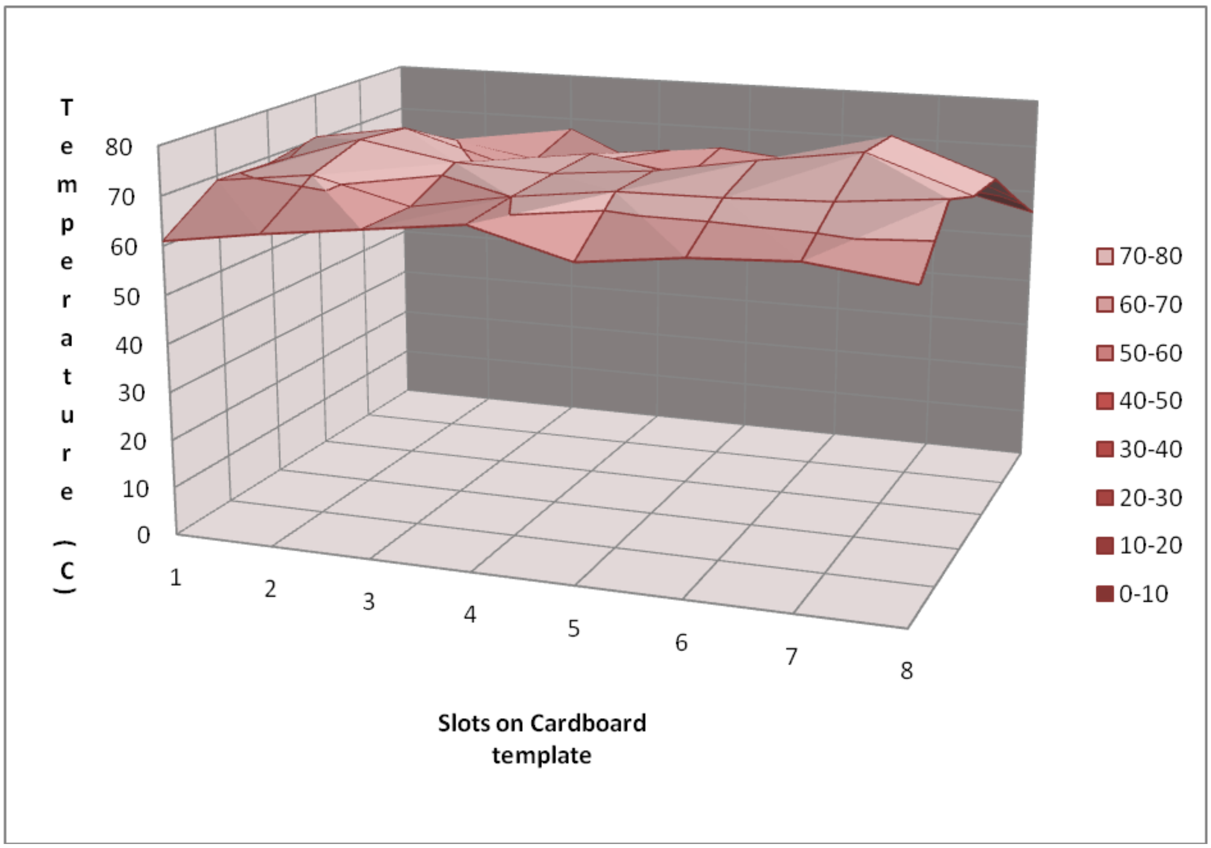


Figure 6. Temperature distribution in microwave cavity (°C)

During our initial experiments, we investigated the use of square versus cylindrical configurations of the thermal containment box. It was observed that the cylindrical set-up (both the single as well as the double cylinder) worked better when compared to the square box in terms of being able to better control the rate of temperature rise. Thermal runaways were much more commonly observed in the square box set-up when compared to the cylindrical arrangement. This encouraged us to utilize the single and/or the double cylindrical set-up for the remainder of our experiments. The thermal containment box was made from one and half inch thick boards of fibrous alumina (Type ZAL-15AA, Zircar Ceramics, Florida, NY) (Figure 4). Silicon carbide materials in semi-circular form (SiC-50, Research Microwave Systems, Troy, NY) were placed inside the thermal containment box to act as a primary susceptor material (Figure 4). The silicon carbide material is capable of coupling to the microwaves at room temperature, thus allowing rapid heating of a ceramic material enclosed within its area. In addition, reticulated zirconia blocks were used as secondary susceptor materials which also served as a floor of the thermal chamber on which the dental zirconia that was to be sintered was placed.

PFM and some all-ceramic dental materials were investigated during our preliminary experiments. All-ceramic (3 mol% yttria-stabilized zirconia) materials were investigated during the initial experiments of this research project and we further evaluated this material for the remainder of the proposed research project. The materials that were investigated can be categorized as a Type II ceramic (according to the ISO 6872, second edition classification). A commercially available microwave furnace (Microwave Research and Services, Inc, MD) was utilized in most of our experiments to sinter the dental materials. Table 5 provides a list of the products that were investigated, the numbers, dimensions of the specimens and the names of the suppliers.

Table 5. List of dental materials, dimensions, and commercial names utilized for both conventional and microwave sintering

Material	Specimen Type, Number and Dimensions			Tradename
All-ceramic (3 mol% yttira-stabilized zirconia)	Irregular shaped specimens	15	Not characterized	Dentsply Ceramco
All-ceramic (3 mol% yttria-stabilized zirconia)	Pellets	42	1.5 mm x 15 mm x 12 mm thickness	(IPS e.max ZirCAD, Ivoclar Vivadent) (CAD-CAM)
All-ceramic (3 mol% yttria-stabilized zirconia)	Strips	16	25 mm x 5 mm x 1.5 mm	(IPS e.max ZirCAD, Ivoclar Vivadent) (CAD-CAM)
All-ceramic (3 mol% yttria-stabilized zirconia)	Tooth coping configurations	4	Variable	(IPS e.max ZirCAD, Ivoclar Vivadent) (CAD-CAM)

5.5. Zirconia

Zirconia, in its native form is a crystalline dioxide of zirconium (74). It is a soft metal in its pure form, and its most important compound is zirconium dioxide or zirconium oxide (ZrO2). In order to achieve molecular stability, zirconium is generally combined with other metallic oxides including MgO, CaO or Y_2O_3 (75). The three most commonly used formulations that have been used till date for dental applications include 3 mol% yttria stabilized tetragonal zirconia polycrystal (3Y-TZP), magnesium doped partially stabilized zirconia (Mg-PSZ) and zirconia-toughened alumina (ZTA). The major benefit with zirconia in dentistry includes its excellent esthetic qualities, strength and biocompatibility. The common phases in zirconium dioxide include monoclinic, cubic and tetragonal (51). These previously mentioned crystalline phases are dependent on sintering temperatures. At room temperature and heating upto 1100 °C, the predominant crystalline phase is monoclinic, between 1100 °C and 1600 °C, the structure is tetragonal and above 1600 °C upto its melting point, the structure is cubic. Yttrium-stabilized zirconia, also known as tetragonal zirconia polycrystal (TZP) is the most commonly utilized combination for biomedical applications (76, 77). Combining zirconium oxide with yttrium provides the material stability (75).

Stresses on a zirconia structure can potentially transform the material from its tetragonal to the monoclinic phase, which is a volumetric phase change (78). However, combining the material with oxides including yttrium can help to prevent this crystalline modification, while providing superior mechanical properties. This previously mentioned step is very essential to zirconia structures used for dental applications for long-term clinical survival (79). The mechanical properties of zirconia is similar to stainless steel, hence it is sometimes referred to as "ceramic steel". Several investigators have studied the mechanical properties of zirconia previously (77). The compressive strength of zirconia is reported to be approximately 2000 MPa. A wide variation in fracture loads have been reported by investigators (77). In spite of this variability in mechanical properties, zirconia has been found to possess mechanical properties that are superior when compared to other ceramic materials including alumina or lithium disilicate ceramics (4). However, processing techniques and environmental effects including exposure to moisture and cyclic loading can lead to a deterioration of the zirconia material during long-term use.

5.5.1. Microstructure of zirconia

Zirconia is a popular biomaterial that is used for dental applications, especially as a core material for dental crowns. Some of the reasons for its increased use includes its ability to withstand repeated functional loads (e.g., during chewing or mastication), besides having superior biocompatibility and esthetics when used as a core material (80). The most commonly used form is zirconium oxide (ZrO_2), which is a metallic oxide. However, in its native state, ZrO_2 is known to be unstable as it can undergo phase transformations due to the application of mechanical stresses. Typically, this includes a change from its tetragonal to the monoclinic phase. This type of phase transformation can render the zirconia mechanically weak, thus leading to structural failure during physiological function. In order to avoid this phenomenon, ZrO_2 is typically combined with various dopants, the most common being yttrium at 3 mol% concentrations. For dental applications, this formulation is known to work satisfactorily in terms of structural and phase transformation stability.

5.5.2. Effect of sintering on the microstructure of zirconia

It has been previously reported that the sintering conditions have a significant effect on the stability and mechanical properties of zirconia (81). Larger grain sizes in the finished product can be found due to higher and longer sintering temperatures. Since grain size is one of the important properties reflective of the mechanical properties of zirconia, it is important to work toward maintaining this property within a certain range. For instance, it has been reported that at the critical grain size of approximately 9 nm, tetragonal zirconia spontaneously transforms into the monoclinic phase (82).

5.5.3. Phase transformation of zirconia

Zirconia undergoes a phase transformation during the sintering process. Typically, this occurs from the monoclinic to tetragonal to cubic phases as a function of increasing sintering temperatures. The phase transformation can usually be confirmed by X-ray diffraction and microscopy studies (83). For example, lower sintering temperatures (e.g., upto 800 °C) would leave the zirconia material in the monoclinic phase, rendering it mechanically weak. When the sintering temperature is increased, a transformation from the monoclinic to tetragonal phase occurs (usually between 1000 °C and 1100 °C), with a consequent increase in mechanical strength (84). This increased strength is observed due to densification of the sintered product. When the sintering temperature is increased to above 1600 °C, the material is transformed into the cubic phase. Some authors have also suggested that sintering 3Y-TZP above 1450 °C can produce a combination of cubic and tetragonal grains (84, 85).

6. Materials and Methods

6.1. Microwave sintering of all-ceramic/zirconia specimens

Twenty green zirconia specimens (Cercon Zirconia, Dentsply Ceramco, PA) were obtained from a dental laboratory. All specimens were individually labeled and bagged in polyethylene bags before and after sintering. The microwave sintering time, power input used and other details for these specimens are provided in Table 6. These specimens were processed in the microwave furnace in an attempt to refine the time-temperature profile that was needed for sintering. All the pellets were labeled and individually bagged in polyethylene bags before and after sintering. CAD-CAM machined green zirconia tooth copings were also utilized for the study (see Table 6 for a list of the number, type, and dimensions of specific dental materials).

Table 6. Specimen details, microwave power input and sintering duration

Specimen Number	Specimen shape	Power input and sintering duration	Cooling time (minutes)
1	Irregular shape, white specimen (Ceramco)	50% for 24 minutes; then varied between 30% - 35% for 1 minute	25
2	Irregular shape; flat specimen (Ceramco) pink dyed specimen	45% for 30 minutes	25
3	Irregular shape, white specimen (Ceramco)	45% for 30 minutes	30
4	Irregular shaped specimen, white color (Ceramco)	50% for 25 minutes, then reduced to 45% for 5 minutes	30
5	Irregular shaped specimen, pink color (Ceramco)	35% for 10 minutes, 40% for 10 minutes, 45% for 10 minutes, 50% for 10 minutes	40
6	Irregular shaped specimen, white color (Ceramco)	40% for 10 minutes, 45% for 10 minutes, 50% for 10 minutes	30
7	Irregular shaped specimen, pink color (Ceramco)	45% for 10 minutes, 50% for 10 minutes	20
8	Irregular shaped specimen, pink color (Ceramco)	50% for 10 minutes, 45% for 10 minutes	20
9	Circular specimen; white (Ceramco)	50% for 30 minutes	25
10	Circular specimen; white (Ceramco)	45% for 30 minutes	25
11	Circular specimen; white (Ceramco)	45% for 30 minutes	35
12	Circular specimen; white (Ceramco)	50% for 30 minutes	35
13	Irregular specimen; white (Ceramco)	60% for 20 minutes	20
14	Irregular specimen; white (Ceramco)	70% for 20 minutes	15
15	Irregular specimen; white (Ceramco)	80% for 20 minutes	10
16	Anterior tooth coping (Town and Country Dental Studios)	45% for 15 minutes, 50% for 15 minutes	30
17	Posterior tooth coping (Town and Country Dental Studios)	45% for 15 minutes, 50% for 15 minutes	30
18	Posterior tooth coping (Town and Country Dental Studios)	45% for 15 minutes, 50% for 15 minutes	30

19	Posterior tooth coping (Town and Country Dental Studios)	45% for 15 minutes, 50% for 15 minutes	30
20	Bend bar (IPS e.max ZirCAD) (Town and Country Dental Studios)	45% for 15 minutes, 50% for 10 minutes	Allowed to cool down to room temperature in thermal box

6.2. Sintering in the Microwave Furnace

Microwave hybrid heating (MHH) was employed to sinter the ceramic samples. The dental material samples were sintered in the microwave and conventional furnaces. A research microwave (Microwave Research and Applications, Inc Model BD DEN) was used for all the experiments (Figure 7). The microwave was equipped with a multi-magnetron 2 kW power supply, having a stainless steel cavity with dual mode stirrers, a platinum sheathed S type thermocouple and Omega controller. The operating frequency of the microwave was 2.45 GHz. Figure 7 shows the furnace that was used for microwave sintering. Individual pieces of zirconia specimens were sintered in the microwave furnace at varying power inputs (i.e., 30%, 32%, 34% and so on). By providing less power, we needed a longer time for the material to sinter. We used the previously mentioned experimental procedure to refine the power input that was most suited to sinter the zirconia dental materials in the fastest time possible. From these preliminary experiments, we were able to obtain complete sintering of the ceramic material in the fastest time possible at 45% power input.

Figure 7. Microwave furnace used to sinter the dental materials (Microwave Research and Applications, Inc, MD)

The microwave furnace was started at a minimal power level before it was gradually increased, as dictated by the desired ramp temperatures, until complete sintering was achieved. All sample-sintering cycles were initiated at room temperature. Each set of the sintered samples was fired only after the oven had completely cooled from the previous run to avoid overheating of the microwave. For the conventional sintering, we used a commercially available furnace (Sintramat, Ivoclar Vivadent, Buffalo, NY) and followed the manufacturer's recommendations for processing zirconia dental materials.

6.3. Microwave Sintering at Different Temperatures

A separate set of specimens was sintered in the microwave furnace at three different maximum sintering temperatures. During this phase of microwave sintering, the power input was set at 100% in order to evaluate the fastest time possible to sinter the ceramics from their green to the fully sintered state. The thermal box set-up was different when compared to our previous experiments. It was also observed that this set-up worked better in terms of containing the heat better and prevented the chamber from being structurally damaged during the sintering process. For the faster sintering process, we utilized two circular alumina boxes of varying diameters. The smaller diameter alumina box was placed inside the larger diameter box. Two rings were believed to be able to contain the thermal energy better when compared to a single cylinder. Both the cylinders were seated on a one inch thick circular base. The top lid of the box also comprised of a one inch thick alumina insert with a hole in the middle to introduce the thermocouple for temperature measurements (Fig 8, 9). The samples that needed to be sintered were surrounded by three silicon carbide susceptors (Fig 8, 9). The entire set-up was placed in the middle of the microwave cavity before it was sintered.

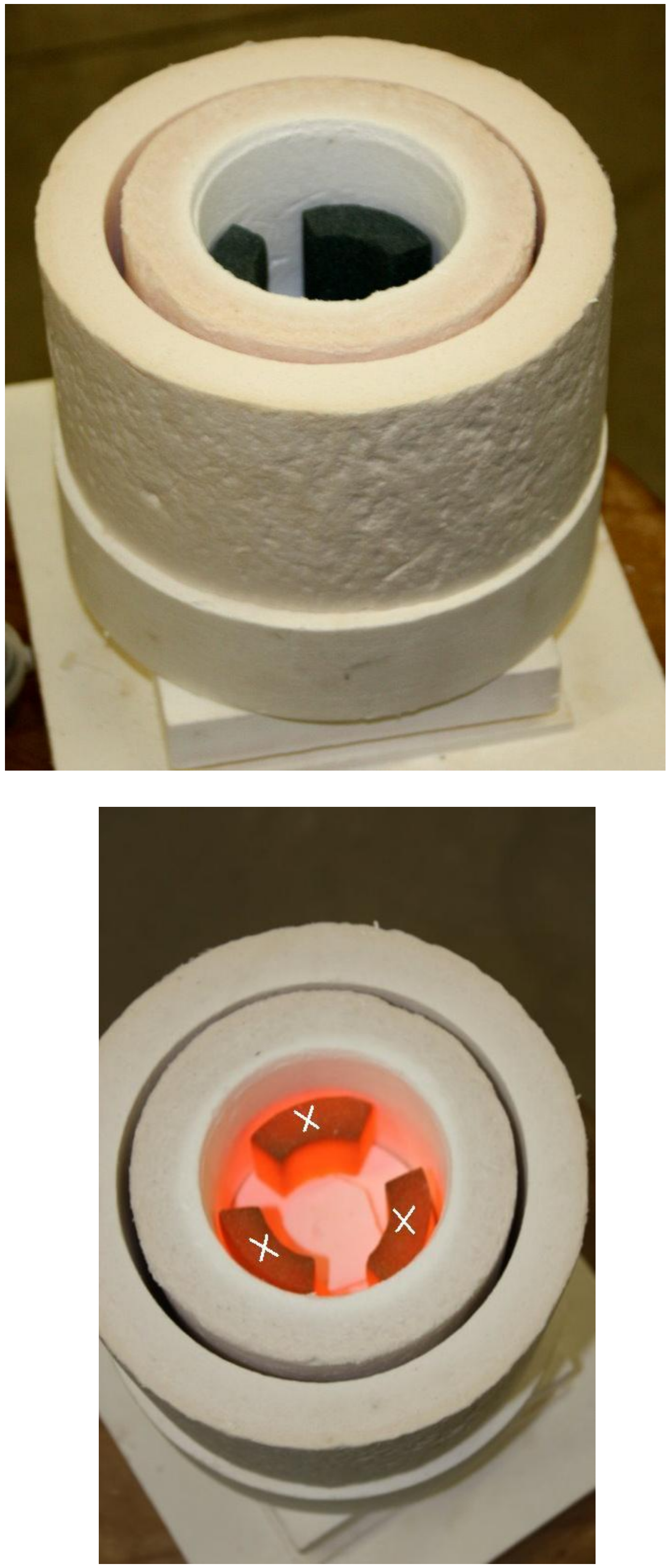


Figure 8. Alumina thermal containment chamber with two cylinder configuration and silicon carbide susceptors (white cross in bottom figure)

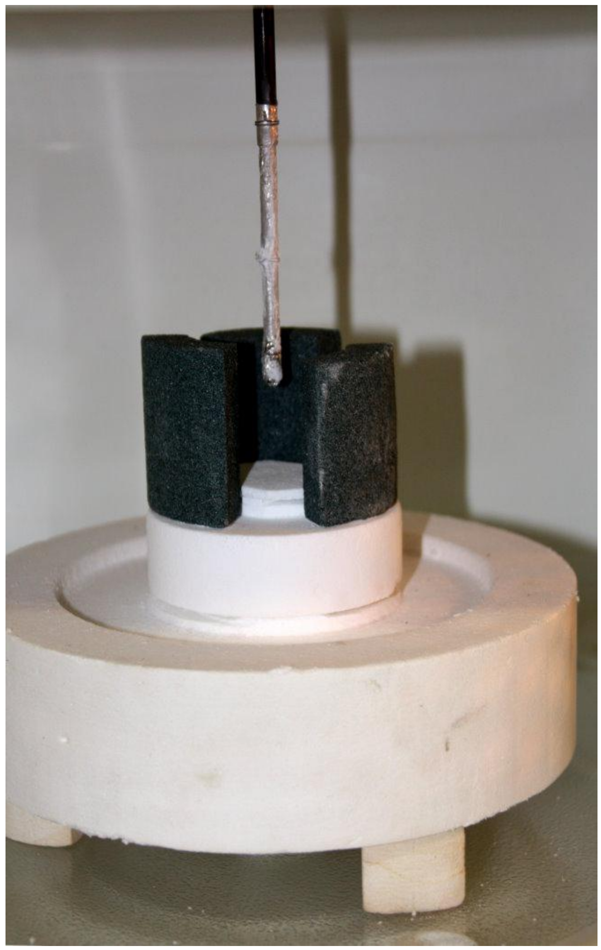


Figure 9. Silicon carbide susceptors and thermocouple in microwave set-up

Table 7 describes the material and sintering details (e.g., maximum sintering temperatures and hold times) for the microwave processed samples. The samples were sintered with and without hold times of 5 minutes at their maximum sintering temperatures. This was done to study whether including hold times would be beneficial to the final properties (mechanical and microstructural) of the dental ceramic materials.

Table 7. Chemical composition, pre-sintered dimensions, maximum sintering temperatures and hold times of zirconia specimens

Specimen Number	Chemical composition IPS e.max ZirCAD (Ivoclar Vivadent, Buffalo, NY)	Pre-sintered dimensions (length x width x thickness in mm)	Maximum sintering temperature (°C)	Hold time (minutes)
1	> 87 % ZrO2, Y2O3, HfO2, Al2O3	15 x 15 x 2	1350	
2	″	15 x 15 x 2	1400	
3	″	15 x 15 x 2	1450	
4	″	15 x 15 x 2	1350	5
5	″	15 x 15 x 2	1400	5
6	″	15 x 15 x 2	1450	5

6.4. Microwave sintering of tooth copings

A total of four zirconia tooth copings (IPS e.max ZirCAD, Ivoclar Vivadent, Buffalo, NY) was obtained from a dental laboratory. In order to determine if the microwave worked optimally for sintering actual tooth copings, we processed these structures according to the time and power inputs established from our previous experiments. The details of the tooth copings are provided in Table 8. The sintering parameters are provided in Table 6. One of these specimens is shown in Figure 10 after it has been microwave sintered.

Figure 10. Zirconia tooth coping with gypsum die

Table 8. Tooth coping material, dimensions and anatomical location

Specimen Number	Material	Dimensions (mm) green state	Location
1	Y-TZP ((IPS e.max ZirCAD, Ivoclar Vivadent)	Thickness = 1.0; Inciso-cervical = 9.54; Mesio-distal = 8.3	Anterior
2	Y-TZP ((IPS e.max ZirCAD, Ivoclar Vivadent)	Thickness = 1.1; Bucco-lingual = 11.7; Mesio-distal = 12.1	Molar
3	Y-TZP ((IPS e.max ZirCAD, Ivoclar Vivadent)	Thickness = 1.1; Bucco-lingual = 11.04; Mesio-distal = 6.35	Premolar
4	Y-TZP ((IPS e.max ZirCAD, Ivoclar Vivadent)	Thickness = 1.0; Bucco-lingual = 10.86; Mesio-distal = 6.42	Premolar

The following experimental procedure was followed to refine the microwave sintering process and to obtain the most desirable (i.e., in terms of appearance, mechanical and microstructural properties) material. Although our preliminary studies indicated that microwaves can be successfully employed to sinter dental ceramics (e.g., zirconia), it was essential that repeated experiments were performed for confirmation of the preliminary results and for a comprehensive investigation. In addition, the proposed microwave sintering experiments with zirconia not only helped us to reconfirm our preliminary results, but it also facilitated us to further refine the optimum time and power inputs that were necessary for processing these materials. We investigated various time-temperature profiles for obtaining the most desirable material properties. In addition, we utilized two different alumina thermal containment chamber configurations to determine which one provided the better finished product. The fastest time (i.e., 25 minutes of sintering time and 20 minutes of cooling time) that was necessary to achieve acceptable characteristics of the ceramic materials was investigated.

In addition to the previously sintered materials, we machined sixteen green/non-sintered zirconia bars, that could be tested for their flexural strength (i.e., three-point bend testing) (Figure 14). The dimensions of the bend bars were adopted from the ISO 6872 standards for testing dental ceramics. The specimens (n=10 and n=6) were conventionally and microwave sintered respectively before their flexural strength was determined. Optimization of the time-temperature profiles was addressed by conducting experiments where the power inputs of the microwave were varied to allow sintering. When the power input of the microwave furnace was maintained at 35% for the entire sintering period, it was observed that the zirconia dental materials were not being sintered optimally. In cases of higher power inputs (e.g., greater than 50%), we found that the zirconia dental materials were warped as well as produced a rough surface. When the power inputs of the microwave was reduced to between 45% and 50% for limited durations during the sintering process, we were able to achieve better quality finished products. This was determined from both visual examination (i.e., smooth surface finish, and no warpage) and microstructural characterization (i.e., SEM and dimensional shrinkage studies). Mechanical characterization (i.e., hardness and fracture toughness measurements) of the microwave sintered specimens was determined as explained further in other sections of this thesis.

6.5. Conventional Sintering

Conventional sintering of zirconia is already being routinely used in dentistry and the time-temperature parameters to obtain fully sintered structures have been established. Due to the existing literature already available, we did not include specimens for the shrinkage measurements from the conventional group. For our experiments, we utilized a commercially available dental furnace (Sintramat – Ivoclar Vivadent) (Figure 11). This furnace is capable of reaching maximum temperatures of 1600 °C by means of a heating element. The maximum power output of the furnace is 3 kW. Conventional sintering takes place at the rate of 15 °C per minute from room temperature upto 1100 °C, 3.5 °C per minute from 1100 °C to 1350 °C and 5 °C per minute from 1350 °C to 1500 °C. The time-temperature profile for conventional sintering of 3 mol% yttria-stabilized zirconia is shown in Figure 16.

Figure 11. Commercially available dental furnace (Sintramat – Ivoclar Vivadent, Buffalo, NY)

7. Measurement of Mechanical and Physical Properties

Measurement of the mechanical and physical properties of dental ceramics is vital to determine its suitability for long-term dental applications. The set of tests that need to be used to determine the properties of these materials can be truncated to the ones described further.

7.1. Bulk Density

Bulk density measurements were performed using a boiling test in accordance with ISO/ASTM standards. Using Archimedes method, the saturated weight (S) was measured. Following this, the volume, bulk density and percentage density (indicates overall pore volume) was calculated as:

Volume (V) = Wet weight (W) – Saturated weight (S)

Bulk Density (B) = Dry weight (D)/ Volume (V)

Percentage Density = (Bulk density/ Theoretical density) X 100

All sintered specimens were used for bulk density measurements.

7.2. Hardness and Toughness Measurements

Hardness and indentation fracture toughness were determined for the microwave and conventionally sintered samples. Once their density was determined, they were prepared for hardness and toughness measurements. Polishing was done on a polishing wheel progressively from grit sizes ranging from 120, 240, 340, 600 and finally upto 1 micron after they were mounted in a quick setting acrylic material (SamplKwik, Buehler, IL) (Figure 12). A Vickers indenter was utilized to determine the Vickers Hardness Number and the Indentation Fracture Toughness (41, 42, 72, 86-92). An equal number of specimens (i.e., n=2 for conventional and n=2 for microwave) were used for the Hardness and Fracture Toughness measurements respectively.

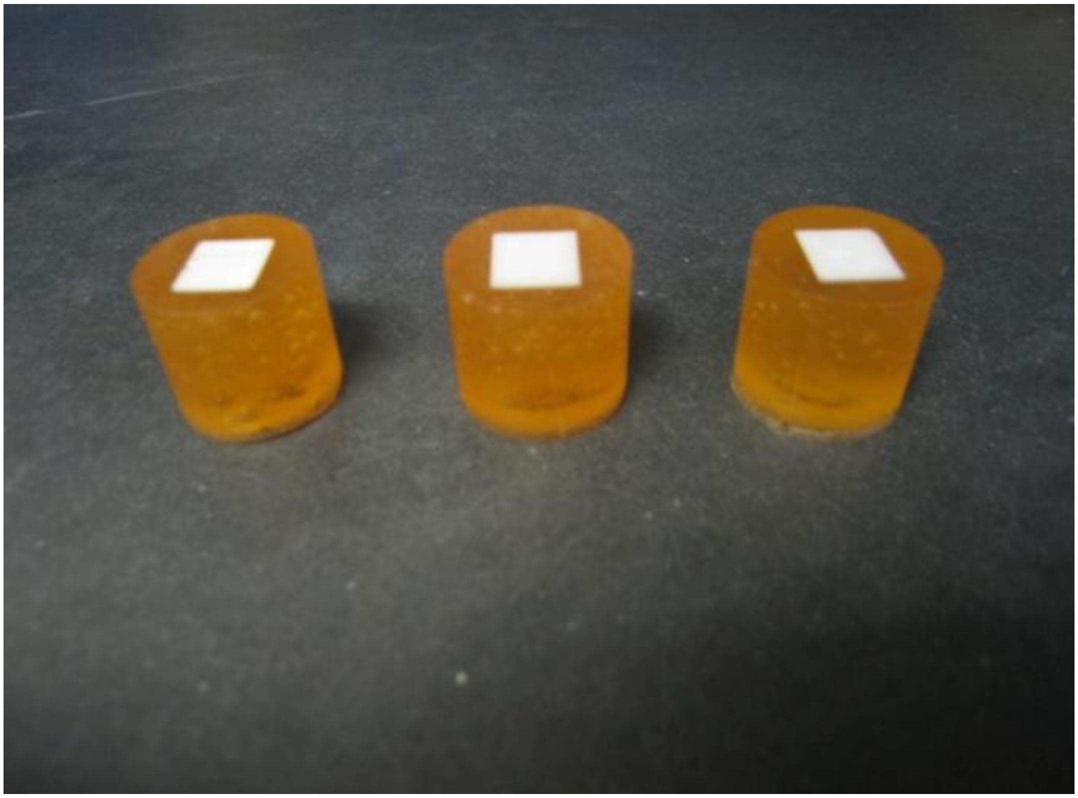


Figure 12. Zirconia tiles mounted in acrylic

The hardness tests were completed on the Zwick 3212 hardness testing equipment. The measurements were taken using a Olympus PMG3 IP software and the images were obtained using a Nomarski filter. A minimum of 8 indents at a load of 100 N were performed for each of the three specimens. The results of the hardness and fracture toughness for these previously mentioned specimens are shown in Table 15. In addition to the specimens described previously, we determined the hardness for six samples sintered at 1350 °C, 1400 °C and 1450 °C with (n=3) and without a hold time (n=3) of 5 minutes at their maximum sintering temperatures. The hardness and fracture toughness values for these previously mentioned specimens is shown in Table 15. Equation 3 was employed to calculate the Vickers hardness number and Equation 4 was used to calculate the Indentation fracture toughness:

Vickers Hardness (Hv) = $1.854\ P/\ d^2$ (3)

where 1.854 is the geometric factor for the Vickers indenter (from sin 68°),
P is the test load (in kg), and d is the mean of both diagonals (in mm).

Fracture Toughness (K_{IC}) = $0.016\ P/c\ 1.5(E/H)^{0.5}$ (4)

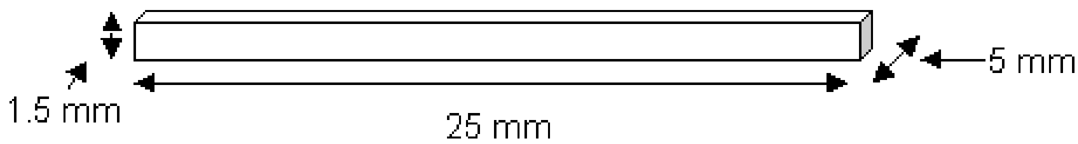
where c = crack length from center of indentation (in meters)
P = Load (in Newton); E = Young's Modulus (in GPa)
Hv = Vickers Hardness (in GPa)

7.3. Mechanical Testing

Three point flexural tests are important for determining consistencies of material quality, and to assure that the strength values are well within the range of those required for successful application as a dental material. Furthermore, mechanical property requirements are prescribed by the ISO 6872 for evaluation of dental ceramics. An Instron Model # 5566 mechanical testing machine, with a maximum load rating of 1000 kgs was utilized for these tests. The computer was capable of controlling the appropriate software for data acquisition and analysis. The methodology in brief is explained further.

7.4. Flexural (Three-Point Bend Test) Strength Testing

Flat substrates of the materials (n = 6 for microwave sintering) and (n = 10 for conventional sintering) was utilized. The flat substrates (green state) were machined using a diamond saw (Buehler Isomet® Low Speed Saw, IL) according to dimensions prescribed by the ISO 6872 standard for dental ceramics (41, 86, 87). The dimensions of the non-sintered substrates were approximately 25 mm in length, 5 mm in width and 1.5 mm in thickness (Figure 13).



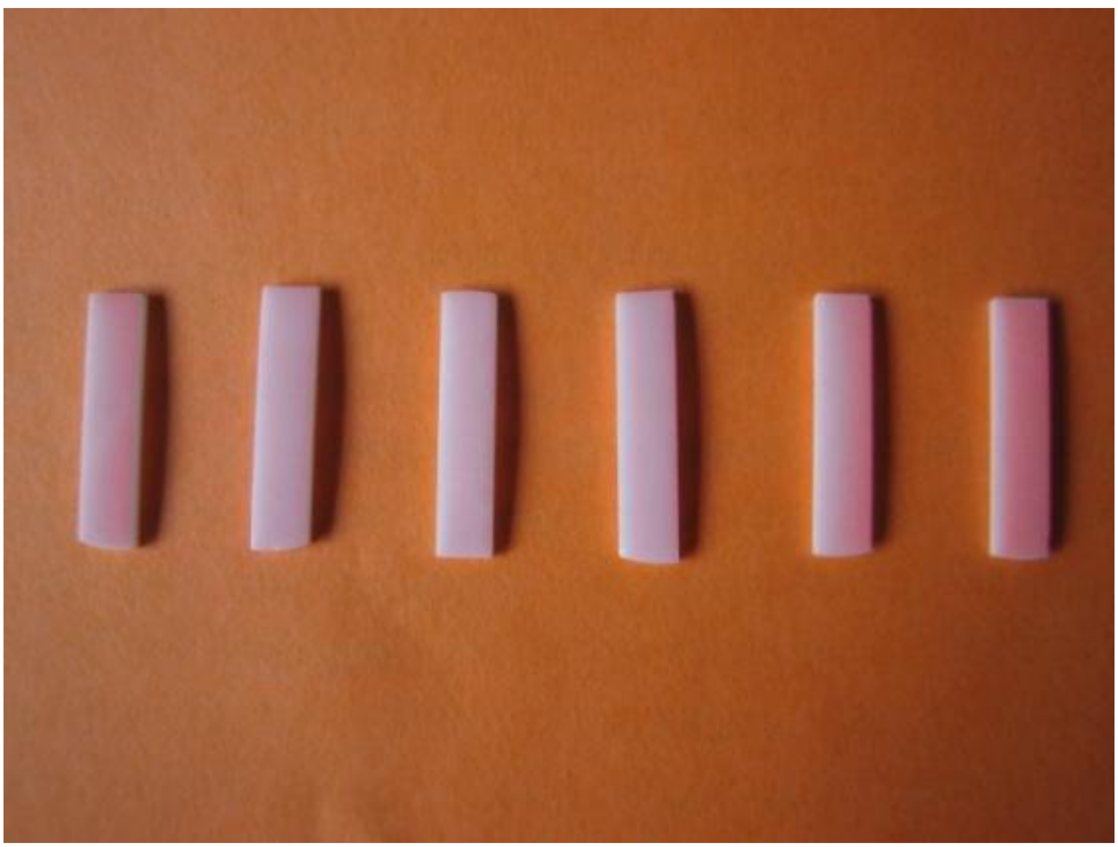


Figure 13. Three-point bend test bars for determining flexural strength

The conventional sintering of the flat substrates was done using a commercially available sintering furnace (Figure 11). A steel fixture was fabricated for testing the specimens in the three-point bend test set-up. The fixture comprised of two anvils on the bottom with a span of 15 mm and one anvil on the top. The radius of curvature for the anvils was 0.8 mm as prescribed by the ISO standard (Figure 14) (41, 86, 87).

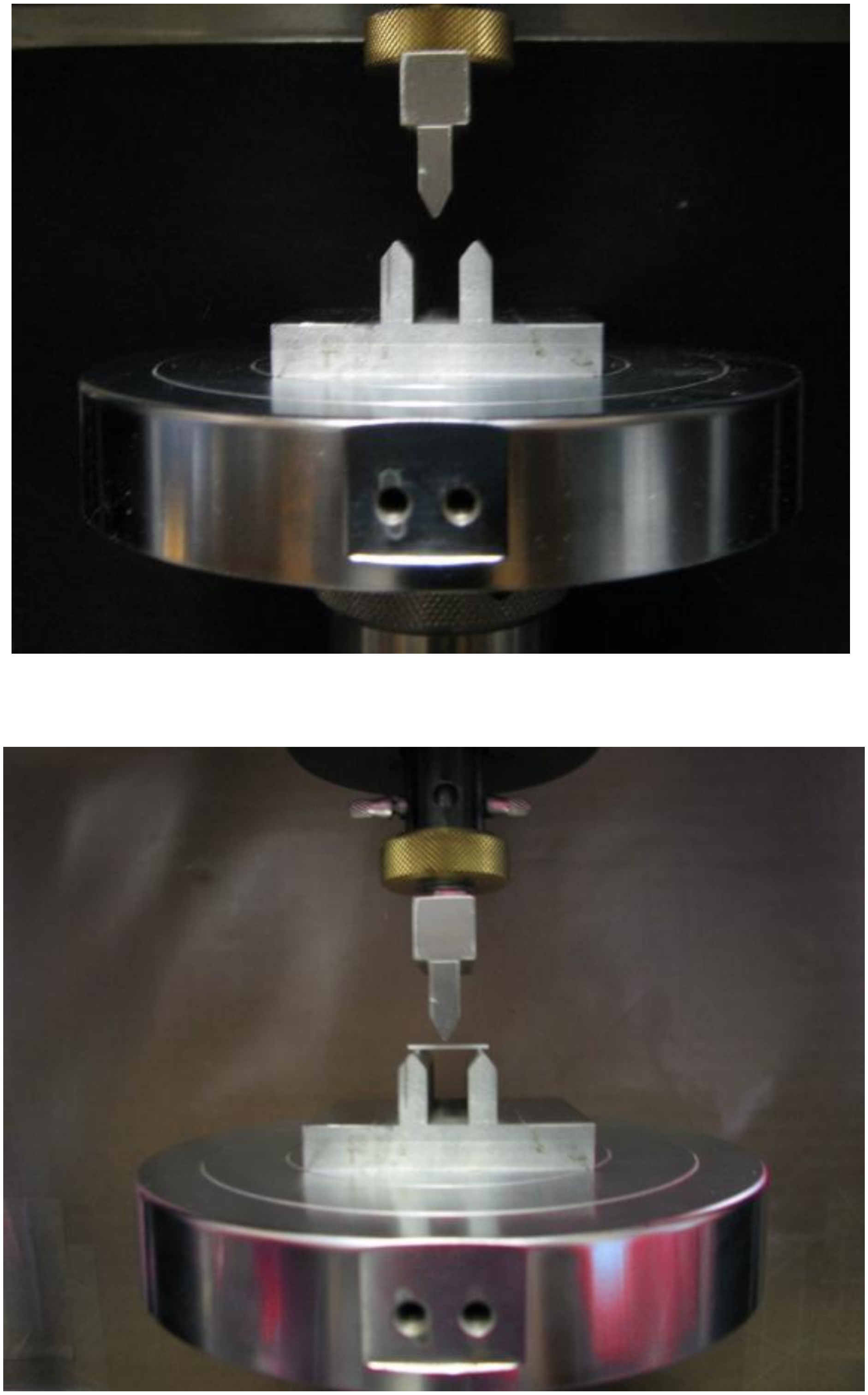


Figure 14. Three-point bend test fixture (top) and set-up (bottom)

A Universal Testing Machine (Instron Corp., Canton, Massachusetts, Model 5566) was used for the three-point bend tests. Both sets (conventional and microwave) of sintered samples were subjected to flexural testing. The specimen dimensions are provided in Table 9. The results of the three-point bend tests for specimens sintered by both conventional and microwave sintering techniques are provided in Table 13.

Table 9. Sintered dimensions of bend bar test strips

Specimen Number	Dimensions (length x width x thickness) in mm; Conventional	Dimensions (length x width x thickness) in mm; Microwave
1	19.56 x 5.27 x 1.48	19.65 x 3.80 x 1.1
2	19.71 x 4.09 x 1.00	19.50 x 3.83 x 1.18
3	19.60 x 4.04 x 1.19	19.09 x 3.85 x 1.22
4	19.81 x 4.29 x 1.16	19.51 x 3.96 x 1.16
5	19.51 x 4.21 x 1.02	19.26 x 3.89 x 1.19
6	20.14 x 4.29 x 1.07	19.78 x 3.68 x 1.24
7	19.84 x 4.2 x 1.18	
8	20.40 x 4.2 x 0.94	
9	20.13 x 4.29 x 1.19	
10	19.61 x 4.28 x 1.16	

Modulus of rupture for all the specimens was determined according to ISO 6872:1995 specifications. The flexural strength was calculated according to Equation 5:

$$\text{Flexure Strength (S)} = 3WI/2bd^2 \qquad (5)$$

where I is the distance between the supports; b is the width of the specimens
d is the depth or thickness of the specimen
W is the maximal load before fracture.

8. Microscopic Examination (SEM)

The microstructure of zirconia is critical to the overall mechanical performance for dental applications. Information on grain size distribution, pore size distribution, and other microstructural characteristics were analyzed, and the overall grain uniformity, which is indicative of potential mechanical properties, was visualized by the use of 2 different microscopes – the Hitachi 3500 Environmental SEM and the Zeiss Supra 40 VP. The zirconia specimens were thermally etched to approximately 150 °C to 200 °C below their maximum sintering temperature for 20 minutes before they were allowed to cool down to room temperature naturally. Following this, they were sputter coated with Gold Palladium for 3 minutes and examined under the Scanning Electron Microscope.

9. Evaluation of Three-Dimensional Shrinkage

Zirconia tooth copings (green state) along with their gypsum dies were obtained from a dental laboratory (Figure 15). Following the microwave sintering, the copings were fitted onto the gypsum dies and visually inspected for their fit. Since the tooth copings are three-dimensional structures, it is difficult to study their shrinkage by traditional visual techniques. Therefore, we used a commercially available software system (Geomagic Qualify, NC) that was capable of accurate, graphical comparisons between digital reference models (i.e., green zirconia tooth coping) and a final dental prostheses (i.e., sintered zirconia tooth coping). The software allowed us to superimpose images of the fully sintered tooth copings onto green/non sintered tooth copings. Further, it allowed us to quantitatively assess the shrinkage of the tooth coping before and after sintering. In addition, a color map that allowed us to study the different areas of shrinkage of the tooth coping was possible with the software (Figure 30). In order to have a comparison with conventionally processed equivalents, similar specimens needed to be sintered in a conventional dental furnace before they could be analyzed. This step was not carried out during this project due to lack of availability of the characterization tool. However, other investigators have previously reported the shrinkage and marginal fit of conventionally sintered zirconia tooth copings (references). This existing data was used for comparison of the shrinkage data from our own studies. The discussion section provides further information related to the shrinkage analysis.

Figure 15. Zirconia tooth copings (green/non sintered)

10. Results

10.1 Density

Table 10 shows the percentage density of the zirconia specimens that were sintered with microwave and conventional techniques at various maximum sintering temperatures. It is evident from these results that maximum density was observed in specimens that were sintered at 1450 °C with a dwell time of 5 minutes. The specimens that were sintered at 1350 °C with and without dwell times of 5 minutes showed the lowest density values. This may most likely be attributed to insufficient sintering or densification. When compared to a conventionally sintered specimen, it was observed that the specimen sintered at 1450 °C was closest in percentage density value to the microwave sintered specimen at similar temperature.

Table 10. Percentage density of microwave and conventionally sintered zirconia specimens at various maximum sintering temperatures (numbers in parentheses denote hold time in minutes)

Maximum sintering temperature (°C)	Percentage Density ± S.D. Microwave	Percentage Density ± S.D. Conventional
1350	95.2 ± 1.0	95.3 ± 1
1400	97.9 ± 0.1	97.2 ± 0.2
1450	98.1 ± 0.3	98.2 ± 0.3
1350 (5)	95.8 ± 0.7	94.6 ± 0.7
1400 (5)	97.3 ± 0.7	97.5 ± 0.4
1450 (5)	98.4 ± 0.2	98.3 ± 0.1

10.2. Sintering Measurements – Conventional sintering

The time-temperature curve for the zirconia specimens sintered in a conventional dental furnace (Sintramat – Ivoclar Vivadent, Buffalo, NY) is shown in Figure 16. The entire sintering process (i.e., from room temperature upto its maximum sintering temperature of

1500 °C) takes approximately 7 hours including the cooling cycle. The sintering parameters for conventional sintering include the following steps. Temperature ramp rates of 15 °C per minute is employed from room temperature to approximately 1100 °C, 3.5 °C per minute from 1100 °C to 1350 °C, and finally, 3..5 °C per minute from 1350 °C to 1500 °C. Once the sample has reached the maximum sintering temperature, it is allowed to cool down to its room temperature naturally.

10.3. Sintering Measurements – Microwave sintering

The time-temperature curves for the zirconia specimens that were microwave sintered at three different maximum sintering temperatures with and without hold times of 5 minutes is shown from Figures 17 to 28. It is observed from Figures 17 to 22 that the zirconia specimens couple to the microwaves at approximately 200 °C to 300 °C. Table 11 shows the time needed for complete sintering and to reach the maximum sintering temperatures for the zirconia specimens from their green or pre-sintered state.

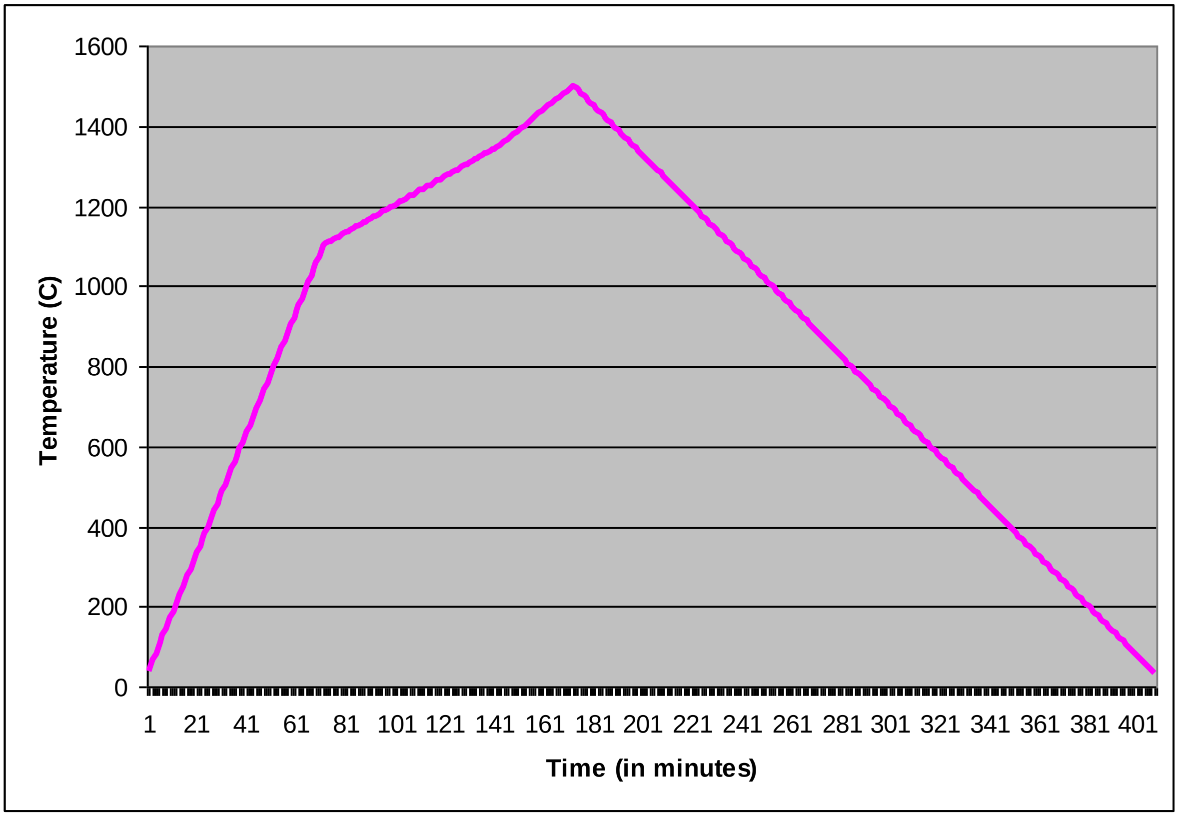


Figure 16. Time-temperature curve for conventionally sintered zirconia at 1500 °C (Sintramat – Ivoclar Vivadent, Buffalo, NY)

Table 11. Maximum sintering temperatures, hold times and time needed to reach maximum sintering temperatures for zirconia specimens (numbers in parentheses denote hold time in minutes)

Specimen Number	Maximum sintering temperature (°C)	Time needed to reach maximum sintering temperature (minutes)
1	1350	12
2	1350	12
3	1400	13.5
4	1400	13
5	1450	14.5
6	1450	15.5
7	1350 (5)	16.5
8	1350 (5)	17
9	1400 (5)	17.5
10	1400 (5)	17.5
11	1450 (5)	19.5
12	1450 (5)	19.5

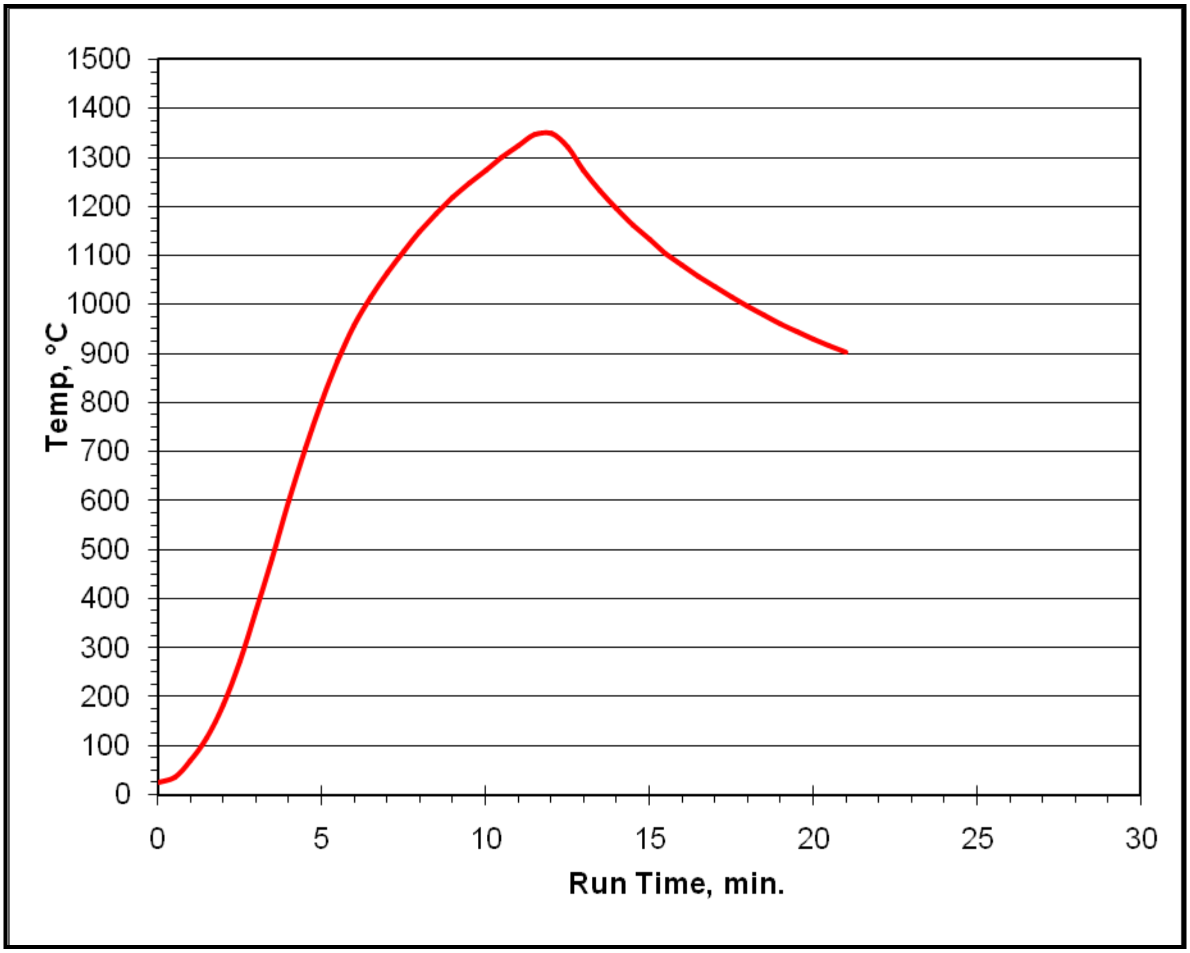


Figure 17. Time-temperature curve for microwave sintered zirconia specimen at 1350 °C with no hold time

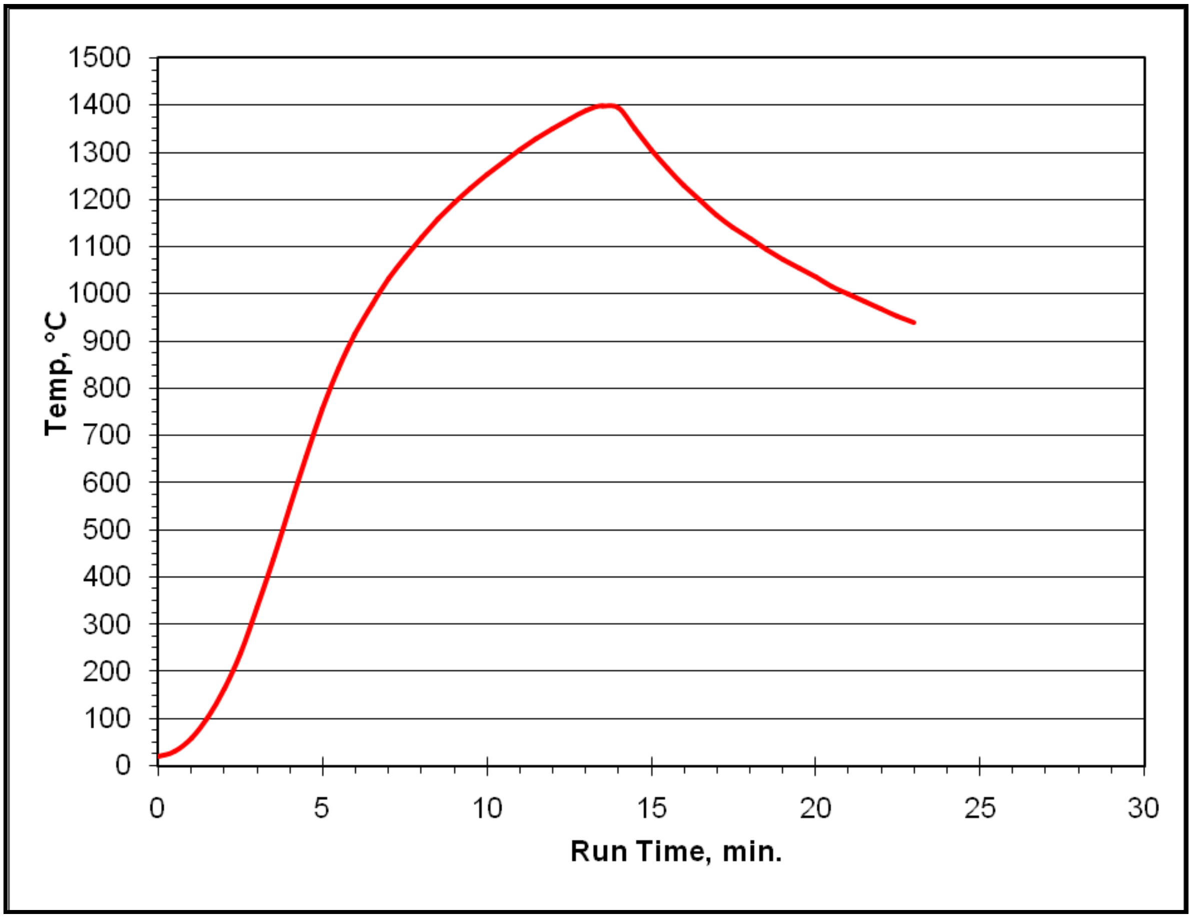


Figure 18. Time-temperature curve for microwave sintered zirconia specimen at 1400 °C with no hold time

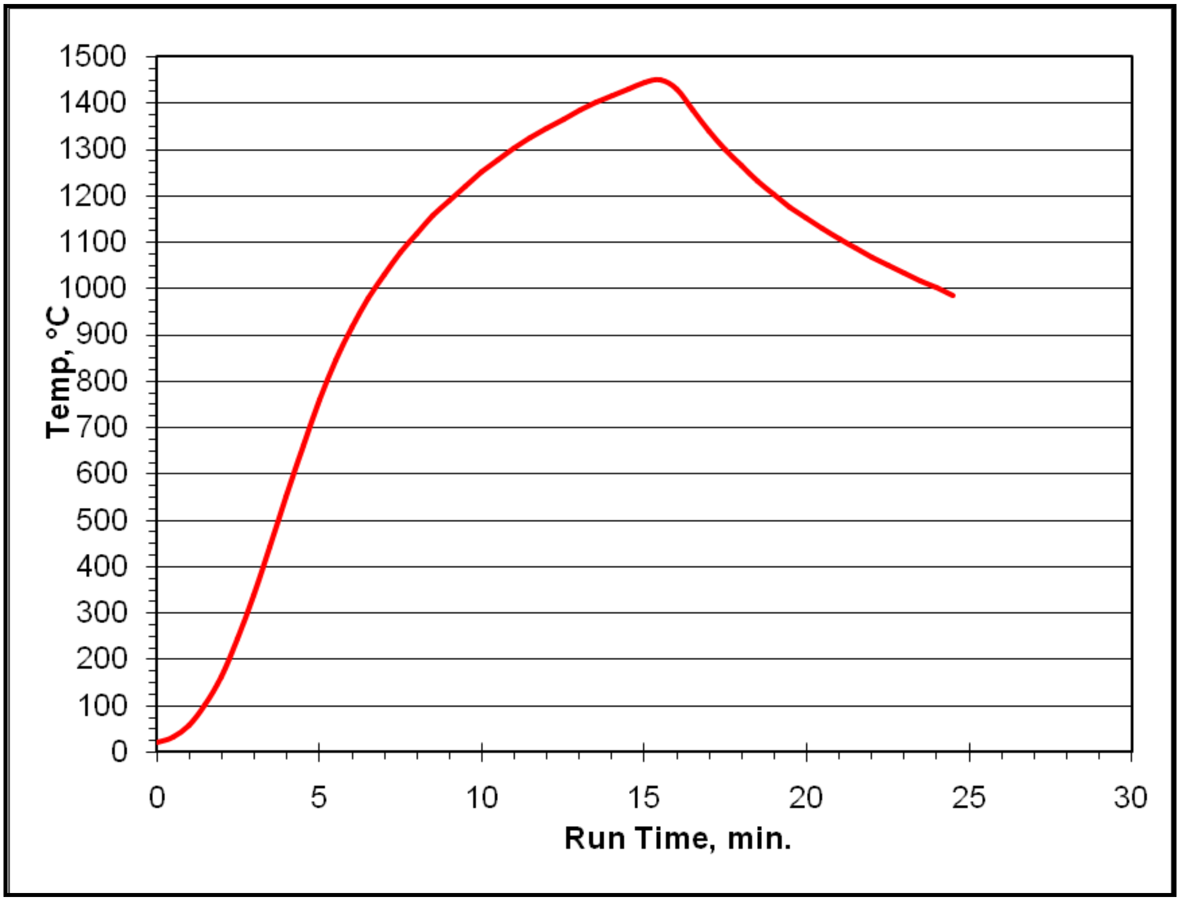


Figure 19. Time-temperature curve for microwave sintered zirconia specimen at 1450 °C with no hold time

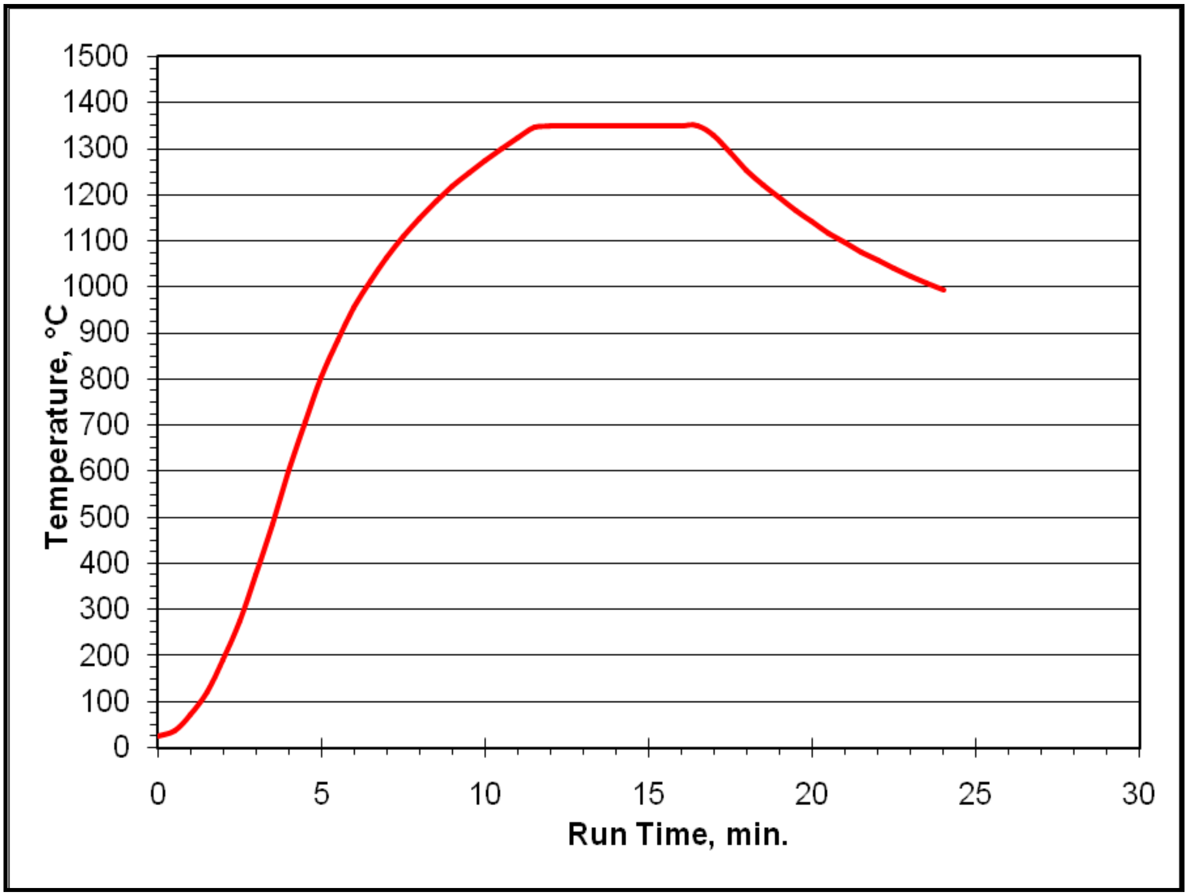


Figure 20. Time-temperature curve for a microwave sintered zirconia specimen at 1350 °C with a hold time of 5 minutes

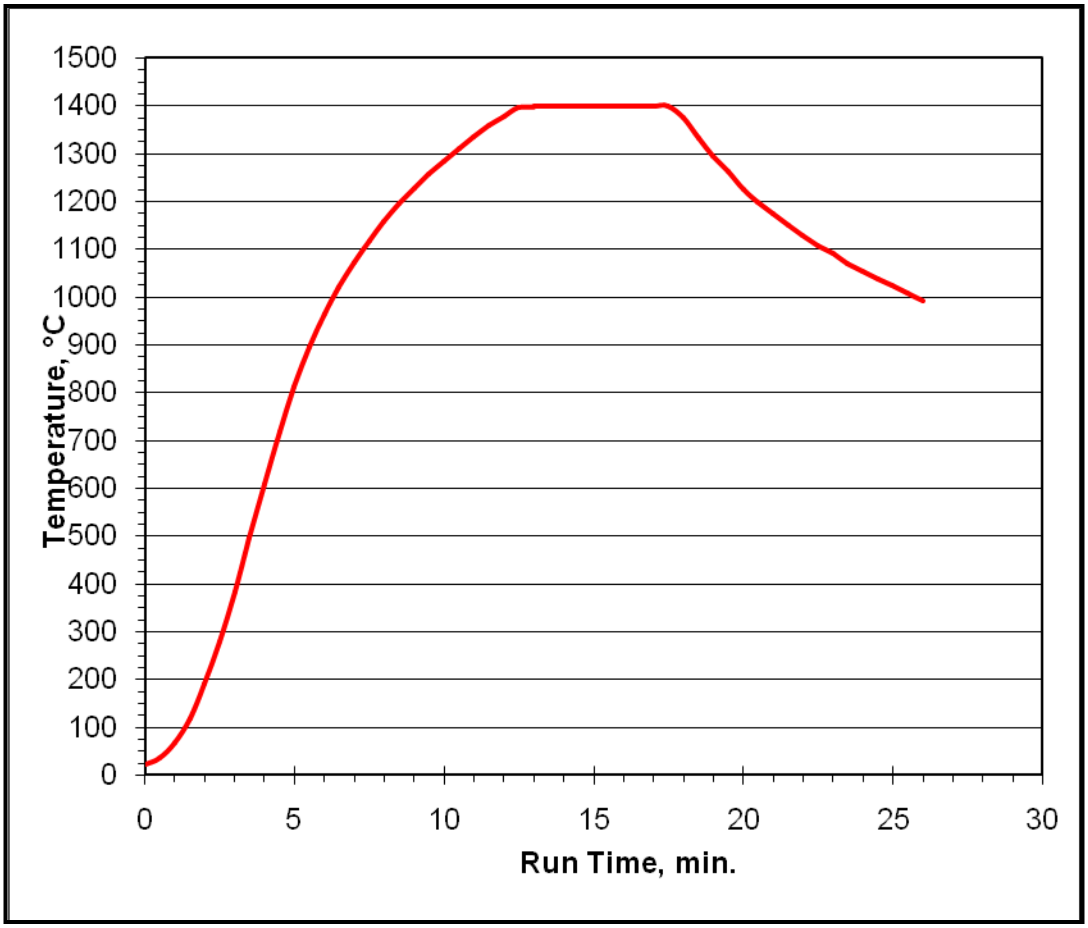


Figure 21. Time-temperature curve for a microwave sintered zirconia specimen at 1400 °C with a hold time of 5 minutes

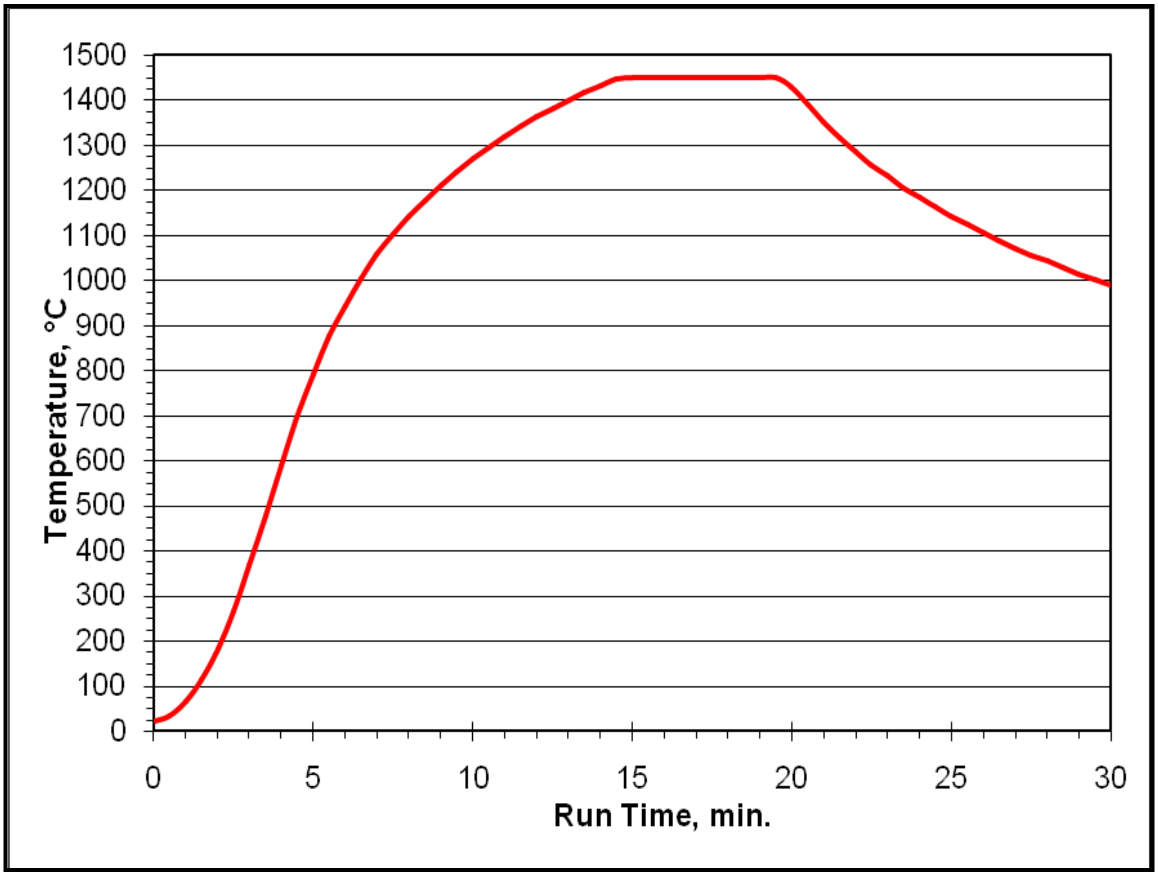


Figure 22. Time-temperature curve for a microwave sintered zirconia specimen at 1450 °C with a hold time of 5 minutes

The rate of temperature rise during the microwave sintering experiments is shown from Figures 23 to 28. From these figures (23 to 28), it can be observed that the ceramic samples coupled with the microwaves at approximately 200 °C. In our experiments, we noticed that the average temperature rise per minute in microwave sintering was approximately 50 °C (Figures 23 to 28).

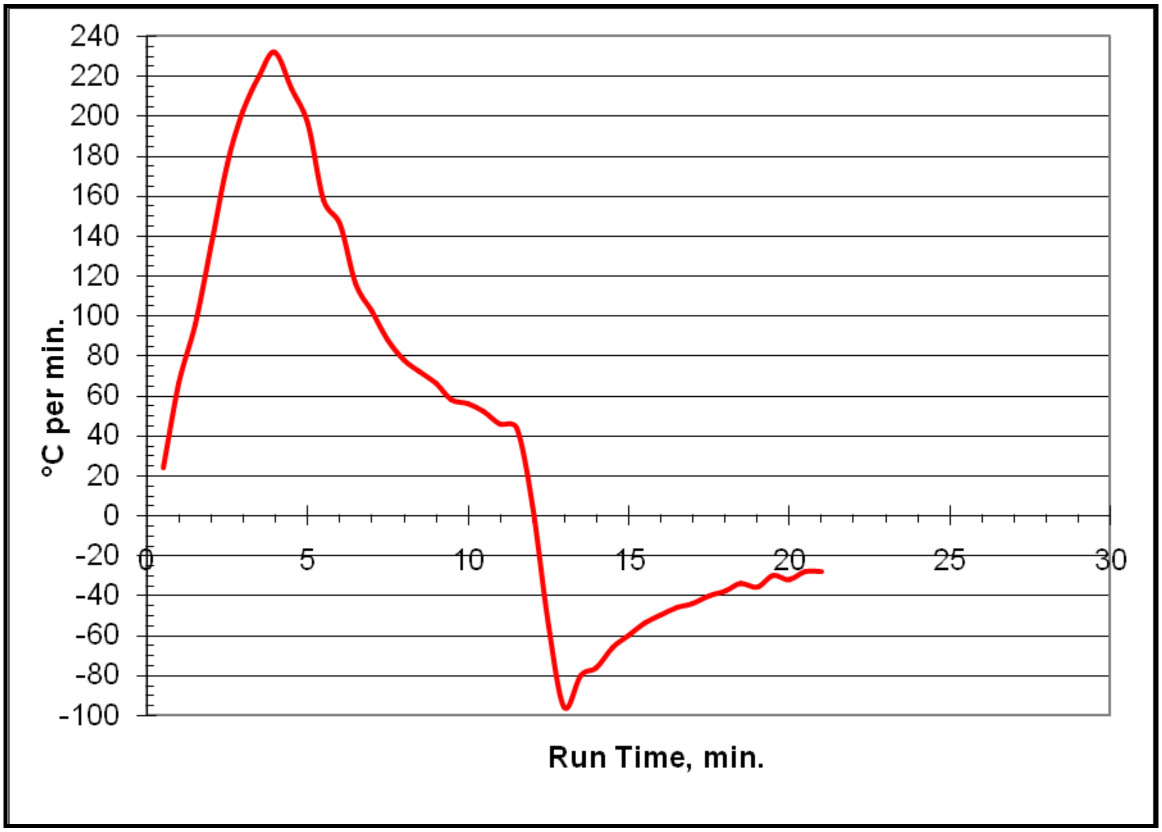


Figure 23. Graph showing temperature rise (°C) per minute during microwave sintering for specimen sintered to 1350 °C with no hold time

Figure 24. Graph showing temperature rise (°C) per minute during microwave sintering for specimen sintered to 1400 °C with no hold time

Figure 25. Graph showing temperature rise (°C) per minute during microwave sintering for specimen sintered to 1450 °C with no hold time

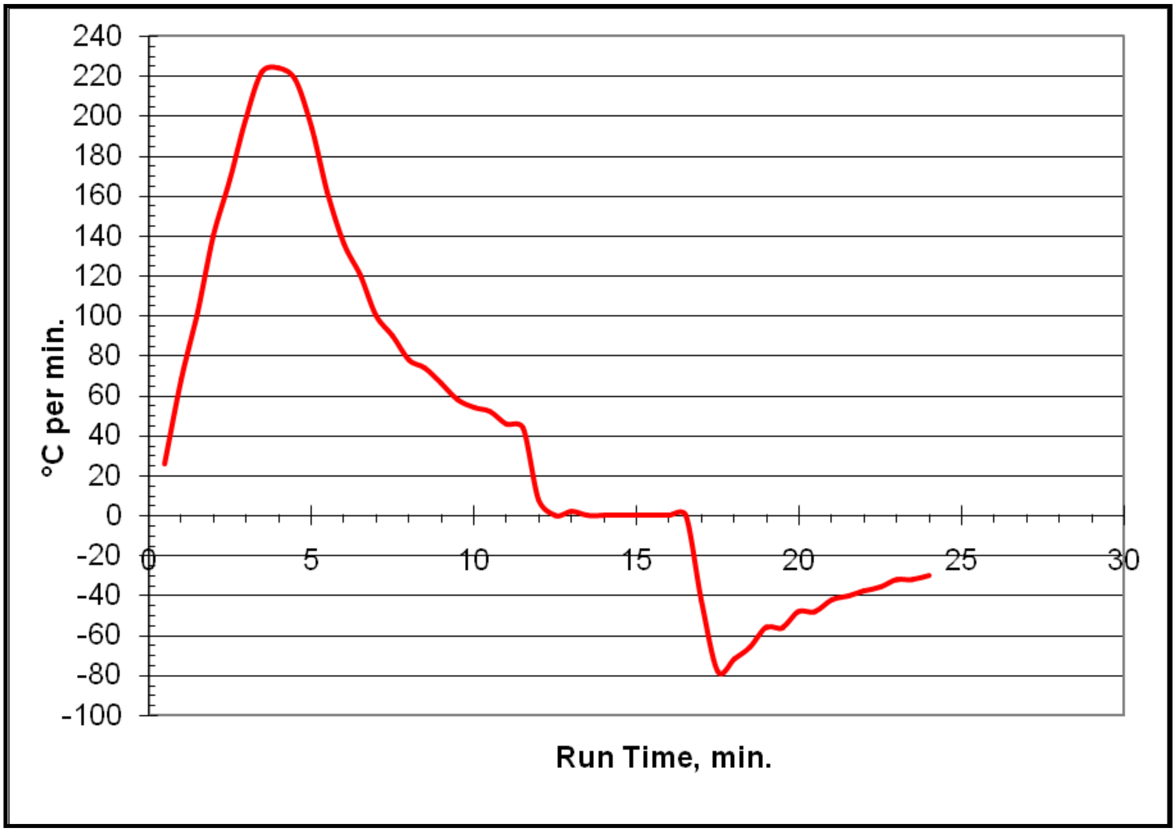


Figure 26. Graph showing temperature rise (°C) per minute during microwave sintering for specimen sintered to 1350 °C with a hold time of 5 minutes

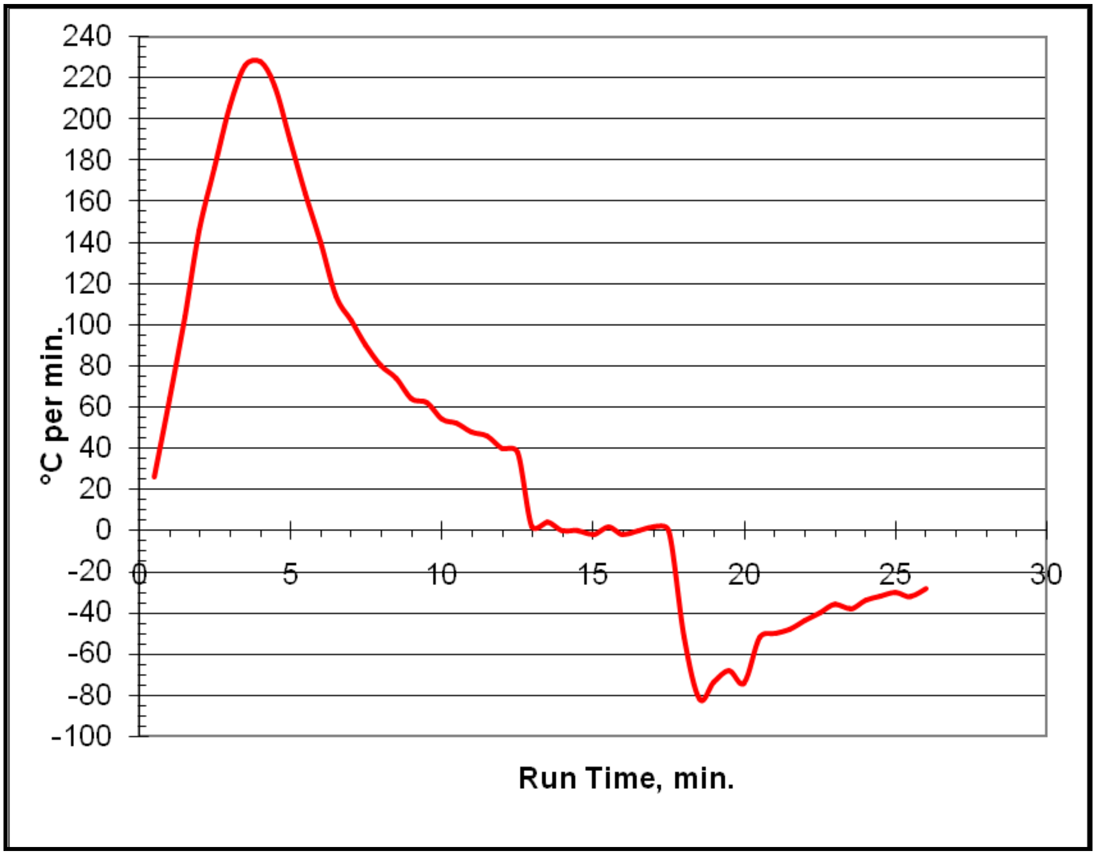


Figure 27. Graph showing temperature rise (°C) per minute during microwave sintering for specimen sintered to 1400 °C with a hold time of 5 minutes

Figure 28. Graph showing temperature rise (°C) per minute during microwave sintering for specimen sintered to 1450 °C with a hold time of 5 minutes

10.4. Sintering Shrinkage

Shrinkage ranging from 11% to 19% was observed for the microwave sintered samples with and without hold times. This range of shrinkage was observed for the specimens that were sintered between maximum sintering temperatures of 1350 °C to 1450 °C (Table 12).

Table 12. Percentage shrinkage of IPS e.max ZirCAD dental zirconia sintered in microwave furnace

Firing Temperature (°C)	Hold Time (mins)	Run A % Shrinkage		Run B % Shrinkage		Average % Shrinkage
		Length	Width	Length	Width	
1350	0			11.7	11.4	11.6
1350	5	14.7	14.8	14.8	14.7	14.8
1400	0	16.1	16.5	15.8	15.9	16.1
1400	5	17.7	17.7	17.9	17.9	17.8
1450	0	18.3	18.4	18.4	18.4	18.4
1450	5	18.9	19.2	18.9	19	19

All specimens sintered with hold times of 5 minutes showed average percentage shrinkages that were greater than similar specimens sintered with no hold times. Furthermore, maximum shrinkage was observed for samples that were sintered at 1450 °C in situations that did and did not utilize hold times, followed by 1400 °C and 1350 °C. This revealed a predictable pattern of shrinkage based on sintering temperatures, with maximum shrinkage occurring as a function of increasing temperatures (Figure 29).

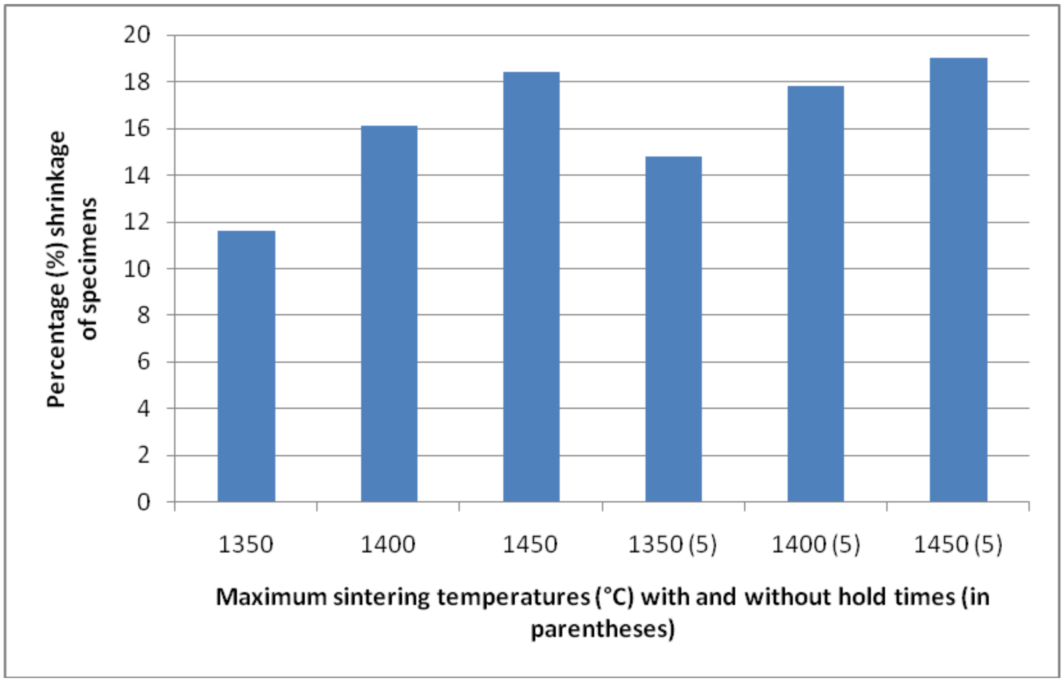


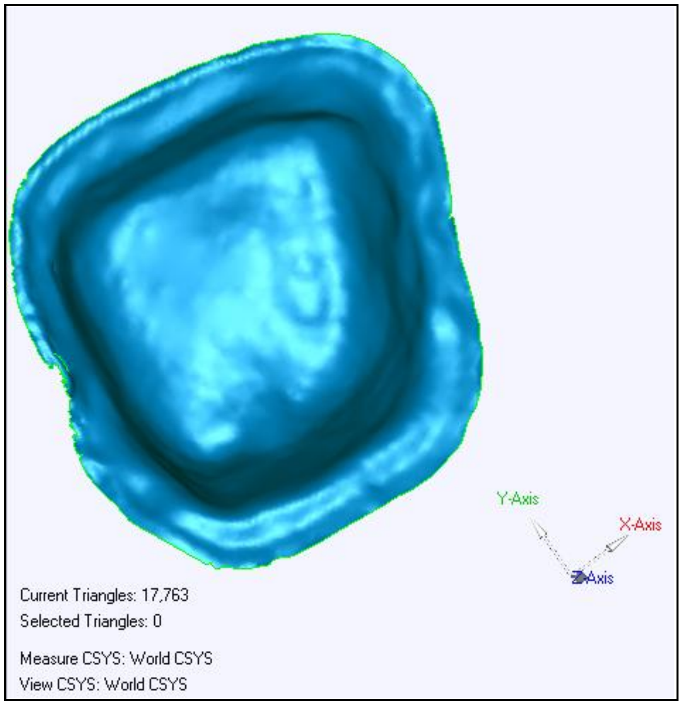
Figure 29. Graph showing the percentage shrinkage of specimens as a function of maximum sintering temperatures (°C)

10.5. Three-Dimensional Shrinkage

Once the zirconia tooth copings were microwave sintered, they were evaluated for the fit on their matching gypsum dies (Figure 30). We did this by visual and manual inspection. Further, the tooth coping margins were visually and manually inspected by a dental laboratory technician. However, as mentioned previously, this type of analysis only provides us with qualitative information related to the fit of the tooth copings on their matching gypsum dies.

Figure 30. Zirconia tooth copings placed on their matching gypsum dies

A software program was utilized to study the three-dimensional shrinkage of the tooth copings as shown in Figure 31 (a, b, c). A description of the results is provided further. Figure 31 (a) shows the pre-sintered/ green coping, while Figure 31 (b) shows the fully sintered tooth coping superimposed on the non-sintered coping. In Figure 31 (c), the green area represents plus or minus 72 microns. The sintered coping in these areas is smaller than the pre-sintered coping. This is signified by the + area (starting from the yellow to the dark red). For example, the gap between the sintered and pre-sintered coping at the top of the positive range is 730 microns. The sintered coping in that area is 730 microns smaller than the pre-sintered coping. In the blue section the sintered coping is larger than the pre-sintered coping. The green range is the closest fitting area.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X-Axis
Z-Axis
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Selected Triangles: 0
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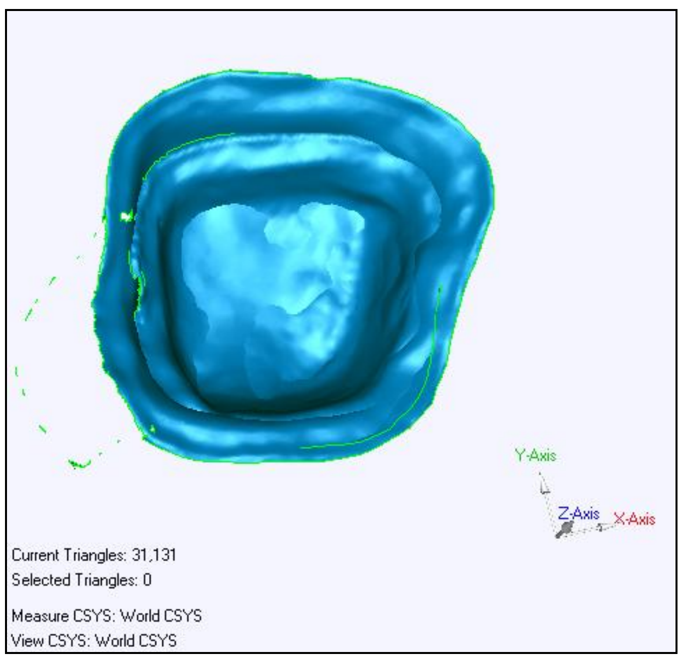
View CSYS: World CSYS

(a)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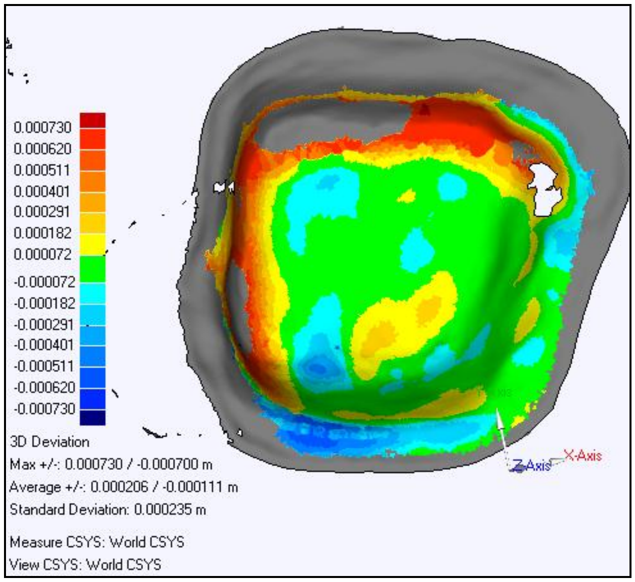
(b)



(c)

Figure 31. (a) – Sintered coping which is the test object; (b) – Pre-sintered is the outside coping and the sintered is the inside coping prior to a best fit analysis; (c) – Color map representing quantitative shrinkage

10.6. Three-Point Bend Test Results

The results of the three-point bend tests are provided in Table 13. Few of the fractured specimens (microwave sintered) are shown in Figure 32. Almost all the specimens fractured in the middle portions. The specimens that were microwave sintered with and without hold times of 5 minutes were also tested for their flexural strength, and their values are shown in Table 14. However, we did not carry out the flexural strength tests for the conventionally sintered specimens from this latter group, but compared the values to data from the literature.

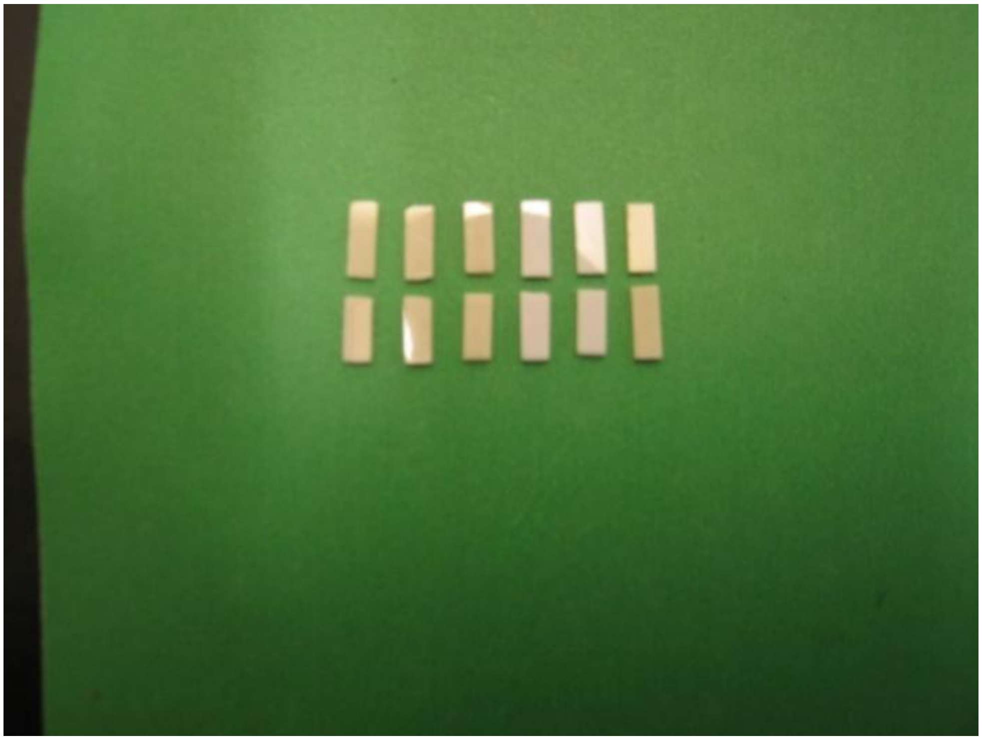


Figure 32. Fractured specimens (after three-point bend test)

Table 13. Three-point bend test results for conventional (Conv) and microwave (MW) sintered samples

	Specimen Number	Maximum load (N)	Maximum stress (MPa)
Conventional	1	182.26	768.31
	2	147.44	811.08
	3	174.17	684.97
	4	198.32	772.98
	5	155.25	797.51
	6	157.74	722.62
	7	172.46	663.52
	8	123.89	751.1
	9	214.4	794.06
	10	185.95	726.46
	Mean	**171.188**	**749.261**
	Std. Dev.	**26.22631**	**49.215877**
	Minimum	**123.89**	**663.52**
	Maximum	**214.4**	**811.08**
	Median	**173.315**	**759.705**
Microwave	1	157.24	769.44
	2	201.83	851.56
	3	208.89	820.2
	4	199.72	843.32
	5	112.33	458.8
	6	222.16	883.39
	Mean	**183.695**	**771.1183**
	Std. Dev.	**41.21372**	**157.6347**
	Minimum	**112.33**	**458.8**
	Maximum	**222.16**	**883.39**
	Median	**200.775**	**831.76**

Table 14. Flexural strength of microwave sintered zirconia specimens with and without hold times of 5 minutes (numbers in parentheses)

Specimen/Sintering temperature (°C)	Load (N)	Thickness (mm)	Strength (MPa)
1350	885.47	1.58	512.35
1350 (5)	719.30	1.32	596.30
1400	796.15	1.25	736
1400 (5)	1141.11	1.28	1006.04
1450	927.50	1.35	978.70
1450 (5)	1144.00	1.21	1128.66

10.7. Vickers Hardness Measurements

The results of the Vickers Hardness measurements are provided in Tables 15 and 16. Table 15 shows the hardness and fracture toughness for a set of specimens that were both microwave (n=10) and conventionally (n=10) sintered and then compared. Table 16 shows the hardness values of microwave and conventionally sintered specimens that were processed at various maximum sintering temperatures. The average Vickers hardness measurements (from three specimens processed at each maximum sintering temperature) is shown in Table 16. The same data is represented in Figure 35. Figure 33 shows an example of the indentation on microwave sintered specimen, while Figure 34 shows an example of the Vickers indentation on a conventionally sintered sample.

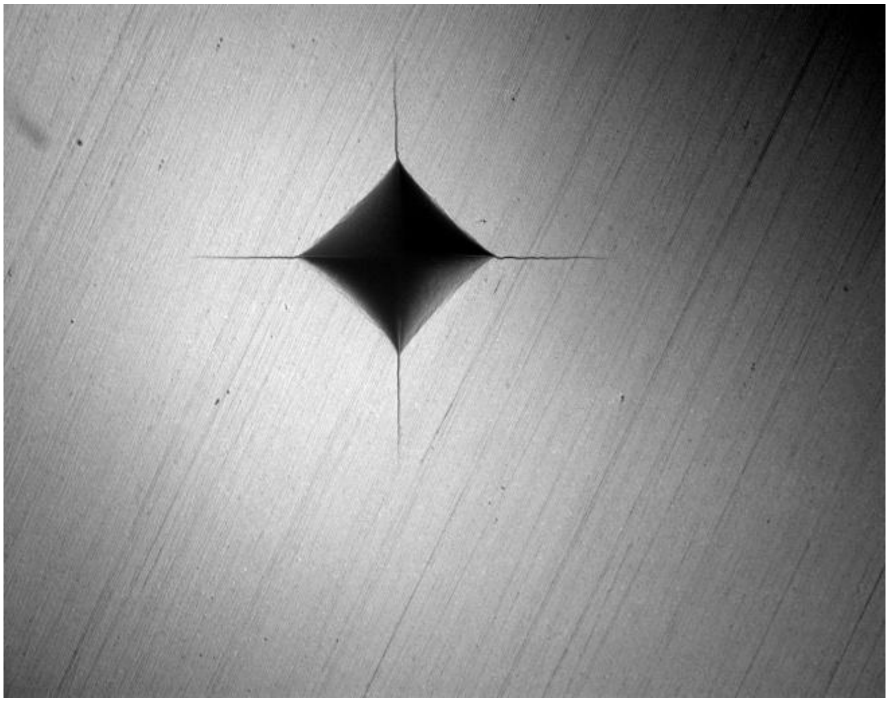


Figure 33. Vickers diamond indentation on microwave sintered zirconia specimen (load = 100 N, indentation time = 10 seconds)

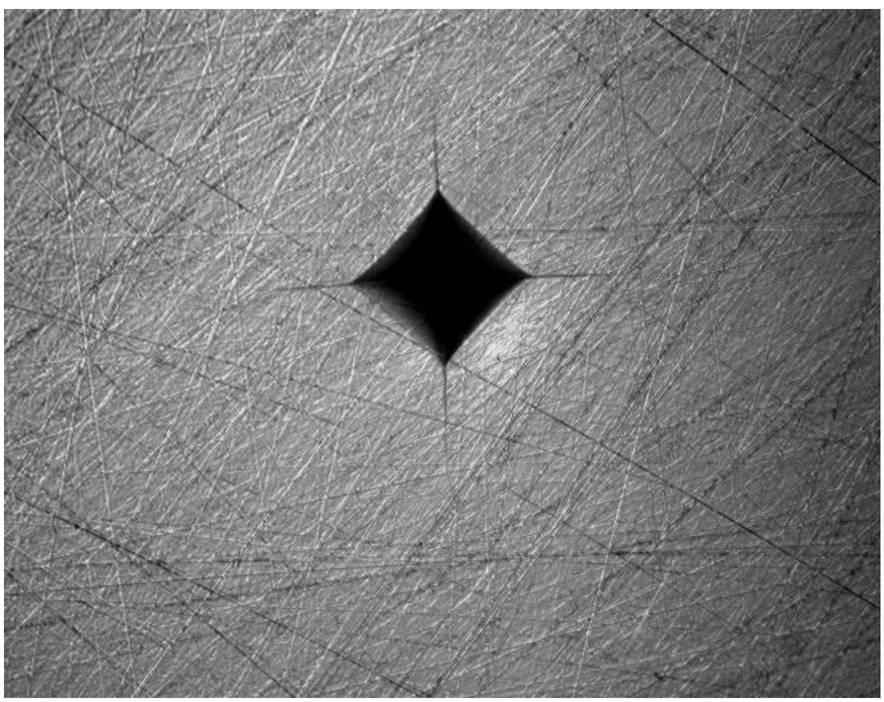


Figure 34. Vickers diamond indentation on conventionally sintered zirconia specimen (load = 100 N, indentaion time = 10 seconds)

Table 15. Vickers Hardness Values of Microwave and Conventionally Sintered Specimens

Specimen Number	Vickers Hardness Numbers (VHN) with standard deviation
1 (Microwave) (n=10)	13.71 ± 0.084
2 (Microwave) (n=10)	13.80 ± 0.160
3 (Conventional) (n=10)	12.52 ± 0.036
4 (Conventional) (n=10)	12.31 ± 0.224

Table 16. Vickers Hardness Values of Microwave and Conventionally Sintered Specimens at Different Maximum Sintering Temperatures With and Without Hold Times (numbers in parentheses denote hold time in minutes)

Specimen number	Maximum sintering temperatures	Average Vickers Hardness Numbers (VHN) with standard deviation (Microwave)	Average Vickers Hardness Numbers (VHN) with standard deviation (Conventional)
1	1350 n=3	6.28 ± 0.075	12.52 ± 0.30
2	1400 n=3	7.07 ± 0.014	12.50 ± 0.15
3	1450 n=3	7.98 ± 0.047	12.31 ± 0.22
4	1350 (5) n=3	10.77 ± 0.071	-
5	1400 (5) n=3	11.63 ± 0.929	-
6	1450 (5) n=3	12.23 ± 0.571	-

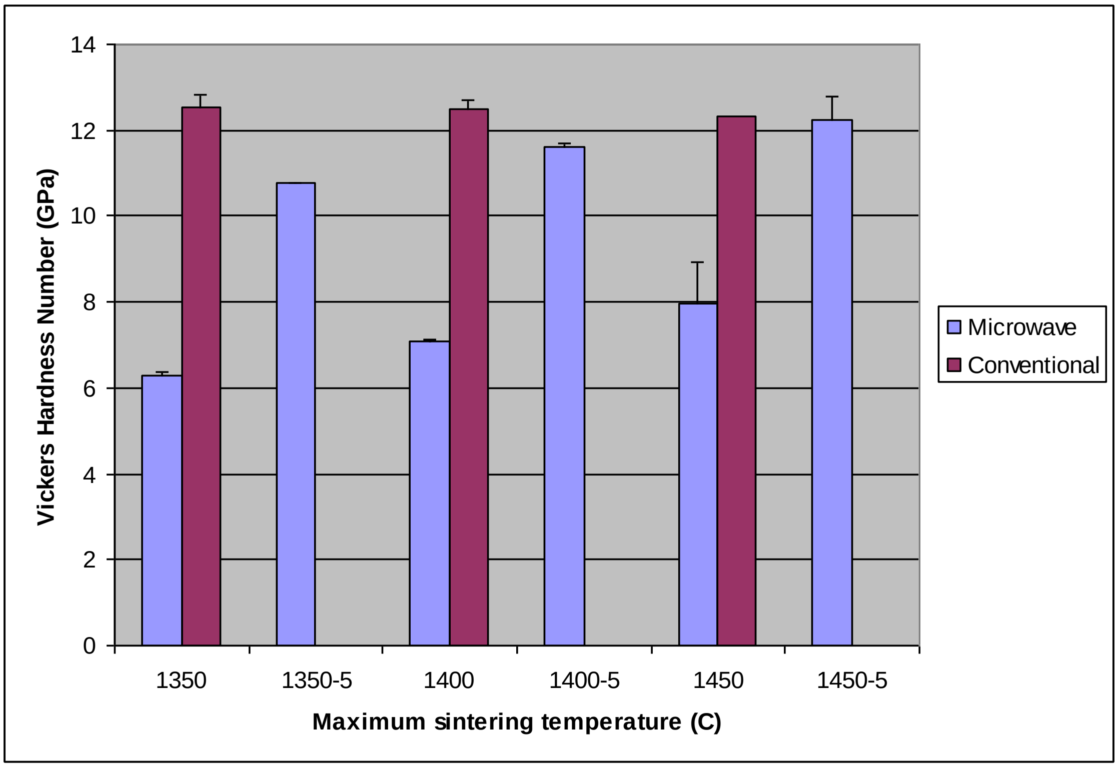


Figure 35. Vickers hardness values for zirconia specimens microwave and conventionally sintered at different maximum sintering temperatures (°C)

10.8. Fracture Toughness Measurements

The results of the fracture toughness measurements are provided in Tables 17 and 18. Table 17 shows the fracture toughness values for a set of specimens that were both microwave (n=1) and conventionally (n=1) sintered and then compared. Table 18 shows the fracture toughness values of microwave and conventionally sintered specimens that were processed at various maximum sintering temperatures. The average fracture toughness values (from three specimens processed at each maximum sintering temperature) are shown in Table 18. The same data is represented in Figure 36.

Table 17. Fracture Toughness Values of Microwave and Conventionally Sintered Specimens

Specimen Number	Fracture Toughness ($MPa[m]^{1/2}K_{1c}$) with standard deviation
1 (Microwave; n=1)	2.13 ± 0.099
2 (Microwave; n=1)	2.19 ± 0.095
3 (Conventional; n=1)	2.73 ± 0.21
4 (Conventional; n=1)	2.81 ± 0.31

Table 18. Fracture Toughness Values of Microwave and Conventionally Sintered Specimens at Different Maximum Sintering Temperatures With and Without Hold Times (numbers in parentheses denote hold time in minutes)

Specimen Number	Maximum sintering temperatures (°C)	Average Fracture Toughness (K_{Ic} – MPa[m]$^{1/2}$) with standard deviation (Microwave)	Average Fracture Toughness (MPa[m]$^{1/2}$$K_{Ic}$) with standard deviation (Conventional)
1	1350 n=3	6.41± 0.10	7.11 ± 0.66
2	1400 n=3	6.72 ± 0.11	6.72 ± 0.43
3	1450 n=3	7.28 ± 0.44	6.81 ± 0.88
4	1350 (5) n=3	6.86 ± 0.0	-
5	1400 (5) n=3	6.86 ± 0.0	-
6	1450 (5) n=3	6.83 ± 0.79	-

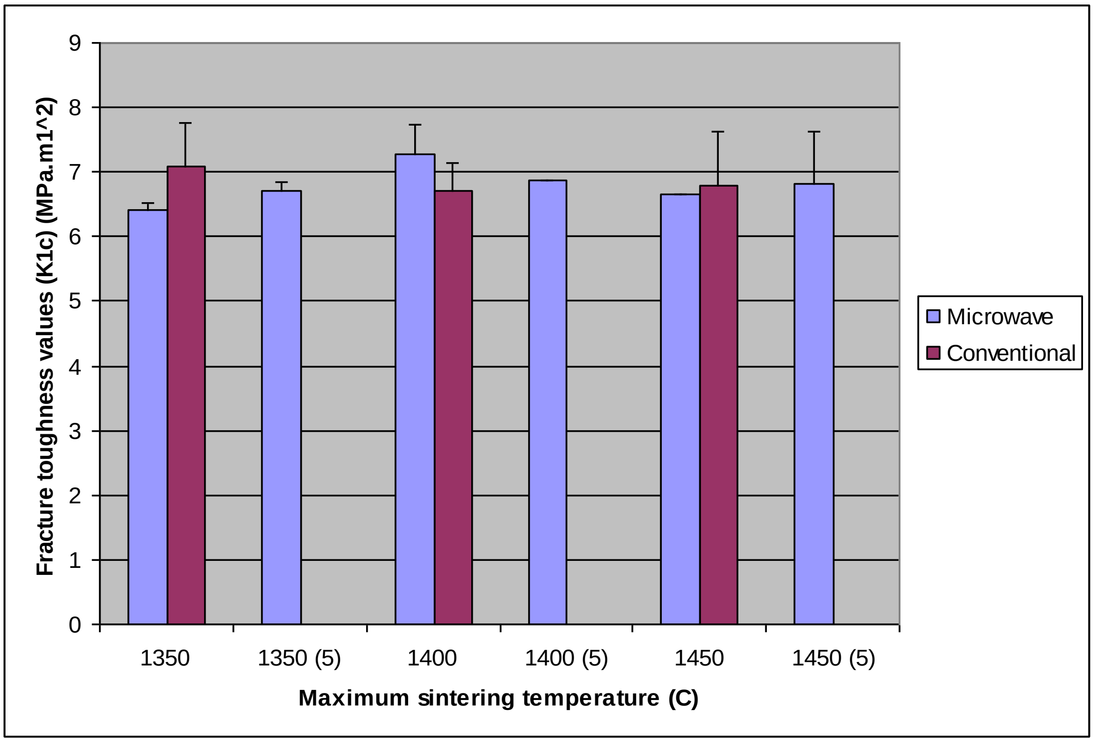
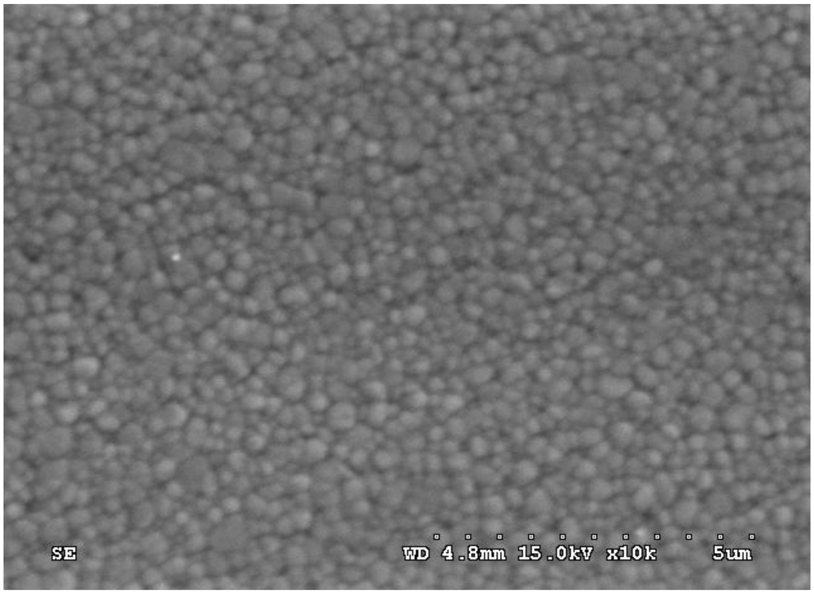


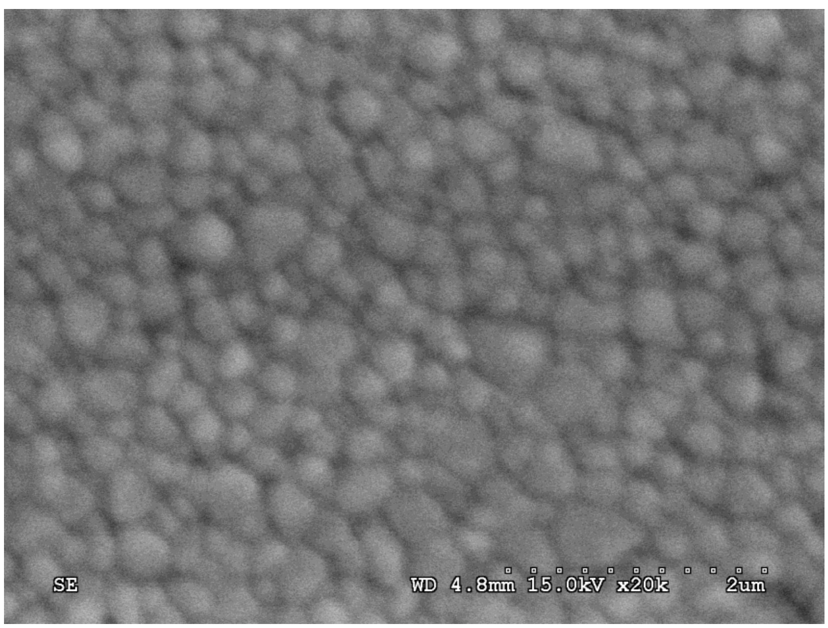
Figure 36. Fracture toughness values for zirconia specimens microwave and conventionally sintered at different maximum sintering temperatures (°C)

10.9. SEM

Microstructural characterization of the microwave sintered Y-TZP dental materials were performed by an SEM analysis. The specimens were characterized for their grain size and distribution. In addition, the specimens were studied for the presence of porosities. Figure 37 (a) and 37 (b) shows the SEM images of a Y-TZP material that was sintered using normal power input and time (i.e., 45% power input for 15 minutes and 50% power input for 25 minutes). The specimens shown in Figures 37 (a), 37 (b) and 45 were sintered in a 2 kW microwave furnace in normal atmosphere with a single alumina thermal containment chamber. Specimens shown from Figures 38 to 43 were sintered in a microwave furnace with a double ring alumina thermal containment chamber.



(a)



(b)

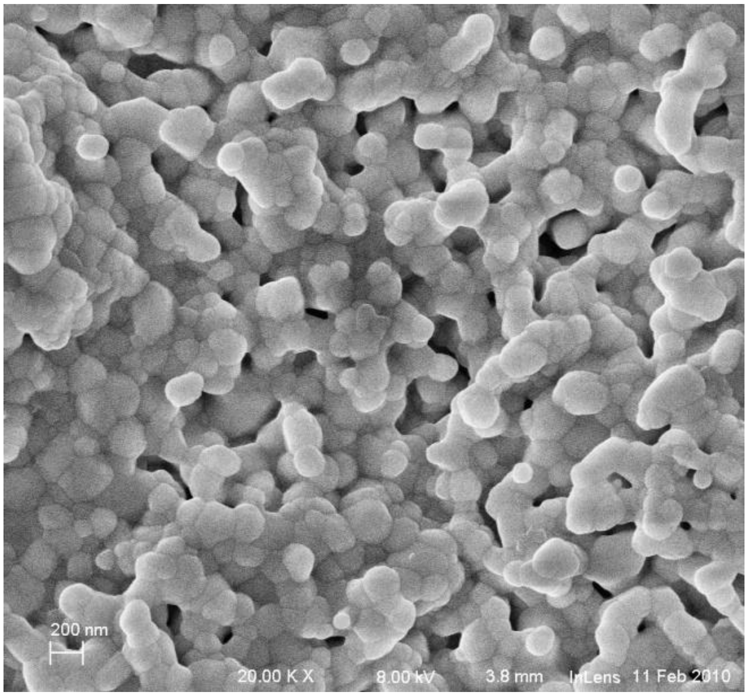
Figure 37. (a) SEM image of normally microwave sintered Y-TZP (x 10k); (b) SEM image of normally microwave sintered Y-TZP (x 20k)

Figures 37 (a) and 37 (b) show even distribution of the zirconia particles when compared to the rapidly sintered counterpart (Figure 45). The average grain size ranges between 0.5 µm to 2µm.

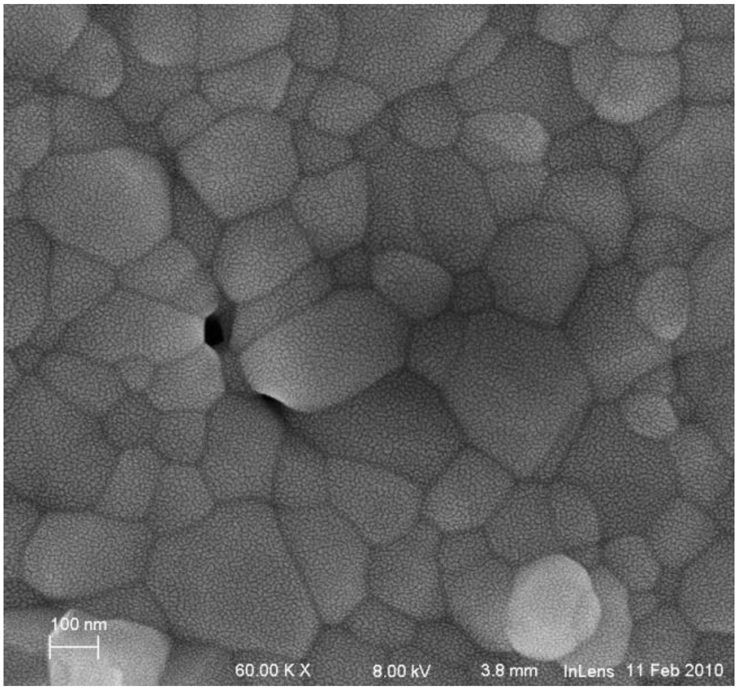
Figures 38, 39 and 40 show the microstructure of zirconia sintered at 1350° C, 1400° C and 1450 °C respectively. Figures 41, 42 and 43 show the microstructure of zirconia sintered at 1350 °C, 1400 °C and 1450 °C with a hold time of 5 minutes respectively. The specimens shown in Figures 38 to 43 were sintered in a 2 kW microwave furnace in normal atmosphere with two circular alumina thermal containment chambers. The average grain size of the zirconia material sintered at 1350 °C ranged between 0.1 µm to 0.3 µm. There was a lack of uniform grain size distribution in this specimen population. Some porosities were observed in this group of specimens (Figure 38 a). Furthermore, some areas of the specimen were not fully sintered when compared to other areas, indicating incomplete sintering. The same was observed in the specimens sintered at 1350 °C with a hold time of 5 minutes (Figure 41).

When the zirconia specimens were sintered with hold times of 5 minutes, it was observed that there was improved microstructure in terms of even distribution of grains, and less porosity. However, sintering the specimens at 1350 °C with and without a hold time of 5 minutes revealed incomplete sintering mixed with fully sintered areas of the specimen {Figures 38 (a), 41 (a) and 41 (b)}c. Figures 40 (a) and 40 (b) show the microstructure of zirconia sintered at 1450 °C. The grain size distribution is somewhat dense; however, there are several larger grains interspersed between smaller grains. Figure 45 shows the

SEM image of Y-TZP material sintered rapidly (i.e., greater than 55% power input, time duration of 15 minutes in a 2 kW microwave furnace with a single cylinder alumina thermal containment chamber). It is evident that the number of porosities is much higher in a rapidly sintered specimen when compared to normally sintered zirconia (Figure 45). Table 19 shows the average grain sizes that were obtained at various maximum sintering temperatures.

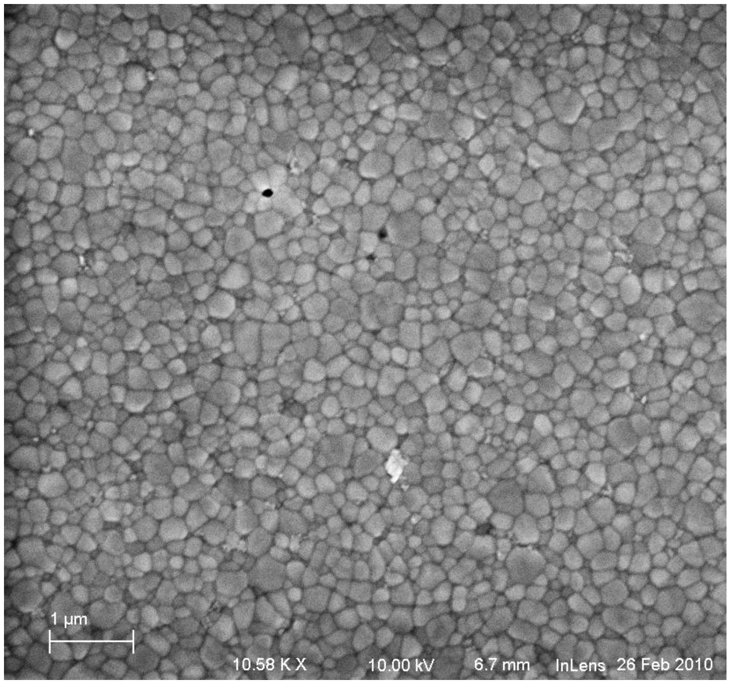


(a)

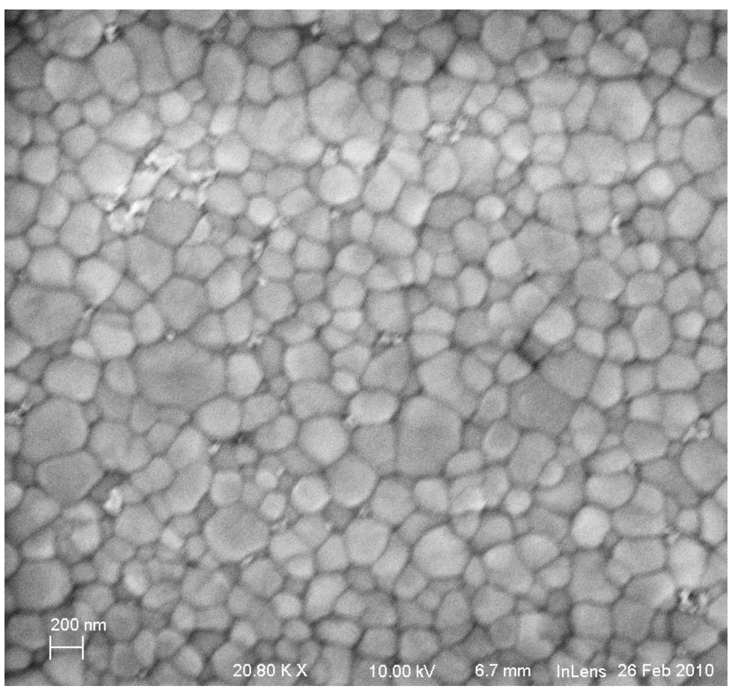


(b)

Figure 38. (a) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1350° C (x 20k); (b) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1350 °C (x 60k)

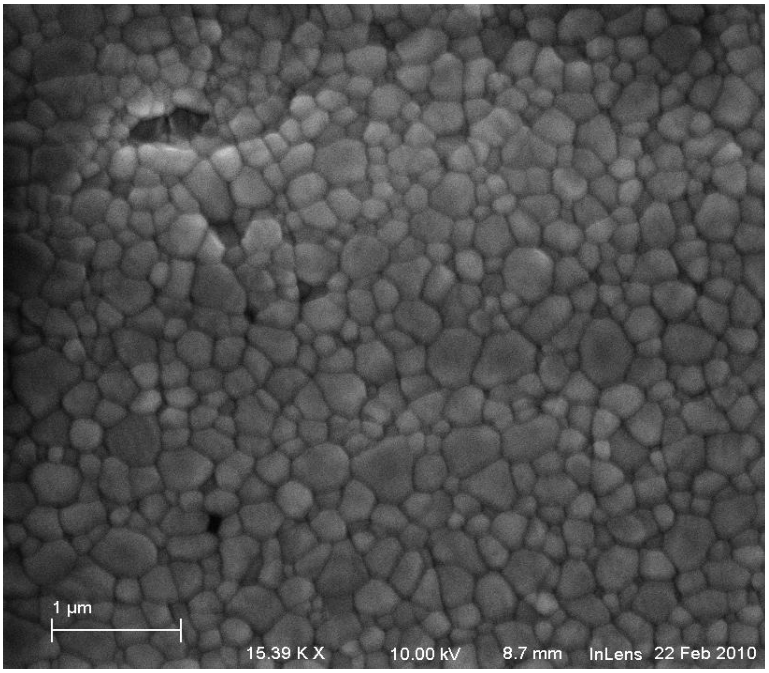


(a)

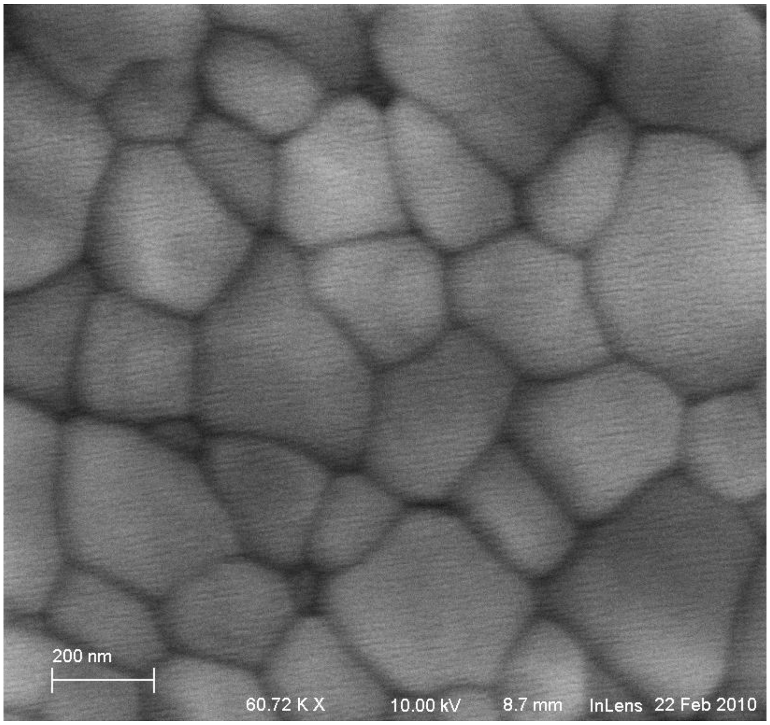


(b)

Figure 39. (a) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1400° C (x 10k); (b) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1400 °C (x 20k)

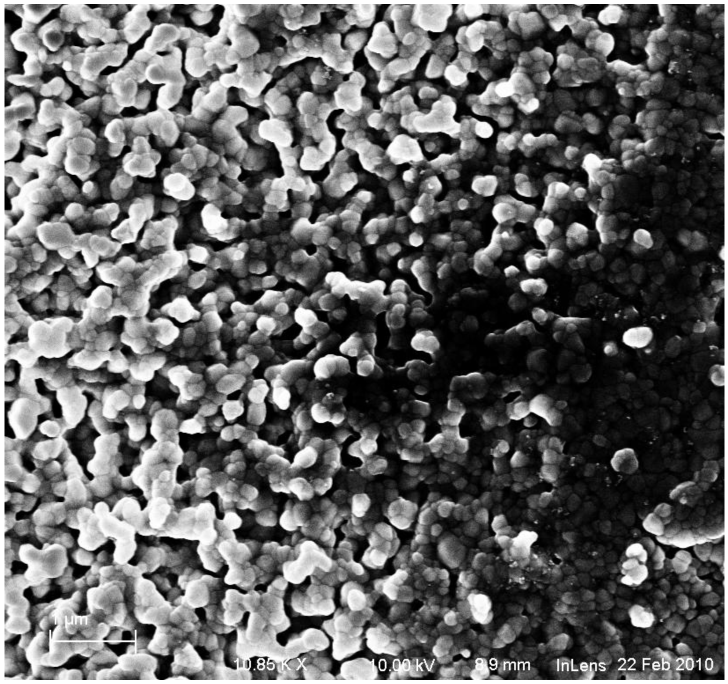


(a)

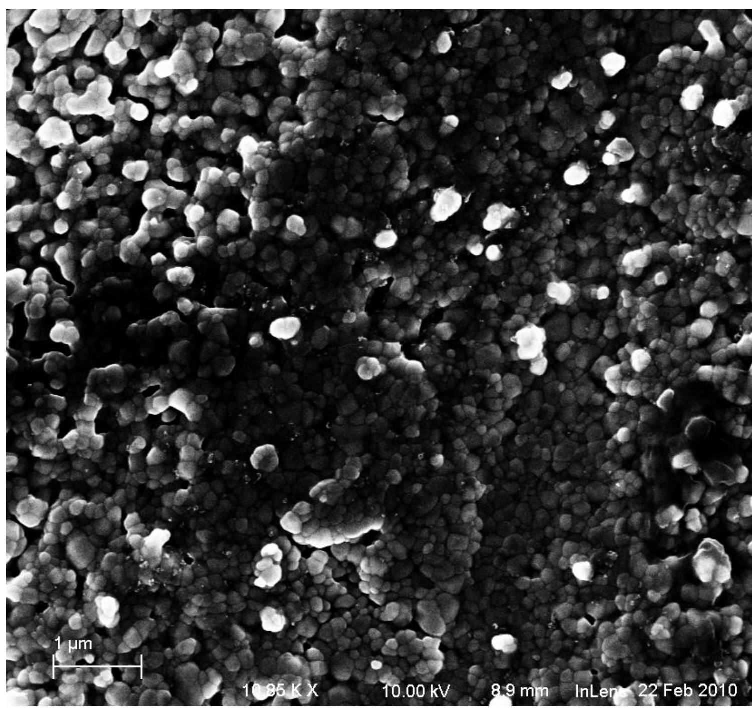


(b)

Figure 40. (a) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1450° C (x 15k); (b) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1450 °C (x 60k)

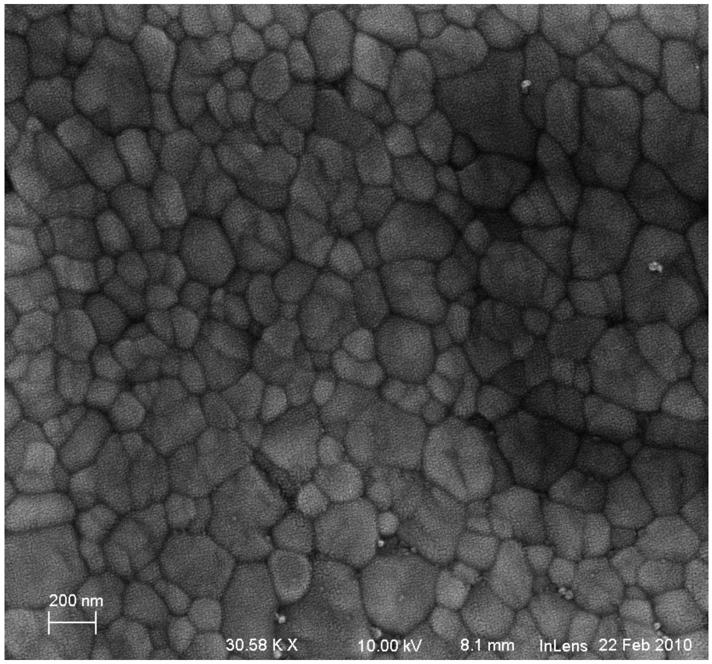


(a)

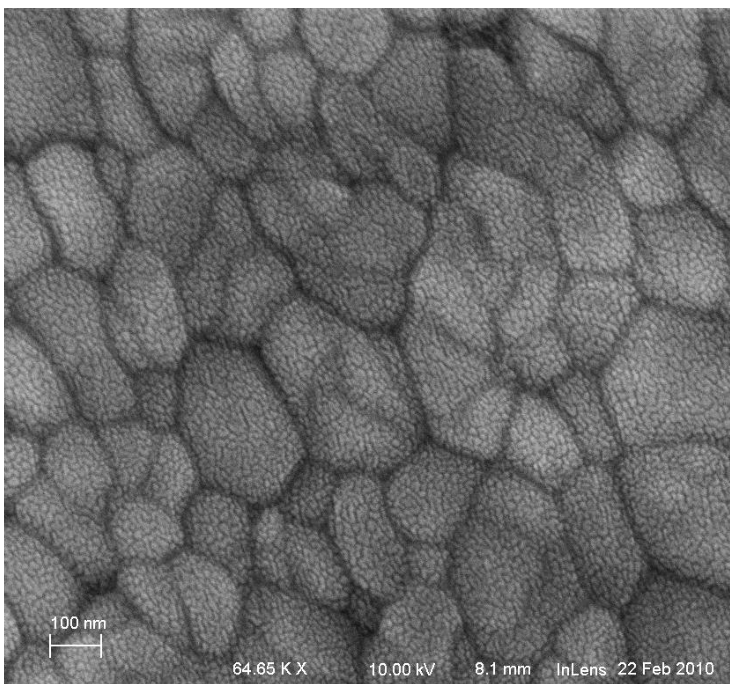


(b)

Figure 41. (a) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1350° C with hold time of 5 minutes (x 10k); (b) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1350 °C with hold time of 5 minutes (x 10k)

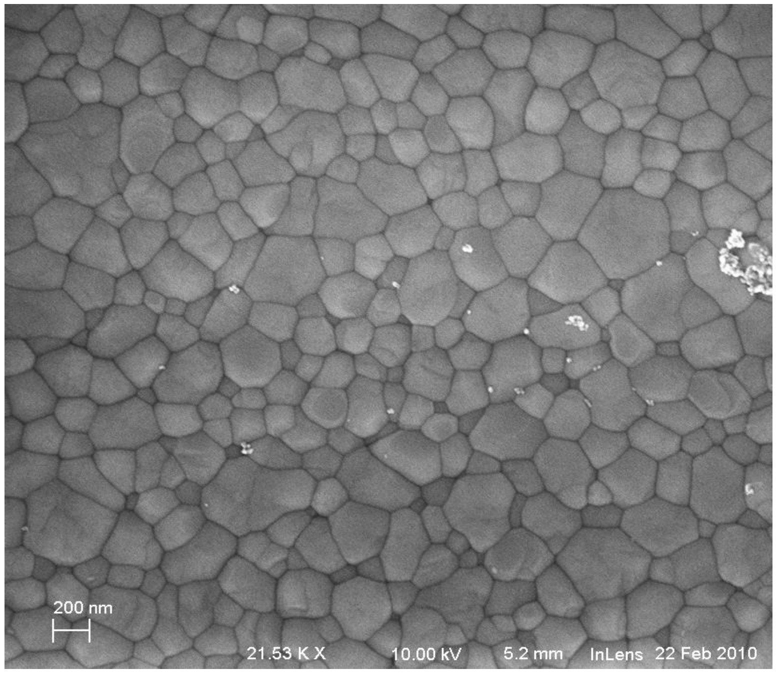


(a)

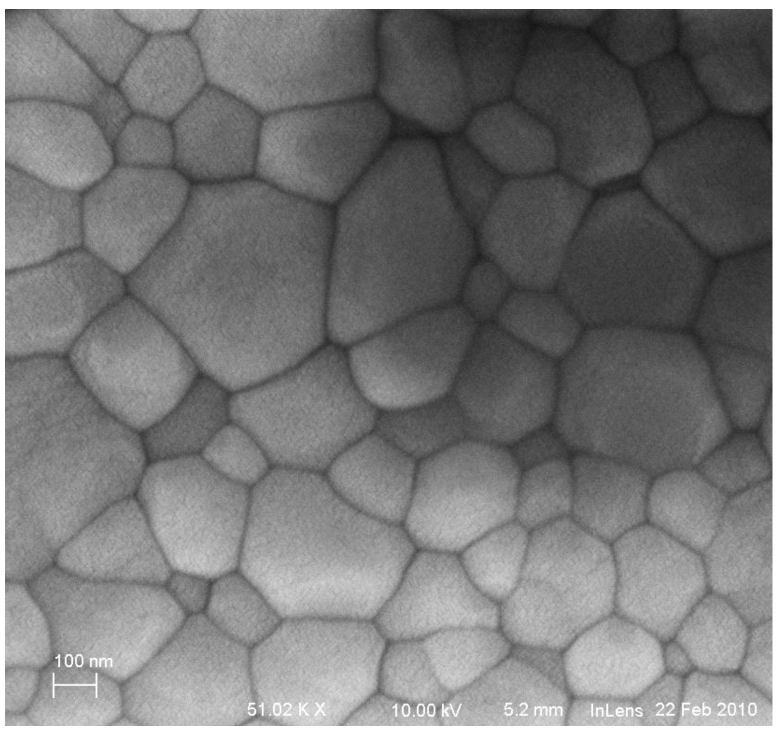


(b)

Figure 42. (a) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1400° C with hold time of 5 minutes (x 30k); (b) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1400 °C with hold time of 5 minutes (x 55k)

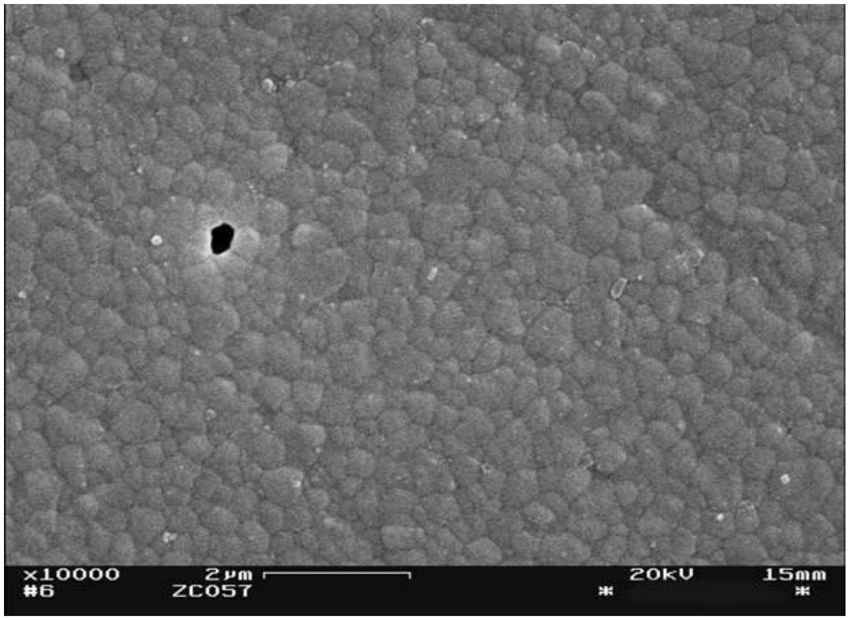


(a)

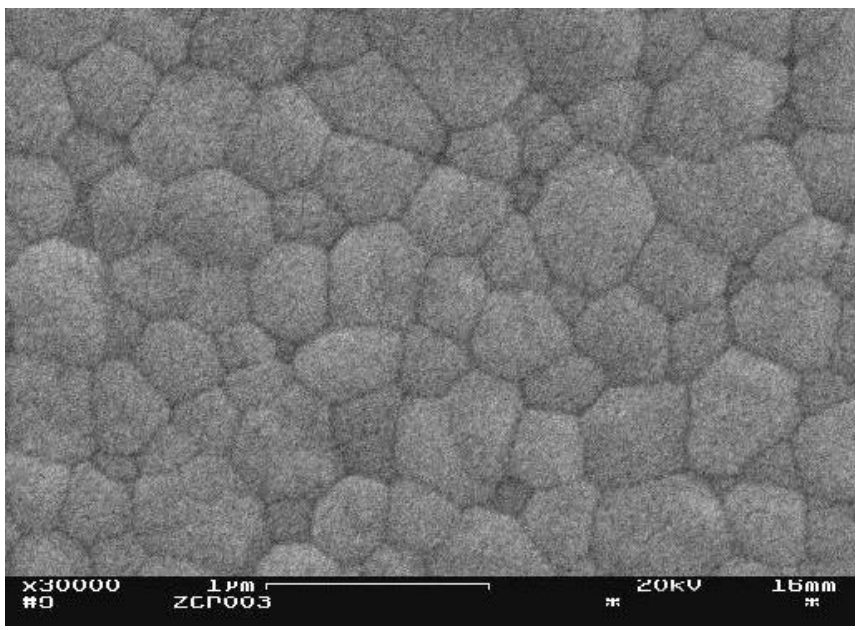


(b)

Figure 43. (a) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1450° C with hold time of 5 minutes (x 20k); (b) Microstructure of microwave sintered zirconia (3 mol% Y-TZP) at 1450 °C with hold time of 5 minutes (x 50k)



(a)



(b)

Figure 44. (a) Microstructure of conventionally sintered zirconia (3 mol% Y-TZP) at 1500 °C (~ 10x) ; (b) ~ 30 x (Courtesy: Thomas Hill, Ivoclar Vivadent, Buffalo, NY)

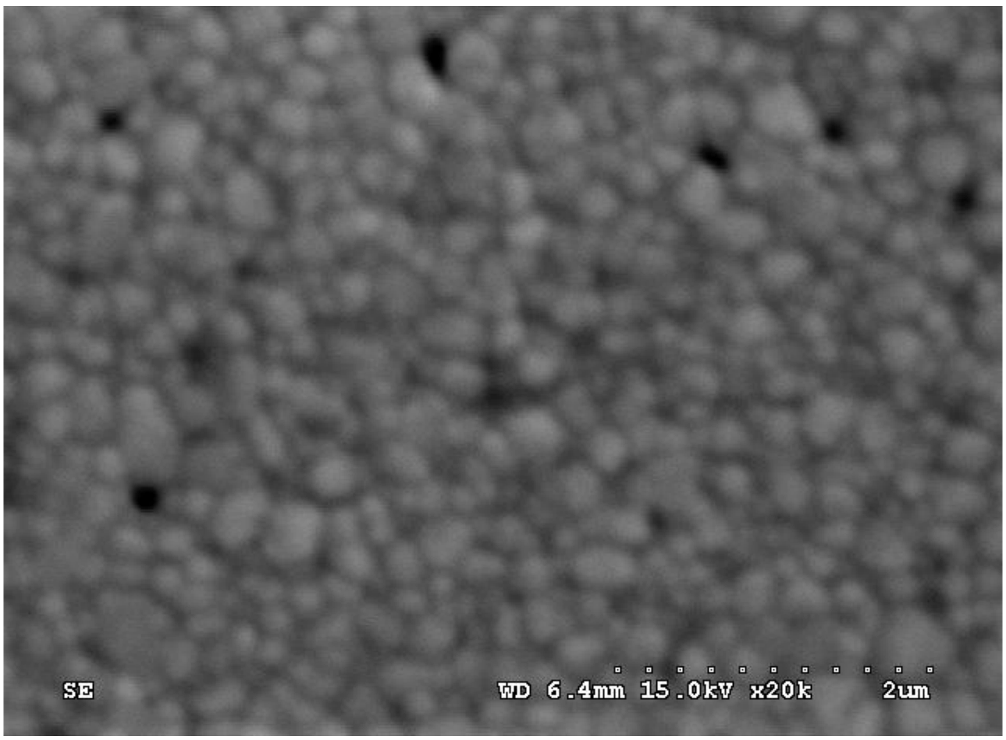


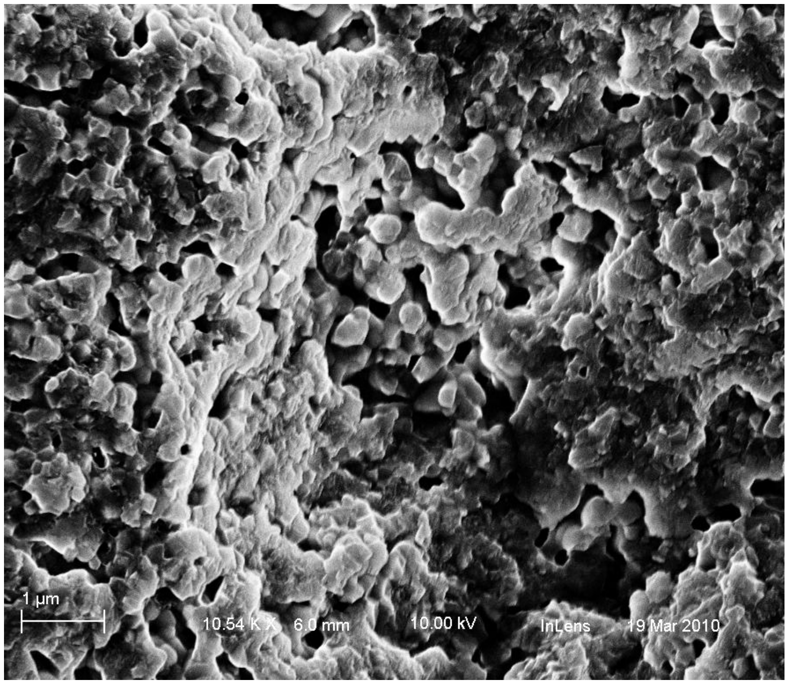
Figure 45. SEM image of rapidly microwave sintered Y-TZP

Table 19. Maximum sintering temperature (°C) and average grain size of microwave sintered 3 mol% Y-TZP (numbers in parentheses denote hold time in minutes)

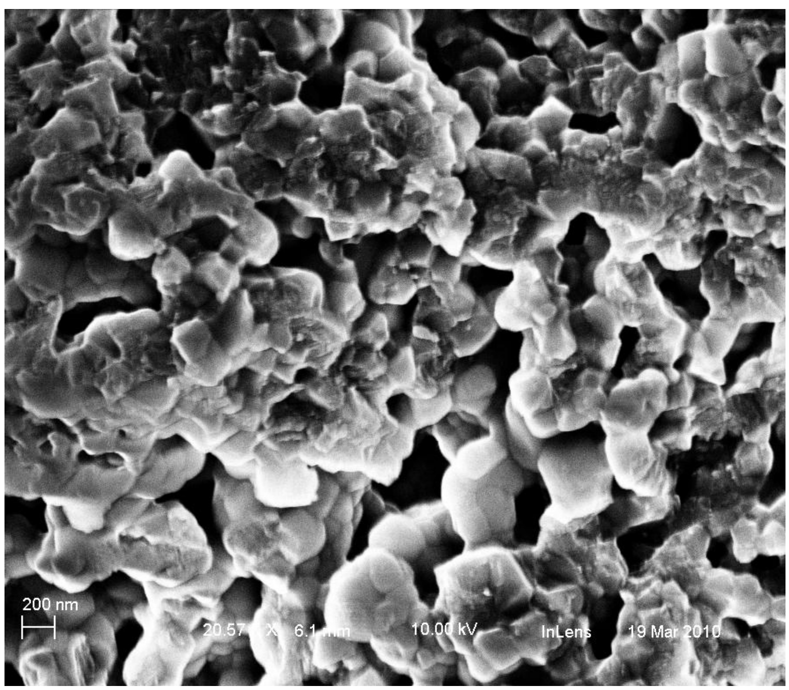
Sintering temperature	Average grain size (μm)
1350	0.05 to 0.4
1400	0.1 to 0.2
1450	0.05 to 0.2
1350 (5)	0.05 to 0.25
1400 (5)	0.1 to 0.2
1450 (5)	0.5 to 0.2

10.10. Fractographic analysis

Dental ceramics have been analyzed previously using fractography (93). In our studies, it was noticed that few specimens (Figure 39) showed particles that were randomly present on the surface of the zirconia sample sintered at 1400° C. In an effort to further analyze the microstructure and fracture pattern within the material, an SEM analysis was carried out for this specimen. In addition, another specimen (1400° C with dwell time of 5 minutes) was also fractured and visualized under the SEM to provide a reference surface. This allowed us to compare the two specimens and to determine if they exhibited different fracture patterns. The results of the analysis showed that the fracture occurred in between the particles, suggesting an intergranular type of fracture. Figure 46 shows the images of the fractured surfaces.



(a)



(b)

Figure 46. (a) Fractured surface of microwave sintered 3Y-TZP specimen sintered at 1400° C; (b) fractured surface of microwave sintered 3Y-TZP specimen sintered at 1400° C with a dwell time of 5 minutes

11. Rapid Sintering of Zirconia Specimens

In an effort to achieve the most rapid sintering, we processed few zirconia specimens (i.e., pellets – IPS e.max ZirCAD; n = 3) by increasing the power inputs of the 2 kW microwave furnace with a single alumina cylinder configuration (Figure 4) to between 60%, 70% and 80% with time durations of 20, 15 and 10 minutes respectively (Table 5). However, following the sintering process, we observed that this power input was too high to achieve optimum results. This was evident from the final observations of the sintered zirconia materials, which developed a rough surface and were warped. In addition, the silicon carbide susceptor material was affected by contamination with the alumina particles from the surrounding chamber wall during the sintering process (Figure 47). The grey/black color of the silicon carbide susceptor was contaminated with the white alumina material (Figure 47). This might have occurred due to the high temperatures developed inside the thermal containment box. It was observed that the surface(s) of the inner portions of the alumina thermal containment chamber melted following the high temperature sintering event. This may have also led to contamination of the silicon carbide susceptor materials. These silicon carbide susceptor materials were replaced with new materials in order to maintain optimum sintering.

Figure 47. Contamination of silicon carbide susceptor with alumina

The results of the previously mentioned experiments helped us to understand that higher power inputs were not suitable for sintering zirconia dental materials optimally with the particular configuration of a single cylinder alumina thermal containment chamber. In addition to these previously mentioned events, the alumina chamber lid had shifted slightly during the high temperature sintering. This may have occurred due to the very high temperatures and pressures that developed inside the alumina chamber (Figure 48). Furthermore, it was observed that the high temperature sintering affected the structural stability of the alumina thermal containment chamber. The lid of the alumina chamber cracked during the rapid microwave sintering experiments (Figure 48). However, these previously mentioned phenomena were not true when a double cylinder configuration was utilized for the microwave sintering experiments.

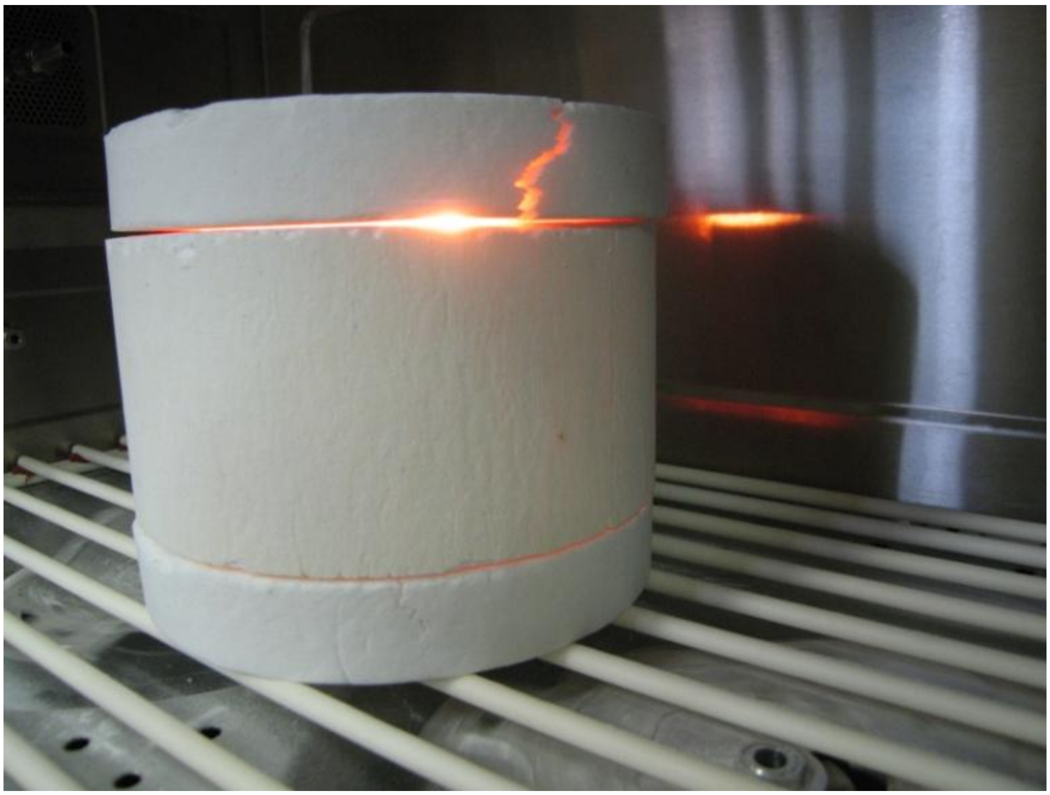


Figure 48. Thermal cracking of the lid of the alumina containment chamber following rapid microwave sintering

12. Data Analysis

The results from the specimens sintered by conventional and microwave sintering experiments were recorded for their optimum characterization qualities, so as to simulate the highest quality dental ceramic materials. All the characterization tests were statistically analyzed using Mann-Whitney Test and the Wilcoxon signed rank sum test where appropriate. The statistical tests were carried out using SAS 9.2 software package.

Descriptive statistics (i.e., mean, standard deviation) for the results are mentioned in Tables 10, 12, 13, 14, 15, 16, 17, 18 for the respective tests. The statistical analysis was carried out using non-parametric tests. The values for density for both sets of specimens (i.e., conventional and microwave) processed at various maximum sintering temperatures was analyzed by the Mann Whitney test due to the non-parametric nature of the data. It was found that the specimens did not vary significantly according to the statistical analysis (p value = 0.29 – Table 21). However, it was noticed that there was a definite increase in density for both sets of specimens as a function of increasing sintering temperatures.

The hardness values for specimens that were sintered by both conventional and microwave techniques showed statistically significant differences between the groups (0.0012). In order to test for variations in the hardness values between specimens that were microwave sintered with and without hold times of 5 minutes, the non parametric analog of the paired t-test (i.e., Wilcoxon signed rank sum test) was utilized. The results showed that the difference between the hardness of specimens sintered by both the previously mentioned techniques was statistically significant (Table 20). Conventionally sintered specimens were not sintered with a hold time of 5 minutes and were therefore not included in the previously mentioned statistical analysis.

The fracture toughness values for specimens sintered by conventional and microwave techniques showed statistically significant differences between the groups (p value = 0.002) (Table 21). However, the fracture toughness values for the specimens sintered at 1450 °C with and without hold time of 5 minutes showed no statistical significance (p value = 0.422) (Table 20). For the flexural strength, the total number of samples was higher in the conventional group (n=10) when compared to the microwave group (n=6). Due to the unequal number of specimens, the resulting data was analyzed using the Mann Whitney test. The results showed no statistically significant differences in the strength values (Table 21).

Table 20. P values for Wilcoxon signed rank sum test to determine difference between hardness (VHN) and fracture toughness (K1c) for microwave sintered specimens at 1350 °C, 1400 °C and 1450 °C with and without hold time of 5 minutes (* < 0.001)

Sintering temperature (°C)	p value
VHN (1350) (n=3)	0.0018*
VHN (1400) (n=3)	0.001*
VHN (1450) (n=3)	0.04
K1c (1350) (n=3)	0.026
K1c (1400) (n=3)	0.0007*
K1c (1450) (n=3)	0.422

Table 21. P values for Mann Whitney test to determine difference between density, hardness, fracture toughness and flexural strength (three-point bend test) for microwave and conventionally sintered specimens at 1350 °C, 1400 °C and 1450 °C (* < 0.001)

Sintering temperature	p value
Density	0.29
VHN	0.0012*
K1c	0.002
Flexural strength	0.2781

13. Discussion

From the microwave sintering experiments, it was evident that the zirconia specimens could be successfully processed at their maximum sintering temperatures in less than 20 minutes (Table 11). However, this was only possible when the alumina thermal containment chamber was placed as a double cylinder (Figure 8). When the same was attempted (i.e., rapid sintering at approximately 15 minutes) with a single cylinder configuration (Figure 4), it was observed that the samples warped and the surface developed blistering. Furthermore, the microstructure of this rapidly sintered material revealed more porosities when compared to the other specimens (Figure 45).

When the single alumina cylinder was used, it was observed that an average of 27 minutes was necessary to reach the maximum sintering temperature when compared to approximately 15 minutes with the double alumina ring configuration. Thus, the specimens required approximately twice the amount of time to reach the maximum sintering temperature with the single cylinder configuration when compared to the double cylinder set-up. Maximum density was observed for specimens sintered at 1450 °C with a dwell time of 5 minutes, followed by 1450 °C and 1400 °C.

The hardness values for the microwave sintered specimens demonstrated a predictable pattern as a function of their maximum sintering temperatures (Figure 35). Both sets of specimens (i.e., with and without hold times) showed a linear rise in the hardness values based on their maximum sintering temperatures, with specimens sintered at 1400 °C and 1450 °C with a hold time of 5 minutes showing the highest hardness. However, it was observed that the values for the specimens sintered at the lowest maximum sintering temperature (i.e., 1350 °C with a hold time of 5 minutes) showed the least standard deviation while the specimens sintered at 1400 °C with a hold time of 5 minutes had the largest standard deviation.

The fracture toughness values were highest for specimens sintered at a maximum sintering temperature of 1400 °C with and without a hold time of 5 minutes. This was followed by 1450 °C with a hold time of 5 minutes, 1450 °C, 1350 °C with a hold time of 5 minutes and 1350 °C. The highest standard deviation was observed for specimens sintered at 1400 °C and 1450 °C with a hold time of 5 minutes; the least standard deviation was observed for specimens sintered at 1400 °C with a hold time of 5 minutes and 1450 °C. The fracture toughness values of the zirconia specimens that were microwave sintered in our experiments were close to published values, although some authors have reported higher values (94, 95). However, the specimens in some of these studies were sintered at slightly higher temperatures when compared to our experiments (96).

The results from the flexural strength tests for specimens sintered by both microwave and conventional techniques showed no statistically significant differences. However, the number of specimens in the microwave sintered group was fewer (n=6) when compared to the conventionally sintered group (n=10). Therefore, increasing the power (i.e., the number of samples) might have had some influence on the results from a statistical perspective. The flexural strength was determined for specimens from both microwave and conventional groups at maximum sintering temperatures of 1450 °C in normal atmosphere. However, the resulting strength values for these specimens were lower than that reported by other investigators (94, 95). In addition, when the group of specimens that were microwave sintered with and without a hold time of 5 minutes were tested for their flexural strength, their values were close to other reported values (Table 14) (94).

The microwave sintered tooth copings were evaluated for their three-dimensional shrinkage as shown in Figure 31. Although it is difficult to analyze three-dimensional shrinkage with requirements for high tolerances, an attempt was made with the Geomagic Qualify software program. However, the introduction of this technique for evaluation of tooth crowns in dentistry is relatively recent and the software might have limitations in terms of exact measurement of structures in three dimensions. Further studies are required to better understand the three-dimensional shrinkage and marginal fit of microwave sintered dental zirconia structures.

We believe that the results from our research have improved the understanding of microwave-dental materials (specifically, dental zirconia ceramics) interactions and processing. Furthermore, we believe that the presented research will have the potential to improve dental care of patients in terms of convenience, efficiency, and reduction of the cost of dental health care. In addition, we will be able to propose better specifications for a microwave furnace, specifically suitable for dental applications in the future. The results of this study will be applicable to the entire dental community (i.e., the dentist, the dental laboratory technician, and the end-user of the product, the dental patient).

Future Research

Total characterization for any given material would be a significant undertaking. Zirconia ceramic materials have been one of the most widely investigated materials in recent times [29, 30]. However, most of these investigations have been carried out for industrial applications and not for biomedical applications. The range of tests required for zirconia ceramics might be truncated to a manageable set that would yield sufficient information relative to its potential reliability for dental applications. One of the areas of research that will provide useful information will be to determine the mechanical properties, especially the fatigue behavior (from cyclic loading similar to human chewing) of microwave sintered dental materials to understand its reliability for dental applications. The microwave sintered zirconia dental materials have not been very well characterized for their dimensional shrinkage behavior for dental applications. Further research to examine these parameters need to be carried out.

Temperature measurement during microwave sintering is one of the most challenging procedures to study. Although current devices (e.g., thermocouples) can record microwave sintering temperatures with some degree of accuracy, they still only provide surface temperature values that are very close to the actual sintering temperature. In order to record the actual sintering temperatures of material(s) being sintered, non-contact temperature measurement techniques (e.g., infrared thermometers) need to be developed further. Some researchers have reported about the use of non-contact temperature recording techniques, albeit further experiments are warranted. Simulations of microwave sintering temperature events are being studied by finite element techniques (97).

Another important area of future research with respect to microwave processed dental ceramics will be the evaluation of its biocompatibility, especially its behavior in moist environments. Although there are some studies related to this (93), a thorough understanding about the environmental influences (e.g., saliva) on the properties of bioceramic materials processed by microwaves is lacking. This might provide additional information related to its applications in dentistry. Alternate techniques for sintering zirconia dental materials including the use of spark plasma sintering is being investigated. Further information about preliminary experiments that were conducted using this previously mentioned technique is mentioned in the appendix. Reproducibility to produce microwave sintered dental zirconia structures with consistency in their overall properties (i.e., physical, microstructural and optical) will be necessary before microwave sintered materials can have wider acceptance from the dental community. Translation of the research findings from the laboratory to the clinic will be possible if this previously mentioned step can be achieved successfully.

Appendix

Investigators have shown that spark plasma sintering can be effective for the processing of various materials (98-100). We sintered 2 different compositions of zirconia powders by spark plasma sintering (Thermal Technology LLC, Santa Rosa, CA). Spark plasma sintering is a pressure-assisted process along with the utilization of force in a vacuum environment. It is already known that SPS requires lower sintering temperatures for the processing of materials when compared to other techniques. Both types of zirconia materials were pressed into pellets from their powder forms (TOSOH USA, INC) using graphite dies. A description of their physical properties is provided in Table 22.

Table 22. Physical properties of zirconia raw materials utilized for spark plasma sintering

					Typical Properties of Sintered Body		
Composition	**Units**	**Specifications**	**Appearance**	**Maximum Sintering Temperature (°C)**	**Density**	**Hardness (Hv 10) 98.07 N**	**Bending Strength (3 point)**
Samples 1 and 2 (weight = ~ 2 grams)							
Y_2O_3	wt%	4.95 ~ 5.35	Granule	1300-1350	6.05	1250	1200
Al_2O_3	wt%	0.15 ~ 0.35					
SiO_2	wt%	Max. 0.02					
Fe_2O_3	wt%	Max 0.01					
Na_2O	wt%	Max 0.04					
Specific surface area	m2/g	13 ~ 19					
Crystallite size	Angstrom	Not specified (maybe 260)					
Samples 3 and 4 (weight = ~ 2 grams)							
Y_2O_3	wt%	3.6 ~ 4.2	Granule	1300-1350	6.05	1250-1280	1200-1210
Al_2O_3	wt%	18 ~ 22					
SiO_2	wt%	Max. 0.02					
Fe_2O_3	wt%	Max 0.01					
Na_2O	wt%	Max 0.04					
Specific surface area	m2/g	12 ~ 18					
Crystallite size	Angstrom	Not specified (maybe 270)					

Samples 1 and 2 were predominantly 3 mol% yttrium stabilized zirconia, while samples 3 and 4 contained approximately 18 to 22 parts by weight percent of alumina as part of their composition.

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