COMPARATIVE STUDY OF MICROWAVE AND CONVENTIONAL SINTERING ON PROPERTIES OF ZIRCONIA

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COMPARATIVE STUDY OF MICROWAVE AND CONVENTIONAL SINTERING ON PROPERTIES OF ZIRCONIA

ABSTRACT

In the past three decades, zirconia based ceramics have been catching great interest especially in biomedical industries due to their excellent mechanical properties combined with biocompatibility and high chemical resistance. Aside from that, the combination of strength, toughness, chemical inertness and low thermal conductivity is advantageous for zirconia to be used in various engineering applications including automotive engine parts, fuel cells, and oxygen sensors. The superior mechanical properties are contributed by transformation toughening. However, one of the major drawbacks for zirconia is its susceptibility to low temperature degradation (LTD) which causes properties deterioration. LTD is highly dependent on the grain size of zirconia. From previous literatures, small grain can be obtained by conventional sintering at low temperature which would also produce less dense ceramics. Microwave assisted sintering has been developed in order to accelerate densification mechanism while decelerating grain growth. In this research, the comparison between microwave sintering and conventional sintering on the mechanical properties and microstructural evolution of 3 mol% yttria-stabilised zirconia were studied. Green bodies were compacted and sintered at various temperatures ranging from 1200 ºC to 1500 ºC. The result showed that microwave assisted sintering was beneficial in enhancing the densification and mechanical properties of zirconia, particularly when sintered at 1200 ºC. It was revealed that as the sintering temperature was increased to 1400 ºC and beyond, the grain size and mechanical properties for both microwave- and conventional-sintered ceramics were comparable thus suggesting that at the sintering temperature where densification mechanism was activated, grain size was strongly influenced by the sintering temperature rather than the sintering mode. In term of ageing behaviour, microwave assisted sintering was observed to delay the degradation process where the monoclinic content is less than 1% after 48 hours of exposure compared to conventionally sintered sample which recorded value more than 5%. However, after 100 hours of exposure to ageing environment, monoclinic content spike up to 31% for microwave- and 24% for conventional- sintered samples. The result suggested that small difference in grain size would give impact on the ageing behaviour of zirconia ceramics.

Keywords: Microwave sintering, Conventional sintering, Zirconia, Mechanical properties, Microstructure evolution

KAJIAN PERBANDINGAN PENGSINTERAN MIKROWAVE DAN KONVENTIONAL TERHADAP SIFAT ZIRKONIA

ABSTRAK

Sejak tiga dekad yang lalu, seramik berasaskan zirkonia telah menarik perhatian besar terutama dalam industri bioperubatan kerana sifat-sifat mekaniknya yang sangat baik digabungkan dengan ketahanan biokaliti dan ketahanan kimia yang tinggi.Di samping itu, gabungan kekuatan, ketahanan, ketidakmampuan kimia dan kekonduksian haba yang rendah memberi kelebihan untuk zirkonia untuk digunakan dalam pelbagai aplikasi kejuruteraan termasuk bahagian enjin automotif, sel bahan api, salutan penghalang haba dan sensor oksigen.Ciri-ciri mekanikal yang unggul adalah disebabkan fenomena yang dikenali sebagai transformasi ketahanan. Walau bagaimanapun, salah satu kekurangan utama untuk zirkonia adalah kerentanannya kepada penurunan suhu rendah (LTD) yang menyebabkan kemerosotan sifat. LTD sangat bergantung kepada saiz bijian zirkonia. Bijian kecil boleh didapati dengan pengsinteran konvensional pada suhu rendah yang pada masa yang sama menghasilkan seramik yang kurang padat. Dalam kajian ini, perbandingan antara sintering gelombang mikro dan sintering konvensional ke atas sifat-sifat mekanikal, evolusi mikrostruktur dan sifat degradasi 3 mol% zttrium yang stabil telah dikaji. Badan hijau dipadatkan dan disinter pada pelbagai suhu antara 1200 ºC hingga 1500 ºC. Hasilnya menunjukkan bahawa pengsinteran gelombang mikro bermanfaat untuk meningkatkan kepadatan dan sifat mekanikal zirkonia, terutamanya apabila disinter pada suhu 1200 ºC. Keputusan menunjukkan bahawa apabila suhu pengsinteran meningkat kepada 1400 ºC dan seterusnya, saiz bijian dan sifat mekanikal untuk kedua-dua pengsinteran gelombang mikro dan konvensional adalah sebanding, dengan itu menunjukkan bahawa suhu sintering di mana mekanisme penyatuan diaktifkan, saiz butir sangat dipengaruhi dengan suhu pengsinteran dan bukannya mod pengsinteran. Dari segi tingkah laku degradasi, sintering gelombang mikro diperhatikan untuk menangguhkan proses degradasi di mana kandungan monoklinik kurang daripada 1% selepas 48 jam pendedahan berbanding dengan sampel disinter secara konvensional yang mencatatkan nilai lebih daripada 5%. Walau bagaimanapun, selepas 100 jam pendedahan kepada persekitaran penenuaan, kandungan monoklinik meningkat sehingga 31% untuk gelombang mikro - dan 24% untuk sampel sintered konvensional. Hasilnya mencadangkan bahawa perbezaan kecil dalam saiz bijian akan memberi kesan kepada tingkah laku degradasi seramik zirkonia.

Keywords: Pengsinteran microwave, pengsinteran konvensional, zirconia, sifat mekanikal, penilaian mikrostuktur

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LIST OF SYMBOLS AND ABBREVIATIONS

Al_2O_3 : Alumina or Aluminium Oxide

ρ : Bulk Density

CIP : Cold Isostatic Pressing

CeO : Ceria

CS : Conventional Sintering

FESEM : Field Emission Scanning Electron Microscope

K_{IC} : Fracture Toughness

LTD : Low Temperature Degradation

MgO : Magnesia

MW : Microwave

m : Monoclinic phase

PSZ : Partially Stabilized Zirconia

μ : Poisson's Ratio

t : Tetragonal phase

t→m : Tetragonal to monoclinic

TZP : Tetragonal Zirconia Polycrystal

Hv : Vickers Hardness

XRD : X-Ray Diffraction

E : Young's modulus

Y-TZP : Yttria-stabilized Tetragonal Zirconia Polycrystals

ZrO2 : Zirconia or Zirconium Dioxide

ZrSiO4 : Zircon or Zirconium Silicate

LIST OF APPENDICES

CHAPTER 1: INTRODUCTION

Ceramics are considered to be both the oldest materials produced by humankind and also among the most recent and sophisticated materials today. Classically, materials can be divided into three main classes; metals, polymers and ceramics. This classification is based on types of atoms in the materials and the bonding between the atoms. Ceramics are associated with “mixed bonding” which is the combination of ionic and covalent, and sometimes even metallic bonding. Most ceramics are compounds of metals and non-metal such as oxides, nitrides and carbides. Ceramic is defined as a non-metallic, inorganic solid (Kingery, 1960). Almost all solid materials which are not plastic, metal, or derived from plants and animals are ceramics. Clay is an important ceramic and is the backbone for traditional ceramic industry such as in the production of brick, pottery and traditional cooking utensils.

In the past decades, the development of enormous potential of advanced ceramics has given rise to the application of advanced ceramics for various engineering demands. Ceramic engineering is the science and technology of creating objects using inorganic and non-metallic materials. Ceramic engineering process is commonly done via sintering at high temperature. Superior combination of mechanical properties, thermal insulation, gas sensing and dielectical properties of ceramics has become the basis for their huge applications in material engineering, electrical engineering, chemical engineering, biomedical, as well as mechanical engineering. Examples of advanced ceramics applications are present in food and chemical industries, aerospace, packaging science, electronic, telecommunication, and medicine. The unique thermal resistant properties of ceramics allow them to be used in many engineering tasks where metals and polymers are not suitable to be used.

One of the widely used ceramics is zirconia. In the past three decades, zirconia based ceramics have been catching great interest especially in biomedical industry. They have several advantages when compared with other biomaterials used in orthopaedics for hip and knee prosthesis due to their outstanding properties such as high elastic modulus, high corrosion resistance, good wear resistance, high fracture toughness, high melting temperature and chemical inertness. Zirconia is known as biocompatible material due to its bioinertness where it does not cause any local nor systemic adverse reaction once it is in contact with body environment (Nogiwa-Valdez, Rainforth, Zeng, & Ross, 2013).

Apart from orthopaedic application, zirconia has also been introduced as dental biomaterial and became very popular as a core material on which porcelain could be enamelled and sintered. Zirconia ceramic is considered to be the best dental material for crown and bridge restoration due to its remarkable strength and fracture toughness.

Aside from applications in biomedical industry, zirconia based ceramics are also widely used in other industries such as in automotive engine parts, refractory components, thermal barrier coatings and fuel cells.

Zirconia can be considered as a promising candidate for automotive engine parts especially in diesel engine due to its low thermal conductivity. They are used as materials for piston crowns, piston liners as well as head face plates. Low thermal conductivity of zirconia helps in reducing heat loss from combustion chamber thus increasing the flame temperature and improves the efficiency of the engine. Apart from that, zirconia possessing high wear resistance would require less routine service and considerably extend the engine life.

Due to its low thermal conductivity and high melting temperature, zirconia materials are used as refractory components and bricks for high temperature furnace in metallurgical processing. Zirconia materials are also used as refractory fibers which provide insulation to separators in hot gas filter and aerospace batteries.

Last but not least, zirconia materials are also used in solid oxide fuel cell. High chemical inertness, phase stability, good mechanical strength and high melting temperature are the requirements fulfilled by zirconia to be used in solid oxide fuel cell. Solid fuel cell is one of the advancements of ceramic materials which offer pollution-free technology to electrochemically generate electricity.

1.1 Problem Statement

In the past three decades, zirconia has received great attention especially in biomedical industry. Apart from possessing outstanding mechanical properties, it is also a biocompatible material due to its excellent bioinertness; i.e. it does not cause any local nor systemic reaction once it is in contact with hard tissues and body fluid. The excellent mechanical properties especially fracture toughness is associated with transformation toughening. The phase transformation during transformation toughening process can put the cracks into compression, retarding the crack growth and thus enhancing the fracture toughness. However, spontaneous and uncontrolled transformation of tetragonal to monoclinic phase could cause a major problem for zirconia ceramics. It is well documented that tetragonal zirconia is susceptible to hydrothermal ageing or low temperature degradation (LTD) when exposed to humid environment at temperature of 60-300 ºC. Severity of LTD increased with the increase in grain size of sintered body. When using conventional sintering, low sintering temperatures generally would produce smaller grain size but at the same time would produce less dense ceramics. Thus, various sintering methods have been developed to accelerate densification mechanism while suppressing the grain growth. One of the methods is by using microwave sintering that involves rapid and volumetric heating. It was reported in the previous studies that the internal heat generation is responsible for the enhancement in densification, hindering grain growth and improving mechanical properties of zirconia ceramics. Previous researchers claimed that microwave successfully produced finer grain size compared to conventionally sintered ceramics. However, different holding time was used during conventional and microwave sintering. Standard holding time used during conventional and microwave sintering are 2 hours and 5-15 minutes respectively. Therefore, the direct effect of microwave in producing fine grain size is not clear whether it is caused by microwave sintering or the effect of short holding time. Thus, the ultimate goal of this research is to compare the microstructure and mechanical properties of microwave with conventionally sintered zirconia when sintered using the same holding time (5 minutes).

1.2 Objective(s)

The main objective of this project is to compare the microstructure of microwave with conventionally sintered zirconia sintered at the same holding time (5 minutes). The primary aims were:

1. To compare the mechanical properties of microwave and conventionally sintered zirconia.
2. To study the effect of microstructural development when using different mode of sintering.
3. To evaluate the degradation properties of sintered zirconia.

1.3 Scope of Study

The study focussed on sintering of zirconia ceramics using microwave and conventional sintering at temperature ranging from 1200-1500 ºC with an interval of 100 ºC. Subsequent to sintering, resulting physical and mechanical properties were evaluated and compared between the two sintering techniques. The phases present in the sintered body were characterized using X-ray diffraction (XRD). Next, the microstructures of the sintered bodies were examined using field emission scanning electron microscope (FESEM). Prior to FESEM imaging, the sintered bodies were grinded, polished and thermally etched. Aside from that, the samples were also evaluated in terms of their mechanical properties including the relative density, fracture toughness, Young’s modulus and Vickers hardness. Last but not least, ageing experiment was carried out in an autoclave containing superheated steam at 180ºC with the pressure of 10 bars in order to evaluate the low temperature degradation of zirconia. The phase transformation was assessed by XRD.

1.4 Thesis Structure

This thesis consists of five chapters which cover the introduction, extensive literature review, experimental procedure, results and discussion, and finally conclusion and future works. Additional information and other experimental data are included in appendix.

The first chapter presents the **introduction** to the current research. It starts with the background of ceramics in general and the importance of advanced ceramics in modern world. Industrial applications and their pros and cons are then discussed with a focus on zirconia-based ceramics, which is an example of advanced ceramics. Zirconia based ceramic is a popular ceramic due to its unique properties involving transformation toughening mechanism. This chapter reveals the major drawback that limits the use of zirconia, which is low temperature degradation (LTD) or known as ageing. The proposed method to overcome LTD by reducing the grain size via microwave sintering is briefly discussed. This chapter also reveals the objectives of the research and the scope of study to achieve the objectives.

The second chapter for this thesis is “**Literature Review”**. This chapter reviews the introduction of zirconia, including its properties and crystal structures, applications and its drawback which is LTD. Zirconia properties, relating to its crystal structures, toughening mechanism and ageing phenomenon are also discussed in detail. In addition, this chapter also reviews previous studies for factors influencing LTD and the methods to overcome it. Non-conventional sintering technique for example using microwave would modify the microstructure of zirconia during the process which in return would affect the degradation properties of zirconia during LTD. The heating principle of microwave- and conventional- sintering was briefly reviewed. This chapter also discussed on the previous studies regarding the effect of microwave assisted sintering on densification, microstructural and mechanical properties for various types of ceramics.

Chapter 3 discusses the **experimental procedures** and the characterization techniques involved in the current research. This includes the material, apparatus and equipment for sample preparation, mechanical and physical properties determination as well as degradation properties evaluation.

The fourth chapter of this thesis reports on the **results and discussion** of the entire research. The comparison between physical, mechanical and degradation properties of microwave sintered with conventionally sintered zirconia are discussed in this chapter.

The last chapter **concludes** the whole research and suggests the works that can be done in the future.

CHAPTER 2: LITERATURE REVIEW

2.1 Summary

Zirconia (ZrO2) is an example of advanced ceramics and is extensively used in a wide spectrum of engineering applications as structural ceramics due to their outstanding mechanical properties such as fracture toughness, mechanical strength, wear resistance and hardness. On top of that, zirconia-based ceramics are objects of great interest in biomedical industry and are widely used as biomaterial especially in orthopaedic for hip and knee prosthesis, due to their bio-inertness and excellent mechanical properties. Apart from biomedical industry, zirconia-based ceramics, which possess excellent mechanical properties, are also widely used in engineering field such as in engine components, sensors, solid fuel cells and thermal barrier coatings.

Transformation toughening is a phenomenon that occurs in zirconia and is responsible for its superior mechanical strength. This phenomenon results to the improvement of flexural strength and fracture toughness by transforming zirconia particles in metastable tetragonal phase into monoclinic phase. However, the effectiveness of transformation toughening can also become counter-productive when the material is exposed to humid environment at a relatively low temperature of 65-300ºC. Uncontrolled transformation toughening or known as low temperature degradation (LTD), which is accompanied by volume expansion, may result to defects in the material such as macro- and micro-cracks (Garvie, Hannink, & Pascoe, 1975).

Considerable amount of researches have been devoted to study the susceptibility of zirconia to LTD. The major factor that affects the LTD behavior in zirconia ceramics is the grain size where severity of LTD increased with grain size. For that matter, various techniques have been developed in order to accelerate densification mechanism while decelerating grain growth. One of the approaches is microwave sintering technology which would modify sintering mechanism, leading to changes in the microstructure development.

Several researchers (Ivashutenko, Frangulyan, Ghyngazov, & Petrova, 2016; Mazaheri, Zahedi, & Hejazi, 2008) have determined that highly dense ceramics without substantial grain growth may be obtained via microwave sintering since the heating rate can be substantially increased while the dwell time is considerably shortened. In contrast, conventional sintering relies on external sources and involves transfer of heat energy via convection, conduction and radiation. Heat energy is generated in an external heating element before it is conductively transferred to the material. Conventional sintering is rather a slow process and takes time to achieve thermal equilibrium.

Extensive amount of researches have been conducted to compare the microstructure of microwave with conventionally sintered ceramics (Benavente, Salvador, Penaranda-Foix, Pallone, & Borrell, 2014; Presenda, Salvador, Peñaranda-Foix, Moreno, & Borrell, 2015). Nevertheless, the degradation properties and mechanical properties are poorly discussed. In addition, previous researchers used different holding time when comparing these two sintering techniques. Holding time for conventional technique was usually 2 hours while microwave sintered ceramics were usually sintered with much shorter holding time; 5-15 minutes . Hence, the effect of microwave in producing fine grain size is not clear whether it is caused by microwave effect or the short holding time used during microwave sintering.

2.2 Zirconia

Zirconium (Zr) is a chemical element discovered by a chemist named Martin Heinrich Klaproth in 1789. It was then isolated by Swedish chemist named Jöns Jacob Berzelius in 1824. The main source for Zr is from Zircon ($ZrSiO_4$). In 1969, zirconia (ZrO_2) was first reported to be used in biomedical application by Helmer and Driskell.

In 1989, Christel utilized zirconia for fabrication of ball head in total hip replacement (Piconi & Maccauro, 1999).

Zirconia is one of the inert ceramics which is widely used in various engineering application and medical implant. Zirconium dioxide (ZrO_2) or Zirconia is a white crystalline oxide. It was categorized as a polycrystalline ceramic having a melting temperature of 2715 °C and a high boiling temperature of 4300 °C. Naturally, zirconia can be found in baddeleyite which contains 96.5% to 98.5% of zirconia. Besides, ZrO_2 can also be produced via series of steps that separate it from impurities in its ore (i.e. zirconium silicate). There are three crystallographic forms naturally existed in pure zirconia which are monoclinic (*m*), tetragonal (*t*) and cubic (*c*). These different phases are the results from dissimilar atomic arrangements which occur at different temperatures even though they possess same chemical composition. Monoclinic (*m*) phase exist at room temperature up to 1170°C. At temperature above 1170 °C, pure zirconia will transform to tetragonal phase and is stable until temperature reached 2370 °C. Above 2370 °C, formation of cubic phase will take place (Kuo, Chou, & Liu, 2016). Amongst these polymorphs, tetragonal polycrystals is known as a structural ceramic due to its superior fracture toughness and strength (Vidyavathy & Kamaraj, 2009).

Figure 2.1: Temperature dependent phase transformation of zirconia ceramics

These phase transformation will be accompanied by volume expansion during cooling and volume shrinkage during heating. During cooling, transformation of cubic to tetragonal phase will results in 2.3 % volume expansion while transformation of tetragonal to monoclinic phase will results in volume expansion of 3-4 %. This transformation also causes zirconia ceramics to exceed their fracture and elastic limits, thus leads to formation of cracks and flaws (Denry & Kelly, 2008).

2.3 Yttria-Tetragonal Zirconia Polycrystal (Y-TZP)

Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) is a part of tetragonal zirconia polycrystals (TZP) family in which all the zirconia particles are in tetragonal (*t*) phase at room temperature. Addition of small amount of yttria oxide allows retention of metastable *t* phase after cooling of the sintered zirconia. For industrial applicability, it is urged to retain zirconia in tetragonal phase at room temperature in order to provide superior mechanical properties. In other words, it is crucial to prevent deleterious $t \rightarrow m$ phase transformation during cooling to room temperature right after sintering process. Monoclinic phase possess very poor mechanical properties due to volume expansion induced cracking which usually occurs during $t \rightarrow m$ phase transformation. Cubic phase on the other hands is unfavourable in many industrial applications since it cause accumulation of yttrium and destabilized the remaining tetragonal.Y-TZP is widely used in many industrial fields due to its excellent strength and fracture toughness. Biocompatibility and aesthetic nature of Y-TZP led to its widespread used especially in dental equipment and orthopedics.

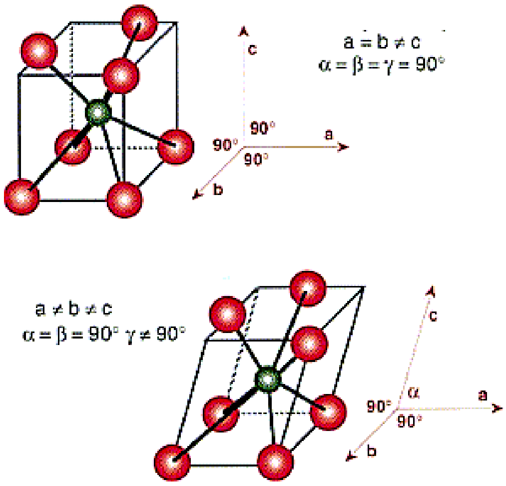


Figure 2.2: Molecular configuration of zirconia. Top configuration shows the tetragonal crystal structure while monoclinic crystal structure at bottom.

Source: (Dambreville, Phillipe, & Ray, 1999)

Elastic strain produces strain energy which plays a vital role in tetragonal phase retention (Lange, Dunlop, & Davis, 1986; Lughi & Sergo, 2010). In Y-TZP matrix, there are two sources which results in elastic constrain. The first one is the difference of crystallographic orientation of adjacent grains of single phase polycrystalline body as shown in Figure 2.3. The difference in crystallographic orientation of neighbouring grains will constrain anisotropic shape change for each grain. The second source of elastic constrain occurs when material contains two phases. When material is made up of two phases, the mixture surrounding the particles will restrain shape change of particles.

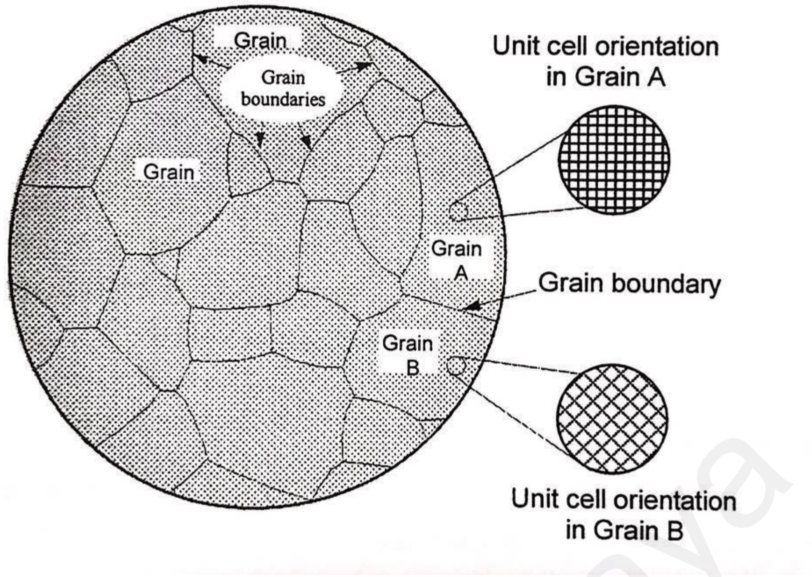


Figure 2.3: Different orientation of particles in adjacent grains of a polycrystalline body.

Source: (Masaki, 1986)

There were a lot of researches reported that proper amount of oxides stabilizer such as yttria oxide (Y_2O_3), cerium oxide (CeO_2), calcium oxide (CaO), copper oxide (CuO) and manganese oxide (MgO) could be added to pure zirconia to hold the tetragonal phase at room temperature (S Ramesh, Meenaloshini, Tan, Chew, & Teng, 2008). These oxides are added to prevent phase transformation at room temperature that may lead to cracks and failures of ceramics. Stabilizer helps in increasing the chemical free energy change, ΔG_C thus lowering *t→m* phase transformation temperature so that tetragonal phase and even cubic phase will not transform into monoclinic at room temperature.

2.4 Transformation toughening

In 1970s, zirconia became one of the most popular ceramic due to discovery of transformation toughening which make them highly sought-after especially for industrial application. Transformation toughening is a characteristic property of zirconia that makes it special when compared to other ceramics. This phenomenon results in the improvement of flexural strength and fracture toughness by transforming zirconia particles in tetragonal phase into monoclinic phase when external stress is applied.

There are numbers of toughening mechanisms which attribute to the transformation toughening such as stress-induced transformation toughening, transformation of strengthen surface layer and microcracking. Stress induced transformation toughening and microcracking are classified as crack tip shielding mechanism. Garvie et al. (1975) reported that transformation of *t-m* phase has a potential to improve both toughness and strength of zirconia in the presence of stress field upon crack propagation. The diffusion-less reaction which results in volume expansion and development of shear strain were identified as opposing the opening of crack, thus strengthen the resistance of zirconia ceramic to crack propagation.

In order for transformation toughening to take place, zirconia particles must be in metastable tetragonal phase. Only metastable *t* particles around crack tips and within stress field will undergo phase transformation. The process of stress induced transformation toughening is shown in Figure 2.4.

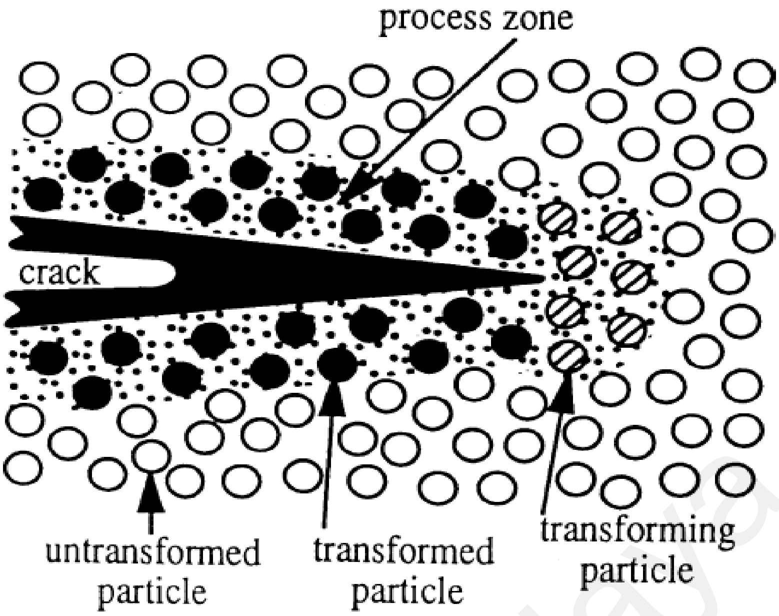


Figure 2.4: Process of stress induced transformation toughening.

Source: (Piconi & Maccauro, 1999)

Transformation toughening mechanism is initiated when stress is induced on the surface of zirconia. In the presence of metastable tetragonal phase around propagating crack, zirconia ceramic will exhibits transformation toughening. Metastable tetragonal (*t*) grains absorb stress produced by propagating crack and transform into monoclinic at room temperature. Simultaneously, volume expansion about 3-4% will take place which will induce compressive stress around crack tip that hinder crack propagation(Piconi & Maccauro, 1999). Aside from that, phase transformation also produce stress field which will rival the stress field that promote crack propagation, thus these stress field cancel each other. Energy is dispelled during phase transformation and also when overcoming compressive stresses cause by volume expansion. This energy dispelled also results in improvement of ceramic’s strength and toughness.

2.5 Low Temperature Degradation (LTD) or Ageing

Despite having excellent mechanical properties, Y-TZP is not in thermodynamic equilibrium at temperature below 900ºC. Uncontrolled phase transformation may lead to properties deterioration which results in microcracks and catastrophic failure of zirconia ceramics. This phenomenon is known as “Low Temperature Degradation” (LTD) or ageing. Y-TZP is susceptible to undergo *t-m* phase transformation. During ageing, tetragonal particles are spontaneously transformed into monoclinic phase in the presence of moist or water. When the transformation took place in a bulk, the compressive stress caused by volume expansion during the transformation will results in further crack propagation thus lead to properties deterioration of zirconia. Therefore, it can be concluded that phase transformation of Y-TZP from tetragonal to monoclinic phase is both favorable and malignant depending on its application and degree of phase transformation. Controlled phase transformation will result in improvement of the mechanical properties of Y-TZP. However, uncontrolled transformation will result in ageing which causes properties deterioration.

Below 900ºC, *t→m* phase transformation is depend on different factors such as tetragonal stabilizing dopant, grain size, temperature as well as water vapor pressure. Ageing phenomenon usually occurs at temperature ranging from 60ºC-500ºC in the presence of steamed or moist environment (Èastkova, Hadraba, & Cihlao, 2004). Sato and Shimada (1985) reported that at ageing temperature of 200-250ºC, maximum phase transformation occurs.

LTD occurs in the presence of water vapor or in moist environment where transformation of metastable tetragonal phase to stable monoclinic polymorph occurs rapidly. The rapid transformation is due to the interaction of metastable tetragonal particles with hydroxyl ions in water (Simon Lawson, 1995). This interaction led to phase transformation which is accompanied by volume expansion as well as microcracking. Interaction of these excess microcracks will then results in decrease in the strength of matrix which will eventually cause failure of ceramic.

2.5.1 Factors influencing LTD

There are many factors that control LTD phenomenon which are grain size, stabilizer content and distribution, grain boundary impurity phase, surrounding temperature and environment factors such as humidity and vapor pressure.

Extensive amount of researches have been conducted to study the factors that affect the ageing phenomenon. From the researches, it was found that ageing is highly dependent on the grain size of zirconia. Tsukuma, Kubota, and Tsukidate (1984) reported that as grain size increase, the monoclinic content also increase which indicates that ageing phenomenon is accelerated. Aside from grain size, stabilizer content for example the amount of yttria added also plays a vital role in improving ageing resistance. Stabilizers will retard the ageing-induced phase transformation by over-stabilizing the tetragonal phase. They concluded that the increased in yttria content will retard ageing process by increasing the critical grain size of zirconia particles. As the critical grain size increased, phase transformation will be retarded thus enhancing the ageing resistance of zirconia.

Ageing resistance of zirconia is greatly influenced by critical grain size of zirconia after sintering. It has been estimated that the grain size of less than critical grain size (approximately 0.2µm) is needed to maintain tetragonal phase in pure zirconia. On the other hand, critical grain size is highly influenced by a few parameters such as amount of stabilizer added, sintering temperature and holding time (Pędzich & Wajler, 2006). Manipulating these parameters will results in optimizing the critical grain size in order to get a high value. High critical grain size means that tetragonal zirconia particles are not easily transformed into monoclinic phase even the grain size is large. If the grain size is below critical grain size, no ageing would occur. As the amount of stabilizer increased, the critical grain size also increases (Singh Ramesh, 1999). In other words, increase in the amount of stabilizer will increase the value of critical grain size. Increase in the critical grain size will retard the phase transformation and thus enhancing ageing resistance. Referring to Figure 2.5, Tsukuma et al. (1984) reported that high yttria content may improve the ageing resistance where monoclinic phase is still absence after 700 h of ageing in air at 300 ºC. In contrast, samples with low yttria stabilizer added exhibit monoclinic phase after less than 100 h of ageing exposure.

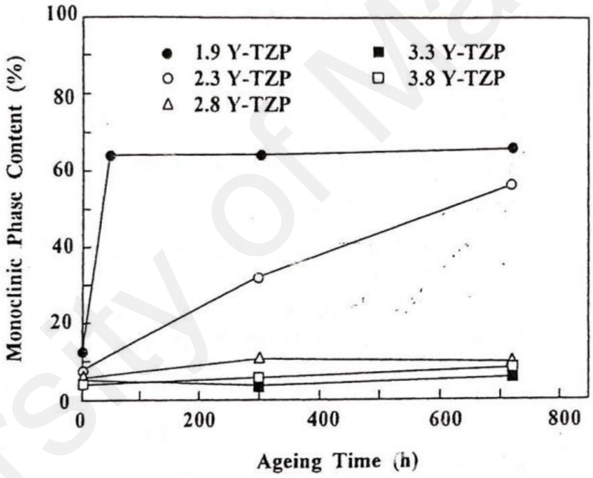


Figure 2.5: the effect of yttria stabilizer content on stability of tetragonal phase aged in air at 300 ºC. The grain size of all samples was ~0.4 µm.

Source: (Tsukuma et al., 1984)

However, S Lawson, Gill, Smith, Dransfield, and Egerton (1993) reported that samples containing very high yttria content might not be beneficial in enhancing ageing resistance. In their study, they found out that a high ytrria content of 4 mol% lead to failure of the samples when subjected to ageing for 100 hours even though the monoclinic content is minimized. The failure of this sample is caused by over-stabilizing the tetragonal phase by adding excess yttria. Over-stabilization caused formation of cubic phase that result in catastrophic failure of the sample during ageing. On the other hand, samples with lower yttria content (2.5 mol% and 3.0 mol%) survived 200 hours of exposure test even with minimum monoclinic content. This result also shows that insufficient yttria added (2.0 mol%) might also lead to failure of sample when exposed to ageing environment.

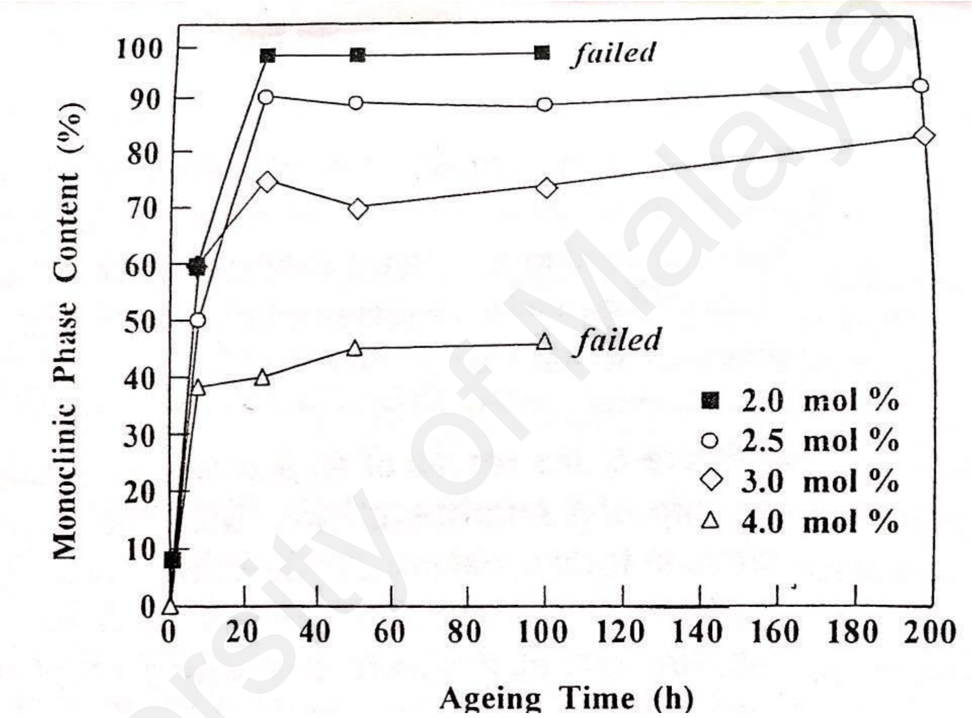


Figure 2.6: The effect of yttria content on monoclinic content aged in superheated water at 180 °C and 1 MPa. All samples sintered at 1500 °C.

Source: (S Lawson et al., 1993)

2.5.2 Ageing mechanism

There are several mechanisms proposed by various researchers to explain the ageing phenomenon in Y-TZP ceramics. Generally, all the theories suggested that the ageing phenomenon is caused by transformation of monoclinic to tetragonal in the presence of water. However, the actual mechanism which is responsible for destabilization of tetragonal phase and lead to phase transformation is still debatable. Researchers suggested a few mechanisms which are responsible for ageing such as corrosion mechanism, destabilization mechanism and stress induced transformation.

2.5.2.1 Corrosion mechanism

There are two basic types in corrosion mechanism which includes stress corrosion of tetragonal phase and corrosion of grain boundary glassy phase. In stress corrosion mechanism, Yoshimura, Noma, Kawabata, and Sōmiya (1989) suggested that once zirconia reacts with water molecules, residual stresses is formed on the surface which is the results from formation Zr-OH. Further accumulation of these residual stresses will lower the barrier for phase transformation to occur and thus lead to development of monoclinic nuclei. There are 4 stages in ageing mechanism (Figure 2.7) suggested by Yoshimura which includes:

Stage 1: Chemical absorption of water at the surface of zirconia ceramic.

Stage 2: Formation of Zr-OH due to reaction of water molecules with zirconia particles. Formation of Zr-OH causes lattice strain on the surface.

Stage 3: Migration of OH ions at the surface and in the matrix lattice results in strains accumulation and thus prepare for nucleation defects.

Stage 4: Nucleation of monoclinic in the tetragonal matrix.

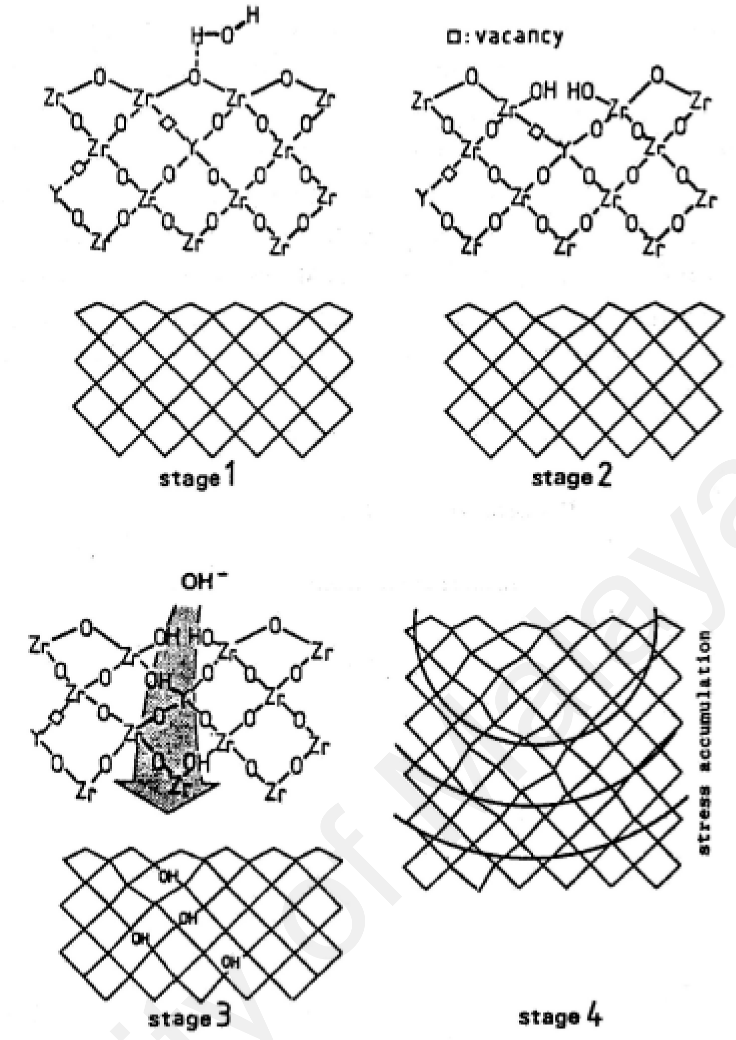


Figure 2.7: Proposed degradation mechanism by Yoshimura.

2.5.2.2 Destabilization mechanism

Aside from corrosion mechanism, researchers also proposed destabilization mechanism to explain the ageing phenomenon. Lange et al. (1986) proposed that once the material is in contact with water, water will drew out a small amount of yttria from a small volume element on the surface of grains, thus destabilizing the region with deficient yttrium which then will result in monoclinic nucleation. Winnubst (1988) support Lange’s theory and observed that tetragonal grains in yttrium deficiency region will transform to monoclinic phase.

2.5.2.3 Stress induced transformation

The third mechanism for ageing is stress induced transformation. This mechanism involves correlation of destabilizing stresses on the tetragonal grain with the phase transformation. Destabilizing stresses are produced during cooling process after sintering. After sintering, ceramic is made up of mixture of monoclinic, tetragonal and cubic phase. These different phases have different thermal expansion coefficient resulting in anisotropy of thermal expansion which create the destabilizing stresses.

2.5.3 Overcoming LTD

Low temperature degradation (LTD) also known as ageing is dependent on various factors such as grain size, addition of dopants, powder manufacturing technique, stabilizer content and distribution, ageing temperature, time and surface modification of the raw material. These factors control the phase stability of tetragonal zirconia in which the optimization of these factors may retard the phase transformation of tetragonal zirconia to monoclinic phase when exposed to ageing environment. It is important to control the phase transformation of zirconia to prevent LTD in order to obtain zirconia ceramic with excellent mechanical properties.

Phase stability of tetragonal zirconia depends strongly on the grain size of the zirconia particles. Earlier workers have been study the effect of grain size on retaining tetragonal phase when exposed to ageing environment (Singh Ramesh, 1999).It can be concluded that one of the ways to avoid LTD is by controlling the grain size of zirconia. Small grain size would be beneficial to ensure tetragonal phase retention after exposure to ageing environment.

Different grain size can be obtained by manipulating the heating temperature during sintering process. Low sintering temperature is needed to suppress the grain growth thus producing ceramics with fine grain size. However, at low temperature, conventional sintering would produce less dense ceramics. For that matter, various sintering techniques were developed to produce highly dense ceramics possessing fine microstructure. Examples of advanced sintering technique are using microwave sintering, spark plasma sintering and vacuum sintering.

2.6 Sintering Route: Conventional (CS) and Microwave (MW) Sintering

Sintering is an important process involved during the fabrication of ceramics. Almost all ceramic bodies are sintered to high temperatures in order to attain densification as well as producing the required microstructures. The properties of ceramics are highly influenced by these microstructures which include:

- The size and shape of grains
- Amount, distribution and size of pores

Densification is the result of sintering where particles change shape to increase their contact area with the neighboring particles, thus reducing porosity through grain growth and boundary movement. Densification and grain growth during sintering lead to shrinkage of the green body or in other words, the green bodies become more compact.

In the present work, the aim is to verify the role of MW sintering in producing highly dense ceramics with fined microstructure. MW sintering was reported to successfully produced ceramics with higher density and at the same time possessing finer microstructure as compared to CS sintered ceramics. Since the mechanical properties of the ceramic are highly influenced by the amount, distribution and size of pores, less porous ceramics obtained via MW sintering is theoretically proven to possess higher density and hardness compared to highly porous sample. Apart from that, fined microstructure would be helpful in suppressing LTD of zirconia.

Last but not least, microwave sintering was reported to reduce the processing temperature, shorter the reaction time apart from improving the densification of ceramics (Thostenson & Chou, 1999).

2.7 Microwave sintering (MW)

Microwave is a type of electromagnetic radiation having frequencies ranging from 0.3 to 300GHz. The wavelength varies from 1m to 1mm depending on the frequencies of the wave. The wavelength of the wave is inversely proportional to the frequency where;

$$\boldsymbol{\lambda = c/f}$$

Note that **λ** is the wavelength of microwave, **c** is the speed of light and **f** is the frequency of microwave.

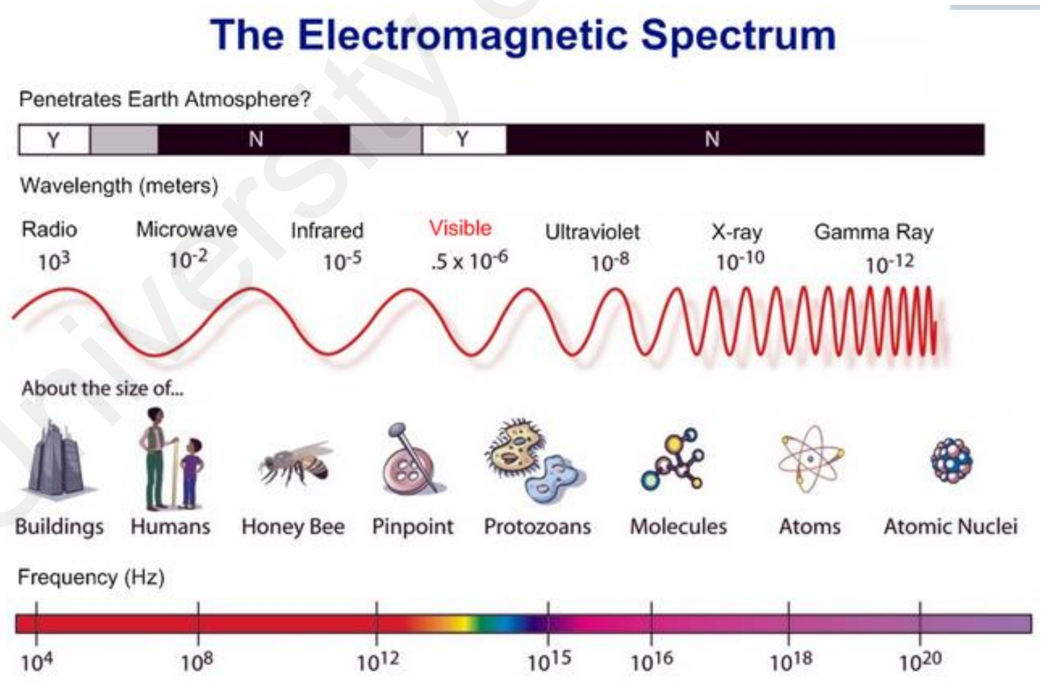


Figure 2.8: Electromagnetic spectrum (courtesy from Wikipedia: Electromagnetic Spectrum)

Microwaves travel at the speed of light in free space and possess similar characteristic to light waves where they are reflected by metallic objects, absorbed by some dielectric materials and transmit without absorption (transparent) to some dielectric materials. In other words, materials can be opaque, absorbable or transparent to microwave (Thostenson & Chou, 1999).

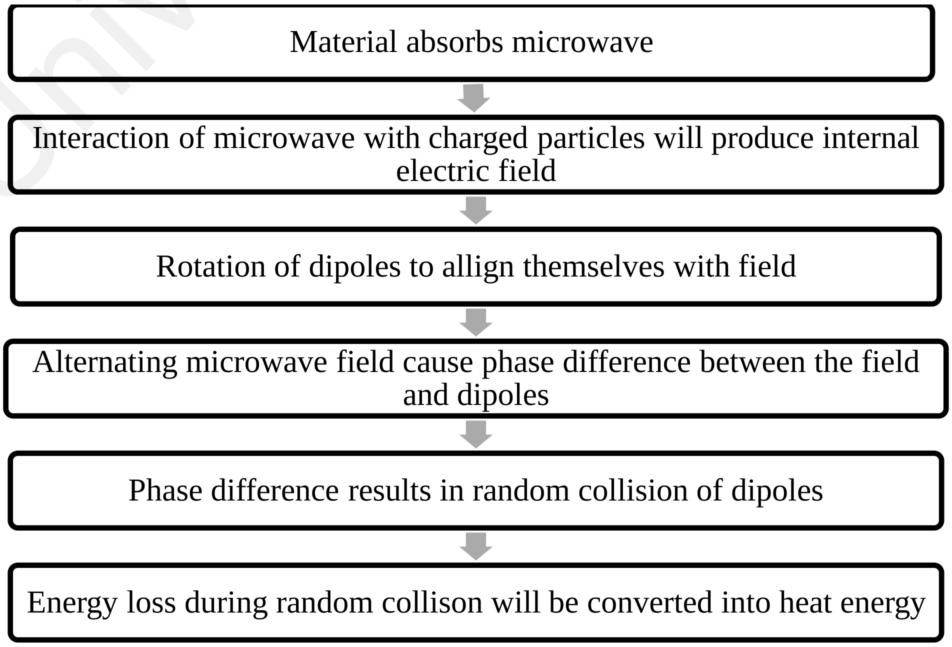
Microwave sintering is fundamentally different from the conventional sintering in term of heat transfer and is consider as a more advanced technique for sintering. Conventional sintering relies on external sources and involves transfer of heat energy via convection, conduction and radiation. Heat energy is generated in an external heating element before it is conductively transferred to the material. Material surface will be heated first, once the temperature increases, the heat will be transferred to the core. Therefore, this sintering technique produces a high temperature gradient as well as internal stress (Babu & Manohar, 2013). Aside from that, conventional sintering is rather a slow process and takes time in order to achieve thermal equilibrium. In spite of that, conventional sintering technique is independent of the nature of the material, thus making it possible to heat any material in a conventional furnace.

On the contrary, for microwave sintering, heat is generated internally in material via molecular interaction with electromagnetic field. Interaction of microwaves with charged particles in the microwave field will produce internal electric field that will then be transformed into heat energy (Borrell, D Salvador, Miranda, L Penaranda-Foix, & M Catala-Civera, 2014).

The key for heating effect is the frequency of microwave which lies in between two extreme frequencies. The frequency is sufficient to cause interaction between microwave field and dipoles which results in the induction of heat energy. If the frequency of the wave is too high, dipoles will not have enough time to react with the wave, results in no dipoles rotation thus no energy transformation would take place. On the other hand, if the frequency of the wave is too low, dipoles will align themselves in phase with the wave. There will be no phase difference between dipoles and the wave, thus there will be no dipoles collision.

Microwave frequency is neither too high nor too low. The microwave frequency is low enough that the dipoles have time to react with the alternating microwave field which will results in rotation of the dipoles. However, the frequency is also high enough that the rotation of the dipoles did not follow the microwave field precisely. As dipoles reorient to align themselves with the field, the field is already changing. This will create phase difference between the field and dipoles. The phase difference will cause random collision of the dipoles in which results in energy loss. The loss of energy during random collision is the main reason for dielectric heating where the loss of energy will be transformed into heat energy.

Heat is generated within the material and not from external sources, thus it is transmits towards outside (Binner, Vaidhyanathan, Paul, Annaporani, & Raghupathy, 2011). Electromagnetic energy will be absorbed by the materials and converted to thermal energy which leads to heating of material as a whole (volumetric heating). The interaction of molecules with microwaves producing heat is summarized as below:



Material absorbs microwave

Interaction of microwave with charged particles will produce internal electric field

Rotation of dipoles to allign themselves with field

Alternating microwave field cause phase difference between the field and dipoles

Phase difference results in random collision of dipoles

Energy loss during random collison will be converted into heat energy

Generally, microwave heating is very rapid as the heating mechanism involves conversion of energy rather than energy transfer. Microwave sintering technique does not involve thermal conductivity mechanism. The sintering process is instantaneous and rapid, and is the function of material under process. Since the heat is generated internally for direct microwave sintering process (inside-out), hence the temperature profile is inversed of the conventional sintering (outside-in). Inverse temperature profile during microwave heating results in materials having hotter interior than the surfaces. Figure 2.9 shows the heating pattern and temperature profile for direct microwave compared to conventional heating respectively.

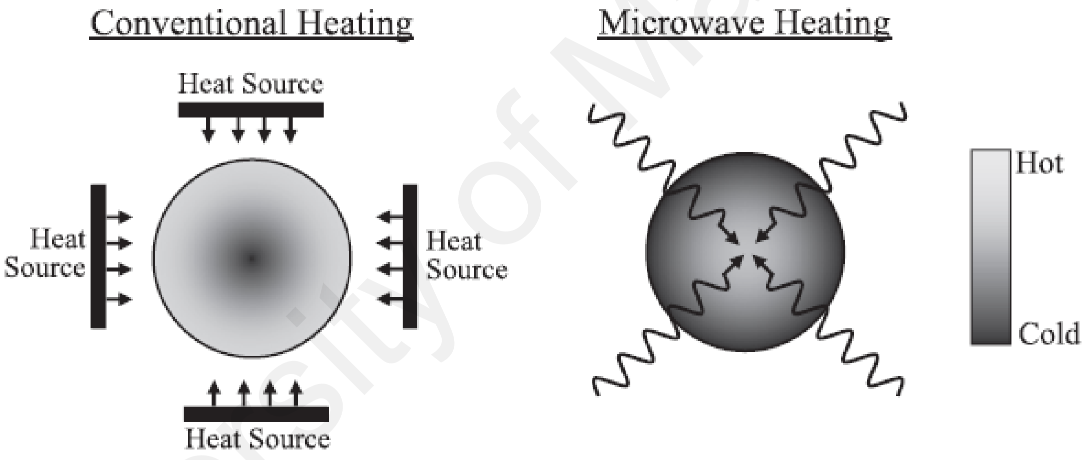


Figure 2.9: Heating pattern of conventional compared to microwave sintering. Source: (Bhattacharya & Basak, 2016)

Direct microwave sintering involves inverse temperature profile where heat is originate from within, thus the interior of the body is hotter than the surface. Even though microwave heating raises the temperature of entire sample through volumetric heating, the heat loss from the surface causes the exterior to become cooler than the core. Thus, one of the disadvantages of this direct microwave sintering is it creates thermal gradient where heat is not distributed evenly in the ceramics (Khalil, 2012).

Hybrid microwave sintering is an alternative way to overcome the problem of thermal gradient suffers during direct microwave heating (Bhattacharya & Basak, 2016). Silicon carbide (SiC) susceptors which are highly loosy material were introduced during hybrid sintering. Figure 2.10 shows the role of susceptors during hybrid microwave sintering. Since zirconia ceramics do not couple with microwave at low sintering temperature (<500 ºC), zirconia will be heated upon its surface via thermal radiance from the susceptors. As the coupling temperature is reached at 500 ºC, zirconia will couple well with microwave and heated internally. Above the coupling temperature, zirconia ceramics will be heated both upon its surface via thermal radiance from susceptors and in its bulk via microwave heating, thus avoiding thermal gradient.

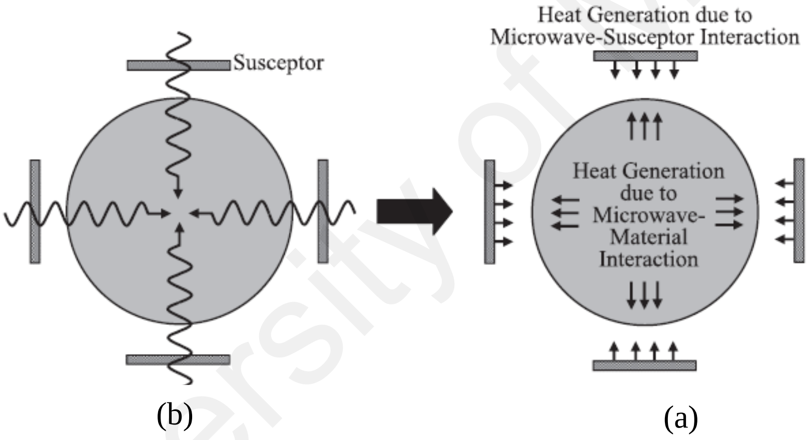


Figure 2.10: Hybrid microwave sintering. (a) Before coupling temperature is achieved, zirconia is heated via thermal radiance from SiC. (b) Two-way heating as coupling temperature is reached.

Source: (Bhattacharya & Basak, 2016)

Besides, hybrid MW sintering also helps in avoiding thermal runaway in which would cause formation of local hotspots and melting of the sample. Thermal runaway would occur during direct MW sintering due to discrepancies in energy absorption of the sample at certain region, thus, results in uncontrolled rapid increased in temperature at that region. Most ceramics are transparent to MW at low temperature. However, as critical temperature is exceeded, ceramics will become more loosy and absorb more microwave as temperature is further increased. During direct MW heating, the core of the sample would have highest temperature due to poorer heat transfer compared to areas near to the surface. This inverse temperature profile where the core has the highest temperature would cause this region to interact and absorb more microwaves compared to other region of the ceramics body. Uncontrolled microwave absorption and rapid increase in temperature may lead to increase of temperature above the desired temperature and in extreme cases would result in melting of the core whilst the outside is still solid. Therefore, the used of susceptors (SiC) during microwave sintering is essential so that the uniform heat distribution may unleashed thermal runaway problem where all the region having the same temperature would absorb same amount of microwave energy (Bhattacharya & Basak, 2016).

Due to the fact that MW heating leads to volumetric heating which enables materials to be heated as a whole, MW heating possesses unique advantage in many industrial field including food and rubber industries as well as drying operations for many products. Moreover, volumetric heating also results in rapid heating where internally generated heat sinters the ceramics instantaneously. Rapid heating via MW sintering results in great energy efficiency, time saving and lowering sintering temperature. These facts make microwave sintering advantageous over conventional sintering for many industrial applications.

2.7.1 Effect of microwave sintering on densification

Densification is the product of sintering where particles change shape to increase their contact area with neighboring particles. This process results in reduction of porosity and is highly dependent on sintering temperature where high temperature is needed to produce highly dense ceramics. Microwave sintering was reported by previous literatures to enhance densification process by lowering the activation energy for densification mechanism to take place (Brosnan, Messing, & Agrawal, 2003). This means that ceramics can achieve high density even at low sintering temperature. Lowering sintering temperature is advantageous since it can reduce energy consumption as well as time efficient.

In 2003, Brosnan et al. (2003) reported the enhancement in densification via microwave sintering compared to conventional sintering of alumina tube. Ramping rate during microwave sintering fluctuates between 45-60 ºC/min while the ramping rate during conventional sintering was fixed at 10 ºC/min without holding time at final temperatures. From their studies, they found out that sintering temperature can be lowered using microwave sintering. It was reported that densification process started at 1100 ºC for microwave and 1300 ºC during conventional sintering. Alumina ceramics were sintered to 95% of theoretical density for both sintering methods. 95% density was achieved by microwave sintering at 1350 ºC while conventional sintering achieved the same density at 1600 ºC. Apart from that, the authors also reported that the ceramics achieved full density at temperature 1400 ºC via microwave sintering while the density of ceramics sintered conventionally at the same temperature was only 52% of theoretical density. The reduction in densification temperature via microwave sintering is the result of lower activation energy for microwave. The activation energy for microwave and conventional sintering were revealed to be 85kJ/mol and 520kJ/mol respectively.

Earlier, Xie, Yang, and Huang (1998) sintered alumina powder using microwave and conventional sintering with holding time 30 minutes and 2 hours respectively. No details on the heating rate were mentioned in their literature. From the results obtained, they reported that microwave sintering would enhance densification of ceramics at temperature below 1400 ºC even with shorter holding time at final temperature. At sintering temperature 1300 ºC, microwave achieved relative density of 97.5% while conventionally sintered alumina only achieved 89% theoretical density. However, as the heating temperature reached 1500 ºC, same density of 99.7% was attained for both methods. This suggested that microwave sintering helps in enhancing densification mechanism at low sintering temperatures. As the sintering temperature is high enough to activate the densification mechanism, same chance of densification can be observed for all samples regardless the sintering route.

Apart from studying the densification of alumina powder, Xie and his team also studied the effect of different sintering mode on densification of ceria doped zirconia (Xie, Wang, Fan, & Huang, 1999). Same result was obtained for this type of ceramic where microwave improved densification of ceria doped zirconia ceramics. At 1300 ºC, the relative densities of microwave and conventionally sintered zirconia are 92% and 85% respectively. As sintering temperature reached 1500 ºC, microwave sintered zirconia attained 99.5% of theoretical density while zirconia sintered conventionally attained 98.3% of theoretical density. It can be concluded that as the sintering temperature is high enough, same chance of densification can be attained for both microwave and conventionally sintered ceramics.

In 2010, Charmond, Carry, and Bouvard (2010) compared the densification of microwave and conventionally sintered 2YZS. The heating temperature and heating rate were fixed for both methods which were 1350 ºC and 25 ºC/min respectively. For both sintering mode, no holding time was set at final sintering temperature. It was revealed that microwave sintered achieved higher density compare to conventionally sintered zirconia ceramics. At the same sintering temperature, the density for microwave sintered was 5.96 g/cm^3 while conventionally sintered zirconia attained density of 5.53

g/cm^3. Their results suggested that microwave sintering might give direct effect on densification of ceramics since other parameters such as heating rate, holding time and sintering temperature were the same for both sintering modes.

Mazaheri et al. (2008) investigated the effect of microwave on densification of 8YZS. Conventionally sintered samples were heated with ramping rate of 5ºC/min without holding time. When using microwave heating, two ramping rate was used which are 5ºC/min for low microwave sintering (LMS) and 50ºC/min during high microwave sintering (HMS). LMS with the same ramping rate and holding time as conventional sintering was used to study the direct effect of microwave sintering on the densification and microstructure of zirconia ceramic. Apart from that, ceramics sintered via LMS and HMS was compared to evaluate the effect of heating rate on densification of microwave sintered ceramics.

At low sintering temperature (1250ºC), LMS produced well sintered sample with less porosity while HMS and conventionally sintered sample are not fully sintered. There is no clear grain boundary in between the grains and the microstructure is very porous as viewed using SEM. From the results obtained, only ceramic sintered via LMS can be well sintered at low temperature. This might be attributed by microwave heating mechanism. Microwave sintering was reported to lower the activation energy thus lowering the sintering temperature (Brosnan et al., 2003). Lowered activation energy explains why LMS can be densified at low temperature while conventionally sintered sample is not fully sintered. Aside from that, in conventional sintering, ceramics are heated via thermal conduction which took longer time thus delaying the densification mechanism. Microwave sintered ceramics are heated via molecular interaction with electromagnetic field which results in volumetric heating. Therefore, LMS is capable of producing denser specimen in shorter time. However, if the heating rate is too high, microwave sintering is also unable to sinter the ceramics especially at low temperature as observed for HMS sintered sample. Ceramics sintered via HMS undergone rapid heating since the heating rate is very high. Accompany with zero holding time, the heating process was very rapid thus there is not enough time for densification mechanism to be activated results in non-sintered ceramics.

Figure 2.11 shows fractional density versus temperature graph for conventionally sintered sample, LMS and HMS samples. From the graph, it was clear that LMS always produced sample with highest fractional density at the same sintering temperatures. There is significant difference in density of LMS sample compared to density of HMS and conventionally sintered samples. In contrast, there was no remarkable difference in densification of HMS and conventionally sintered sample.

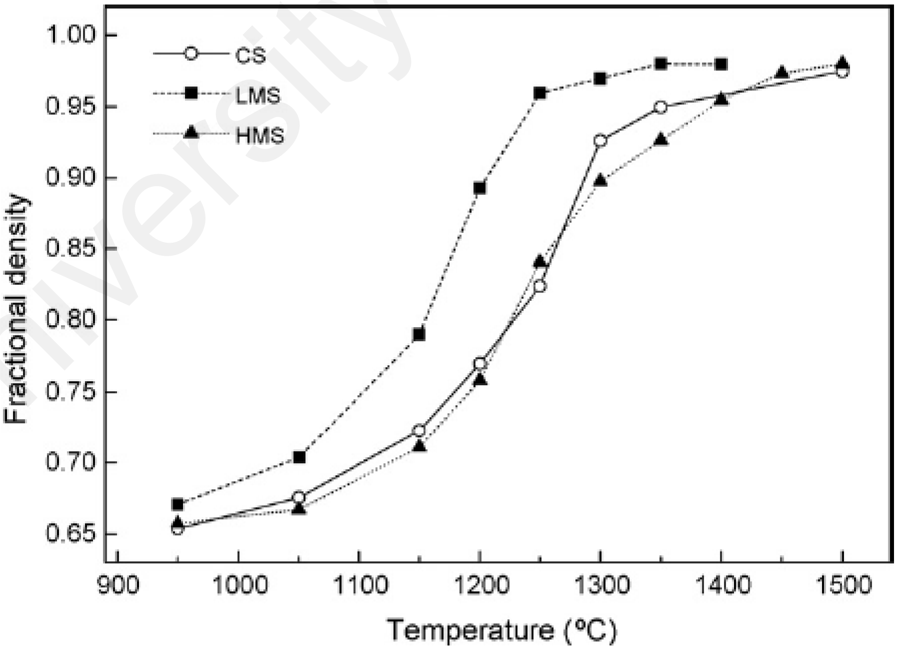


Figure 2.11: Fractional density versus temperature graph for conventionally sintered sample, LMS and HMS samples. (Mazaheri et al., 2008)

Mazaheri et al., (2008) concluded that microwave heating improve the densification at low sintering temperature especially when using low heating rate. The improvement in densification of ceramic is attributed by rapid and volumetric heating in microwave sintering. Heat is generated internally via molecular interaction when using microwave, thus activating densification mechanism at lower temperature in much shorter time. However, HMS produced less dense sample compared to LMS at low temperature since the high heating rate causes lack of time to activate the densification mechanism. Above 1300ºC, all samples have the same chance of densification where the temperature is high enough to activate the densification mechanism accompanied by longer sintering time to reach the higher temperature.

Recently, Ivashutenko et al. (2016) studied the effect of microwave sintering on densification of 3YTZP. They found out that density of microwave sintered ceramic sintered at 1400 ºC was 5.86 g/cm^3 while conventionally sintered ceramic only achieved density of 5.6 g/cm^3 at the same sintering temperature. Based on previous literatures, it can be inferred that microwave sintering helps in improving densification of ceramics via volumetric heating accompanied by reduction of activation energy which help in minimizing the sintering temperature and processing time.

2.7.2 Effect of microwave sintering on grain size

There have been a lot of studies comparing the grain size of microwave to conventionally sintered ceramics. Some reported that microwave sintering would hinder the grain growth especially at high sintering temperature. They reported that ceramics sintered via microwave sintering at the same temperature would have finer grain size as compared to ceramics sintered using conventional method. In contrary, some studies reported that the grain sizes are comparable for both methods at same sintering temperature and suggested that grain size is strongly influenced by sintering temperature regardless the sintering method. There are several factors that are interrelated which affect the grain size of sintered ceramics including sintering temperature, density and holding time.

Ivashutenko et al. (2016), Borrell et al. (2014)and Presenda et al. (2017) reported that microwave sintering would produce finer grain size at the same sintering temperature compared to ceramics sintered via conventional sintering. Ivashutenko et al. (2016) conducted experiment to study the sintering of 3YSZ via microwave and conventional sintering. Ceramics were sintered to desired temperature using microwave furnace operated with ramping rate 50 ºC/min and 10 minutes holding time at final temperature. On the other hand, conventionally sintered zirconia was sintered at slower ramping rate; 10 ºC/min, with 3 hours holding time at final temperature. They found out that at same sintering temperature, microwave sintering produced finer microstructure. At 1400ºC, the grain size for microwave sintered zirconia was 220nm while the grain size for conventionally sintered zirconia was 340nm. Nevertheless, their inference which concluded that microwave sintering helps in producing finer grains can be debatable since the holding time used during microwave sintering is shorter compared to the holding time set for conventional sintering. Besides, the heating rate for microwave sintering is so much higher which suggests that the ceramics undergone rapid heating. Rapid heating accompanied with short holding time might be the main reason for producing fine grain structure since grains did not have enough time for grain coarsening process to take place. Therefore, the direct effect of microwave sintering in producing fine grains is still unclear.

Earlier, Borrell et al. (2012) sintered 3Y-TZP at 1400 ºC using microwave and conventional method. They proved that microwave is helpful in hindering the grain growth. The grain size of microwave and conventionally sintered zirconia sintered at the same sintering temperature are reported to be 225 nm and 256 nm respectively. However, direct effect of microwave sintering in hindering the grain growth is also not clear since the holding time and ramping rate used during these two sintering method are much differ. Ramping rate for microwave sintering is 30 ºC/min while 5 ºC/min was used for conventional sintering. Furthermore, 10 minutes and 1 hour holding time was set during microwave and conventional sintering respectively.

Presenda et al. (2017) sintered 3Y-TZP ceramics at temperature 1200 ºC and 1300 ºC. Similar to Ivashutenko et al. (2016) and Borrell et al. (2014), longer holding time and relatively higher ramping rate were used for conventional sintering. Holding time for microwave and conventional sintering are 10 minutes and 2 hours respectively. Ramping rate for microwave sintering was set at 100 ºC/min and 10 ºC/min for conventional sintering. They reported that microwave sintering produced smaller grain than conventionally sintered zirconia sintered at same sintering temperature. However, they did not mention the detail for the results whether the difference in grain size for both methods is significant or not. Shorter holding time and higher ramping rate during microwave sintering results in reduction of processing time which might be the main cause that hinder the grain growth. From the results obtained by Ivashutenko, Borrell and Presenda, it is yet to be proved that microwave sintering gives direct effect on producing fine grain size for ceramics materials. Therefore, it is crucial to conduct a study to compare the grain size of microwave with conventionally sintered ceramics sintered at fixed holding time and comparable heating rate.

In another report by Presenda et al. (2015), they revealed that the grain size of microwave and conventionally sintered 3Y-TZP is quite similar even though the holding time and ramping rate is different for both methods. The holding time for microwave sintering was way shorter, 10 minutes compared to 2 hours using conventional sintering. Besides, the ramping rate for microwave was 100 ºC /min while 10 ºC /min for conventional sintering. From the results obtained, microwave sintered ceramics has slightly finer grain with difference of 9 nm. The results suggest that the grain size is highly influenced by sintering temperature rather than heating mode and holding time. The results obtained by Presenda et al. (2015) is in contrast with results obtained by Ivashutenko et al. (2016) where Ivashutenko reported significant difference in grain size for microwave and conventionally sintered zirconia with different holding time and ramping rate.

Similar to the results obtained by Presenda et al. (2015), Charmond et al. (2010) also revealed that the grain size is highly dependent of sintering temperature, not the heating mode. In their experiment, they fixed the heating temperature at 1360 ºC and the heating rate at 25 ºC/min. There is no holding time at the final temperature. Based on the results obtained, the grain size of conventionally sintered zirconia is 220nm while microwave possessed slightly larger grain, 230nm-270nm. The results obtained from Presenda and Charmond suggested that sintering mode, holding time and heating rate did not give significant effect on the grain size. The main factor influencing the grain size of sintered zirconia is the sintering temperature.

In contrast to other literatures, Xie et al. (1998) reported that the grain size of microwave sintered alumina powder is larger than the grain size of conventionally sintered powder. In their experiment, they sintered the ceramics with 30 minutes holding time at the desired temperature for microwave method and 2 hours hold for conventional sintering method. At 1300 ºC, microwave sintered ceramics possessed grain size of 1.2µm while conventionally sintered ceramics only possessed grain size of 0.7µm. Larger grain size obtained for microwave compared to conventionally sintered ceramics was corresponds with their high density. Microwave sintered ceramics achieved density of 97.5% at sintering temperature of 1300ºC while ceramics sintered conventionally at that temperature only achieved 89% of theoretical density. Higher density of microwave sintered zirconia results in larger grain size. As sintering temperature was further increased to 1500 ºC, ceramics sintered using both methods attained 99.7% density. Since the density is equal, the grain size for both methods is also comparable which is around 2.5µm. From their results, they concluded that the grain size is highly dependent on density. On the other hand, a year after they published the previous literature, Xie conducted another experiment to study the grain size of microwave and conventionally sintered ceramics. This time, they used ceria doped zirconia (Ce-Y-ZrO_2). They sintered the ceramics to 99.5% theoretical density and both methods achieved the same density at 1550 ºC. The results is in contradicts with their previous results where grain size is independent to the density of ceramics. At the same theoretical density, microwave sintered zirconia has finer grains (0.65µm) compared to conventionally sintered zirconia possessing grain size of 1.15µm. They concluded that microwave sintering helps in hindering grains growth at final densification stage. One of the main reasons for grain growth hindering via microwave heating is the rapid heating and accelerated diffusion of microwave by zirconia at high temperature (Xie et al., 1999).

Mazaheri et al. (2008) also conducted experiment to study the effect of microwave sintering and also the heating rates during microwave sintering on the grain size of 8YSZ. Conventionally sintered samples were heated with ramping rate of 5ºC/min without holding time. The same ramping rate was used for low microwave sintering (LMS) in order to study the direct effect of microwave sintering on the microstructure of sintered zirconia. Apart from that, an experiment for high microwave sintering (HMS) with ramping rate of 50ºC/min was also conducted and the microstructural results were compared to the results obtained during LMS.

It was reported that HMS produced finest grain size followed by conventional sintering and LMS. Sintered to 1350 ºC produced samples with grain size of 0.4µm using HMS, 1µm using conventional sintering and 2.09µm using LMS. LMS produces largest grain size compared to other methods. Figure 2.12 shows the grain size variations for LMS, HMS and conventional heated samples. From the figure, it was clear that as temperature increases, the grain size of all samples increases regardless the method used. However, LMS method produced sample with largest grain size even at low temperature. Comparing LMS and conventionally sintered sample having the same ramping rate (5 ºC/min), there is significant difference in grain size. Grain size of LMS increases drastically at 1200 ºC while grain size of conventionally sintered sample increases drastically after temperature reached 1300ºC. This might be due to LMS undergoing volumetric heating thus densification mechanism and grain growth are activated earlier than conventionally sintered sample. On the other hand, no drastic changes in grain size for HMS samples. This might be due to short sintering time when using high ramping rate. Therefore, samples do not have enough time to undergo grain coarsening, resulting in samples having very fine grain even at high temperature.

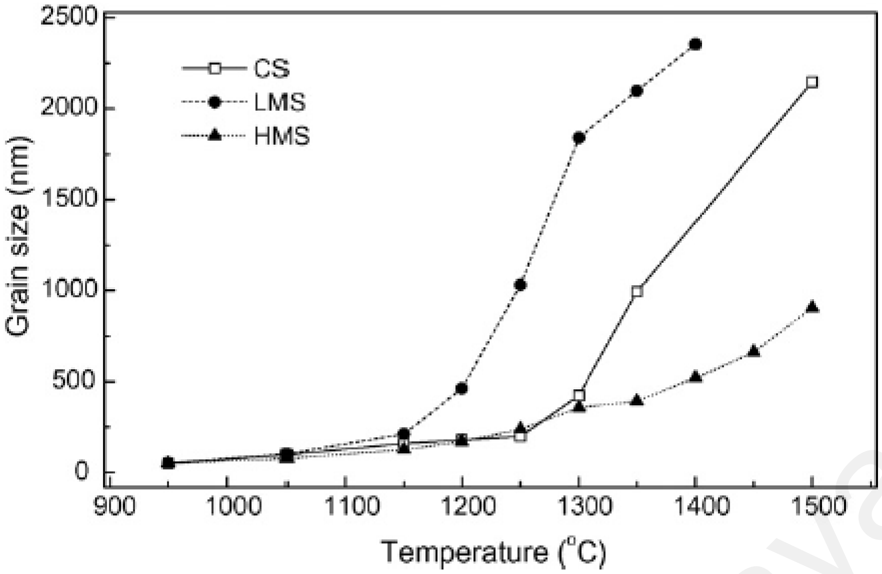


Figure 2.12: The grain size variations for LMS, HMS and conventional heated samples

Based on the results obtained by Mazaheri et al. (2008), it can be concluded that microwave did not give direct effect on the grain growth of ceramics. Samples heated via microwave sintering might also have large grain if the heating rate is too low. Low heating rate will results in long processing time. Since the densification mechanism starts way earlier for microwave compared to conventional sintering, ceramics sintered via microwave would undergo grain coarsening process way earlier which in return produced larger grain than conventionally sintered ceramics.

The effect of holding time has been studied by S Ramesh et al. (2011) and Kwa et al. (2015) using conventional sintering. They reported that longer holding time will result in larger grain size. S Ramesh et al. (2011) compared the grain size of conventionally sintered YTZP for 12 minutes with 2 hours holding time. At the same sintering temperature, 1350 ºC, the grain size for 12 minutes holding time is 0.19µm while 2 hours holding time produce grains with average grain size of 0.32µm. Kwa et al. (2015) compared 1 minutes to 12 minutes and 2 hours holding time. Based on their results, the grain size is the same for 1 minute and 12 minutes holding time. As the holding time was set to 2 hours, significant difference in grain size can be observed. For example, the grain size of 3Y-TZPs sintered with 1 minute and 12 minutes holding time is 0.33µm while 2 hours holding time has the grain size of 0.4µm at the same sintering temperature.

2.7.3 Effect of microwave on mechanical properties

Mechanical properties of ceramics are usually dependent on density and also grain size where small grain size would enhance the strength of ceramics especially in terms of hardness and Young's modulus (Benavente et al., 2014). However, in most cases where mechanical properties of microwave is compared to conventionally sintered ceramics, small difference of grain size would give significant effect on the mechanical properties of microwave sintered ceramics where the mechanical properties are always higher than ceramics sintered conventionally. Unfortunately, none of the literatures explain the mechanism behind the significant improvement of mechanical properties via microwave sintering. Apart from that, previous literatures only focused on comparing the densification and microstructure of microwave to conventionally sintered ceramics while the mechanical properties were poorly discussed.

Xie et al. (1999) reported the effect of microwave sintering on the mechanical properties of ceria doped zirconia. They studied the flexural strength and fracture toughness of ceramics when sintered via microwave and conventional methods. They observed that sintering at the same temperature and holding time (1500ºC and 15 minutes hold) using microwave sintering would produce ceramics with higher flexural strength and fracture toughness. The flexural strength for microwave and conventionally sintered zirconia are 1195 MPa and 950 MPa respectively. Microwave sintered ceramics also have higher fracture toughness which is 13.7 MPa.m$^{1/2}$ while the fracture toughness of zirconia sintered conventionally was only 11.2 MPa.m$^{1/2}$. They concluded that the higher strength in microwave sintered ceramics was contributed by finer grain sizes and higher density.

Besides comparing the densification and microstructure of conventional to LMS and HMS sintered zirconia, Mazaheri et al., (2008) also compare the mechanical properties of the tested samples. In term of hardness and fracture toughness, HMS was reported to possess highest fracture toughness. Fracture toughness of ceramic was reported to be linked with grain size and grain size distribution. Uniform and fine grain produced ceramics with high fracture toughness. Aside from that, smaller grain size also results in ceramics having higher hardness.

Recently, Ivashutenko et al. (2016) revealed that 3YTZP sintered using microwave sintering possessed higher hardness than ceramics sintered conventionally at the same sintering temperature. At sintering temperature of 1400 ºC, the hardness of microwave and conventionally sintered zirconia are 12.6 GPa and 9.5 GPa respectively. The enhancement of hardness for microwave sintered ceramics was reported to be related to grain size where grain size of microwave sintered was recorded to be 220nm compared to 340nm for conventionally sintered zirconia. The big difference in grain size where microwave sintering produced finer microstructure might be the main reason for the improvement of hardness via microwave sintering.

In 2014, Benavente et al. (2014) also concluded that microwave sintering produced alumina-zirconia nanocomposite with higher hardness, fracture toughness and Young's modulus in comparison to conventionally sintered ceramics. However, the results were not mention in details. Presenda et al. (2015) also mentioned about the improvement of hardness and fracture toughness of 3YTZP via microwave sintering. When sintered at 1300 ºC, the hardness of microwave and conventionally sintered ceramics are 15 GPa and 13 GPa respectively. Fracture toughness was recorded at 6.8 MPa.m$^{1/2}$ for microwave and 6.2 MPa.m$^{1/2}$ for conventionally sintered zirconia. The enhancement of mechanical properties was believed to be caused by grain size where the grain size of microwave sintered zirconia is finer compared to conventionally sintered zirconia.

However, the difference in grain size was not really significant where microwave sintered ceramics recorded grain size of 194nm while conventionally sintered ceramics recorded grain size of 203nm. In this case, 9nm difference in grain size might not cause big difference in mechanical properties. This suggest that enhancement of mechanical properties of ceramics via microwave sintering might be due to microwave effect on microstructural development of ceramics. Unfortunately, the mechanism behind the microwave effect in improving the mechanical properties has yet to be discussed.

CHAPTER 3: METHODOLOGY

3.1 Introduction

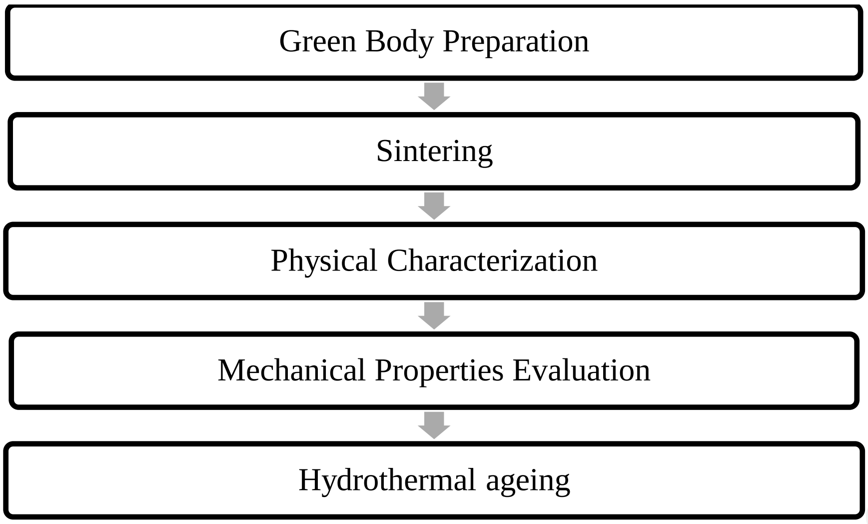
The focus of this work is to study the effect of different sintering techniques on microstructure, mechanical properties and ageing resistance of sintered zirconia. The two techniques used were conventional and microwave sintering. This chapter covers the standard experimental procedures used in conducting the entire project. Aside from that, proper description on the equipment and raw material used are also presented. This chapter also reveals the methods used for analysis of the results.

The entire process can be divided into three parts; sample preparation, sample characterizations and ageing evaluation. In sample preparation, as received powder was pressed and sintered. After sintering, the sintered bodies were characterized to study their microstructure, phase identification and mechanical properties. The characterization methods used are as shown in Table 3.1.

Table 3.1: Characterization methods

Sample characteristics	**Characterization Method**
Surface morphology/ microstructure evaluation	Field-Emission Scanning Electron Microscope (FESEM)
Phase identification	X-ray Diffractometer (XRD)
Bulk density measurement	Water emission technique using electronic balance
Hardness	Vickers indentation technique
Young Modulus	Sonic resonance technique
Fracture toughness	Vickers indentation fracture toughness

The last part of the project is to evaluate the degradation properties of the sintered samples. The overview of the process involved in the entire project is as follow:



3.2 Green Body Preparation

In this present work, 3 mol% of yttria- stabilized tetragonal zirconia polycrystalline (Y-TZP) obtained from Kyoritsu Corporation Japan was used as starting powder. The highly pure powder had a total impurity concentration up to 0.1 wt% with SiO_2, TiO_2, Al_2O_3 and Fe_2O_3 as major impurities. The powder was uniaxially pressed into discs (20 mm diameter x 3 mm thickness) and rectangular bar (32 mm x 13 mm x 4 mm) samples at a pressure of 3 MPa using a manually-operated hydraulic bench press (SPX Hydraulic Technologies, Rockford, Illinios, USA). The disc samples were weighed 2.5 g each while rectangular bar were 3.0 g each. Hardened steel mould set was used during the compaction process. During this process, WD-40 was used to clean the die wall prior to powder compaction in order to avoid lamination of powder particles on the die wall.

Uniaxial pressing was followed by cold isostatic pressing (CIP) (Riken Seiki, Japan) at 200 MPa for 1 minute. The purpose of using CIP is to induce uniform shrinkage and improve densification of zirconia ceramics by applying high pressure in all direction on the green body.

3.3 Sintering

Sintering is a process of compacting and forming a solid mass of material by heat and/or pressure without melting it to the point of liquefaction. During sintering process, the atoms in the material diffuse across the boundaries of the particles, fusing the particles together to form one solid piece. Sintering is a crucial process involved in fabrication of ceramics where heat is applied to a powder compact to impart the ceramics strength and integrity. Ceramic bodies are usually sintered at high temperature below their melting points in order to attain excellent densification as well as producing the required microstructure. In order to produce ceramic with excellent mechanical properties various sintering processes have been studied. In the present work, microwave sintering was carried out in a multimode 6 kW microwave furnace operating at frequency of 2.45 GHz. The microwave was autorun with ramping rate/ heating profile as shown in the Figure 3.1 below. Sintering temperatures were set at 1200 ºC, 1300 ºC, 1400 ºC and 1500 ºC with 5 minutes holding time at the final temperature. 10 samples were prepared for each temperature.

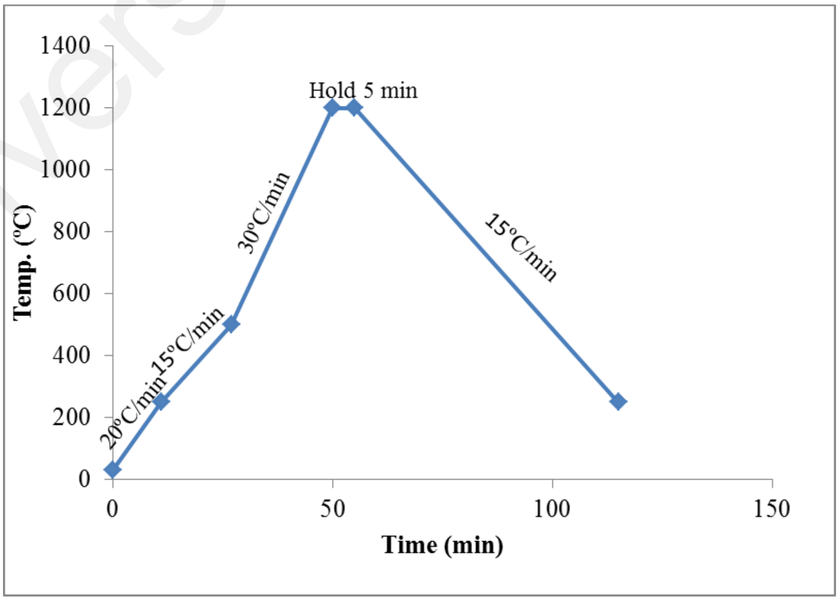


Figure 3.1: Heating profile during microwave heating.

Microwave sintered samples were then compared with conventionally sintered samples in term of their microstructure, mechanical properties and degradation properties. Conventional sintered samples were sintered in a box furnace at the same sintering temperatures and holding time as microwave sintered samples. Standard ramping rate for conventional sintering was used which is 10 ºC/min. The highlight of microwave sintering method is the ability to shorten the sintering time, thus energy efficient. For example, in order to sinter zirconia sample at temperature 1200 ºC, 239 minutes is needed when using conventional method. On the other hand, only 115 minutes is needed to complete the sintering process at the same sintering temperature when using microwave sintering. The sintering profile for microwave and conventional sintering at 1200 ºC with 5 minutes holding time is illustrated in Figure 3.2.

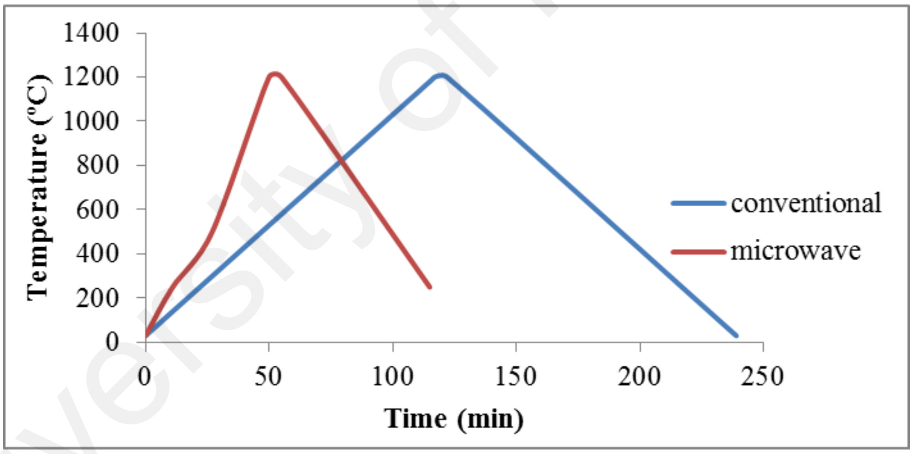


Figure 3.2: Heating profiles during microwave and conventional sintering.

3.4 Grinding and Polishing

Sintered disc samples were grinded and polished in order to obtain optical reflective surface. Silicon carbide (SiC) papers of different grades starting from 120 (coarsed), 240, 600, 800 and 1200 (fine) grade were used successively. Subsequently, the samples were polished using 6 µm and 1 µm diamond paste. Polished samples were then thermally etched at temperature 50ºC below the sintering temperature for 30 minutes prior to FESEM imaging. The purpose of thermal etching is to evaporate glassy phase along the grain boundaries, thus exposing the grains during microstructural imaging.

3.5 Bulk Density Measurement

Bulk densities of the sintered samples were determined via water emission technique based on Archimedes principle. An electronic balance with retrofitted density determination kit was used in the experiment. Distilled water was used as immersion medium. The experiment was started by recording the mass of the samples in air, followed by recording the mass of samples immersed in water. The difference in the weight were recorded and used to calculate the bulk densities of the samples using Archimedes equation (1):

$$\boldsymbol{\rho_{object} = \frac{W_a}{W_a - W_w}\, x\, \rho_{water}}$$

(3.1)

Where:

ρ_{object} is the density of object

W_a is the weight of sample in air

W_w is the weight of sample immersed in distilled water

ρ_{water} is the density of distilled water

The relative density is then calculated by taking 6.07 g/cm^3 as the theoretical density of KZ 3YF. The equation for relative density is as follow (2):

$$\boldsymbol{Relative\ density = \frac{bulk\ density}{theoretical\ density}\, x\, 100\%}$$

(3.2)

3.6 Young’s Modulus Determination

Sonic resonance technique was used to measure the flexure resonance frequency of rectangular bar samples. Flexural resonance frequency is an important parameter in calculating the Young’s Modulus (E) of the samples. Once the resonance frequency is experimentally determined, the modulus of elasticity or known as Young’s Modulus can be calculated using equation (3) based on standard test method ASTM C1259-2008e1 (2008). Gindo Sonic, type MK5 ‘Industrial’ J. W. Lemmens from Belgium is a commercial testing instrument used in the process. This instrument is equipped with transducer which monitors and evaluates the vibrational harmonic of the samples, thus calculating the resonance frequency of the sample. The experiment was carried out by tapping the samples followed by monitoring the resonance frequency using the transducer. The test was repeated five times for each sample to obtain a steady resonance frequency.

$$\boldsymbol{E = 0.9465\left(\frac{mf_f{}^2}{b}\right)\left(\frac{L^3}{t^3}\right)T_1}$$

(3.3)

Where,

b = bar width

m = bar mass

L = bar length

t = bar thickness

f_f = flexural resonance frequency of the bar

T_1 = correction factor for resonance flexural mode to account the finite thickness of bar, Poisson's ratio etc. are calculated as shown in equation (4):

$$\boldsymbol{T_1 = 1 + 6.585(1 + 0.0752\mu + 0.8109\mu^2)\left(\frac{t}{L}\right)^2 - 0.868\left(\frac{t}{L}\right)^4 - \left[\frac{8.34(1 + 0.2023\mu + 2.173\mu^2)\left(\frac{t}{L}\right)^4}{1 + 6.338(1 + 0.1408\mu + 1.53\mu^2)\left(\frac{t}{L}\right)^2}\right]} \qquad \textbf{(3.4)}$$

Where,

μ = Poisson's ratio for Y-TZP, considered as 0.23 (Musikant, 1991).

3.7 Vickers Hardness Determination

Hardness of the sintered samples is determined via Vickers Hardness method. During the testing process, a pyramidal diamond indenter (Mitutoyo AVK-C2, USA) was used to make indentation on the samples. 10 kg load was applied slowly for 10 seconds during the indentation process. Figure 3 shows the schematic diagram for typical result of the indentation process on the samples' surface. Generally, the typical result for indentation appears to be square with two diagonals having similar length (D1=D2). Typically, for ceramics sample, cracks will be emanated from four corners of the indent. Crack lengths (L1, L2, L3 and L4) were recorded to be used for fracture toughness calculation.

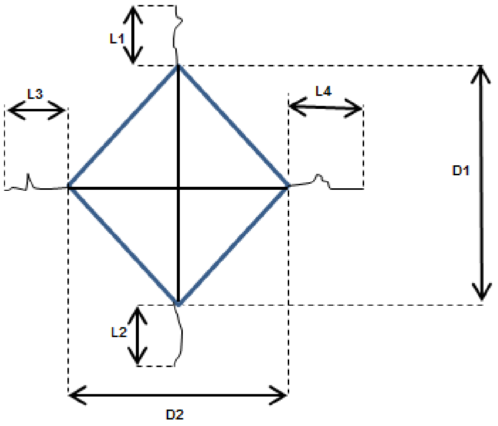


Figure 3.3: Typical indentation result formed on ceramics surface.

Indentation process was repeated five times and the average mean diagonal value, D was calculated. The Vickers hardness (H_V) of ceramic was then calculated using equation (5);

$$H_V = \frac{1.854P}{D^2} \quad (3.5)$$

Where,

P = Indentation load

D = mean diagonal; $\frac{D1+D2}{2}$

3.8 Fracture Toughness Determination

During Vickers hardness test, the length of four cracks at each corner, L_1 L_2 L_3 and L_4 are measured. Fracture toughness of the ceramics, K_{IC}, which corresponds to the indentation is calculated using equation (6) derived from Niihara et al (1982).

$$K_{IC} = 0.035 \left(\frac{L}{a}\right)^{-\frac{1}{2}} \left(\frac{E\Phi}{H_V}\right)^{\frac{2}{5}} \left(\frac{H_V}{\Phi}\right) a^{\frac{1}{2}}$$

(3.6)

Where,

L = mean crack length; $\frac{L1+L2+L3+L4}{4}$

E = Young's Modulus

Φ = Constrain factor (taken as 3 for tough ceramic, Evans & Charles, 1976)

3.9 Microstructure Evaluation

Microstructural evaluation of the sintered bodies was carried out in Faculty of Engineering University Malaya using Field Emission Scanning Electron Microscope (FESEM). FESEM imaging is used to study the morphological properties or the microstructure of the sintered bodies. Prior to FESEM imaging, the sintered bodies were thermally etched at temperature 50 ºC below sintering temperature. Heating and cooling rate was set at 10 ºC/min with 30 minutes holding time at the maximum temperature. The purpose of thermal etching is to delineate the grain boundaries during microstructural imaging.

The advantage of using FESEM compared to conventional scanning electron microscope (SEM) is the ability to produce higher resolution image. This is due to different probes used where FESEM probe is sharper compared to the probe used for SEM. The field emission gun emits the electrons from a much smaller area and thus allowing electron beam to be perfectly focused on the samples. During the process, samples were put on carbon tape and mounted on a stage. 1kV voltage was used with magnification ranging from 3000X to 20000X. Three images were taken at each magnification at various spot.

Once high quality images were obtained, average grain size of the samples was calculated. Line intercept method proposed by Mendelson (1969) was used to calculate the average grain size in accordance with ASTM E112-96. The micrographs were printed on A4 size papers. Few lines were drawn and the number of intercepts between grain boundaries and lines were counted. The average grain size was then calculated based on Mendelson equation (7):

$$\bar{D} = 1.56\bar{L} \qquad \text{and} \qquad \bar{L} = \frac{C}{MN} \tag{3.7}$$

Where,

$\bar{D}$ = Average grain size

$\bar{L}$ = Measured average interception length over the number of grains

C = total length of test line

M = magnification of photomicrograph

N = number of intercepts

3.10 X-Ray Diffraction (XRD) Analysis

The phase presence in the sintered samples were analysed using X-ray Diffractometer (XRD) which is a non-destructive analytical technique. XRD relies on the particle nature of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern without damaging the sample. Once the X-ray from the source hits the atoms in the crystal lattice, X-rays will be deflect and scattered at different angles which provides the information of the atomic arrangement of the sample. This information on the atomic arrangement was used to determine the phase presence in the crystal structure as different phase possess different atomic arrangement. PANalytical Empyren XRD machine was used in this research. The machine was operated at 40 mA and 45 kV with Cu-Kα as x-ray radiation source. The samples were scanned at diffraction angle, 2θ, in the range of 27° to 36° with step size and step scan of 0.02º and 0.5º/min respectively. For Y-TZP ceramics with tetragonal (t) phase, strongest peak can be observed at $2\theta \approx 30.2^{\circ}$ $(1\ 1\ 1)_t$. Two strong peaks can be observed for Y-TZP ceramics with monoclinic phase which are at $2\theta \approx 28.2^{\circ}$ $(1\ 1\ \bar{1})_m$ and $2\theta \approx 31.5^{\circ}$ $(1\ 1\ 1)_m$ .The peaks obtained from XRD analysis were compared with the standard references; ICSD 98-006-2994 (tetragonal) and ICSD 98-006-2993 (monoclinic).

The relative amount of tetragonal and monoclinic phase was determined using the relationship established by Toraya et. al in equation (8):

$$V_m = \frac{1.311X_m}{1 + 0.311X_m}$$

(3.8)

Where,

V_m = volume fraction of monoclinic phase

X_m = integrated intensity ratio of monoclinic

$$X_m = \frac{I(11\bar{1})_m + I(111)_m}{I(11\bar{1})_m + I(111)_m + I(111)_t}$$

(3.9)

Where I is the peak intensity and the subscripts t and m represent the tetragonal and monoclinic phase respectively. Once the volume fraction of monoclinic phase (V_m) is obtained, the volume fraction of tetragonal phase can be calculated (10).

$$V_t = 1 - V_m$$

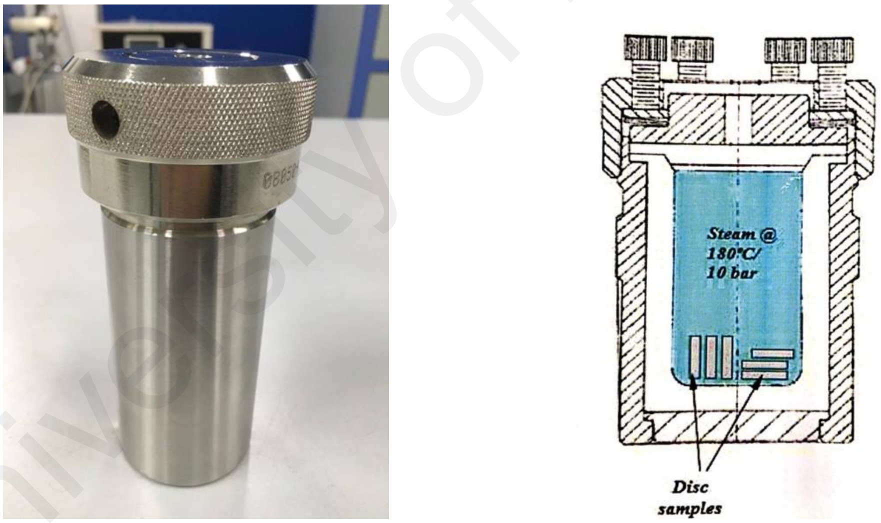
Or

$$V_t\% = 100\% - V_m\%$$

(3.10)

3.11 Ageing Experiment

The ageing behavior of conventional and microwave sintered zirconia at different sintering temperature was examine by exposing the disc samples in autoclave condition for duration up to 200 hours. Samples are placed in an autoclaves vessel or also called acid digestion bomb obtained from Parr Instrument, USA. The vessel was filled with 10ml distilled water before it is place inside an oven set at 180ºC/10 bar. Under this condition, distilled water will be transformed into superheated steam. At different intervals of ageing (1 hour, 3 hours, 6 hours, 9 hours, 24 hours, 48 hours, 100 hours and 200 hours), all samples were taken out for physical inspection and phase analysis using XRD. Last but not least, FESEM imaging was conducted to study the morphology of aged samples.



(a) (b)

Figure 3.4: (a) Photograph of autoclaved vessel or acid digestion bomb (b) cross section view of the vessel.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

This chapter reveals the findings of this current research including the results for phase analysis of as sintered samples, microstructural analysis as well as mechanical properties characterization. Last but not least, this chapter also uncovers the results for degradation properties after the sintered samples were exposed to ageing environment. The results of microstructural, phase stability and mechanical properties of the microwave sintered bodies such as density, Young's modulus, Vickers hardness and fracture toughness were compared to conventionally sintered zirconia.

The results obtained reveal that microwave sintering gives positive effects on densification of ceramics. For example, microwave sintered sample achieved >99% of theoretical density at 1300 ºC while ceramics sintered conventionally need higher sintering temperature to achieved the same theoretical density. Aside from that, improvement of mechanical properties via MW can also be seen especially at low sintering temperatures. As sintering temperature was increased above 1400ºC, the grain size and mechanical properties for both microwave and conventionally sintered ceramics are comparable suggesting that at high sintering temperature where densification mechanism is activated, grain size is strongly influenced by sintering temperature rather than sintering mode.

Ageing experiment was first conducted for samples having largest grain size which are ceramics samples sintered at 1500 ºC followed by samples sintered at 1400 ºC. Both conventionally and microwave sintered ceramics sintered at 1500 ºC failed after 100 hours of ageing. On the other hand, samples sintered at 1400 ºC showed fully *t* grains after 200 hours of ageing. No further ageing experiment was conducted for samples sintered below 1400 ºC since they have smaller grain size. Generally, it can be concluded that samples sintered below 1400 ºC having small grain size were prone to ageing.

Despite comparable mechanical properties and degradation properties of conventional and microwave sintered samples especially at high sintering temperature, it can be highlight that microwave sintering proved to be effective in reducing processing time thus reducing energy consumption and cost. Total sintering time during microwave and conventional sintering were shown in Table 4.1:

Table 4.1: Total sintering times for microwave and conventional sintering.

Temperature (ºC)	Sintering time (min)	
	Microwave	Conventional
1200	115	239
1300	119	259
1400	122	279
1500	125	299

4.2 Phase composition (XRD analysis)

XRD analysis were conducted on sintered samples indicates that all samples exhibited fully tetragonal phase regardless of sintering methods and temperatures. Figure 4.1 shows the XRD patterns of samples sintered using microwave and conventional sintering at temperature ranging from 1200 ºC to 1500 ºC. Figure 4.1 shows that only *t* peak presence in all sintered sample. No trace of monoclinic phase contents showed the effectiveness of the starting powder in controlling tetragonal phase stability at all sintering temperatures.

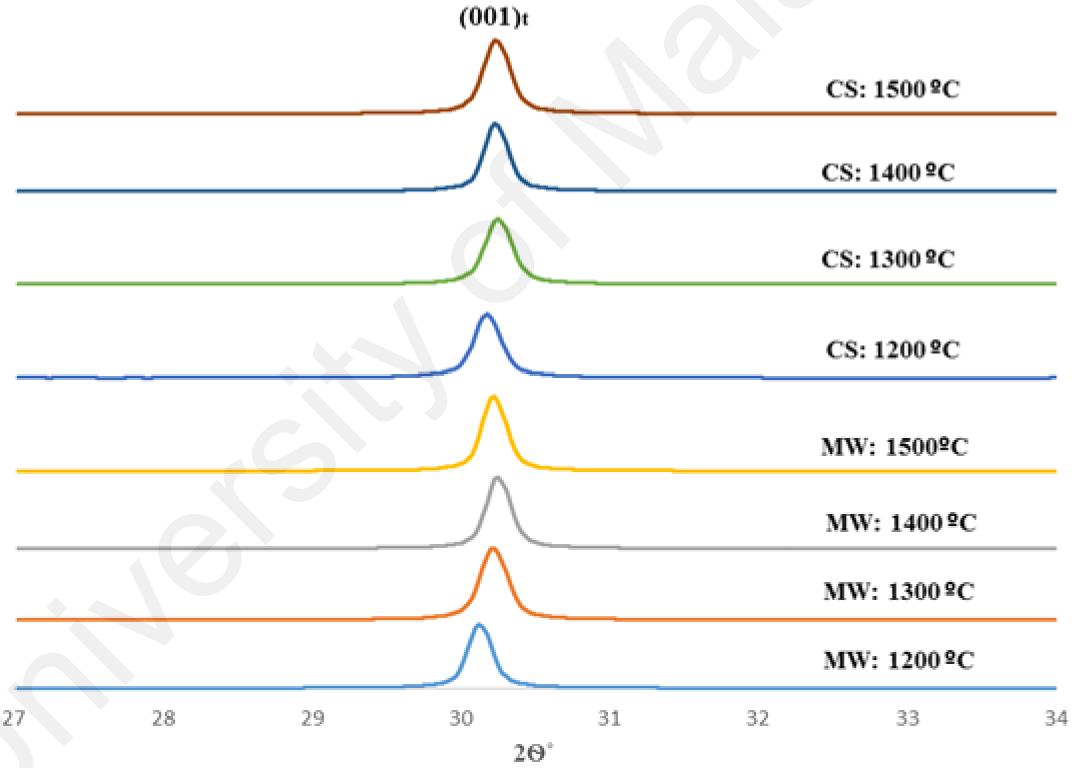


Figure 4.1: XRD patterns of samples sintered via microwave and conventional method at temperature range of 1200ºC -1500ºC.

4.3 Microstructural Evaluation

Referring to the FESEM images in Figure 4.2 , there is significant difference between the microstructure of MW and conventionally CS-sintered sample at temperature 1200 ºC with 5 minutes holding time as shown in Figure 4.2 (a and b). At this low temperature, in comparison to the CS sample, the MW-sintered sample revealed complete grain structure with smooth surface and clear grain boundaries. A distinct grain boundary is not observed for the conventional sintered sample at 1200 °C and this indicates that sintering is not complete at this low temperature.

Despite having the same sintering temperature and holding time, the microstructure of microwave are completely different from conventionally sintered sample. The significant difference in microstructural development at this low temperature might be attributed by the difference in the sintering method. Microwave sintered ceramics is heated internally via molecular interaction with electromagnetic field as microwave penetrate the ceramics (Agrawal, 2006). Electromagnetic energy is converted into heat energy to heat the ceramics from inside. This result in volumetric heating where the heat produced in the whole bulk of material will help in activating the sintering mechanism in a shorter time. Furthermore, the heating rate for microwave is relatively high compared to conventional sintering. Combination of high heating rate and volumetric heating via microwave sintering allows ceramic to be sintered at a lower temperature in a shorter time. In contrast, conventionally sintered ceramics is heated via conduction where external heat source will heat the surface of the ceramics first, as the surface temperature increases, the heat will be transferred to the core. Aside from non-uniform sintering, heat conduction from the surface to the core also requires time, thus delaying the activation of sintering process as observed for the 1200 ºC sintered sample in this work.

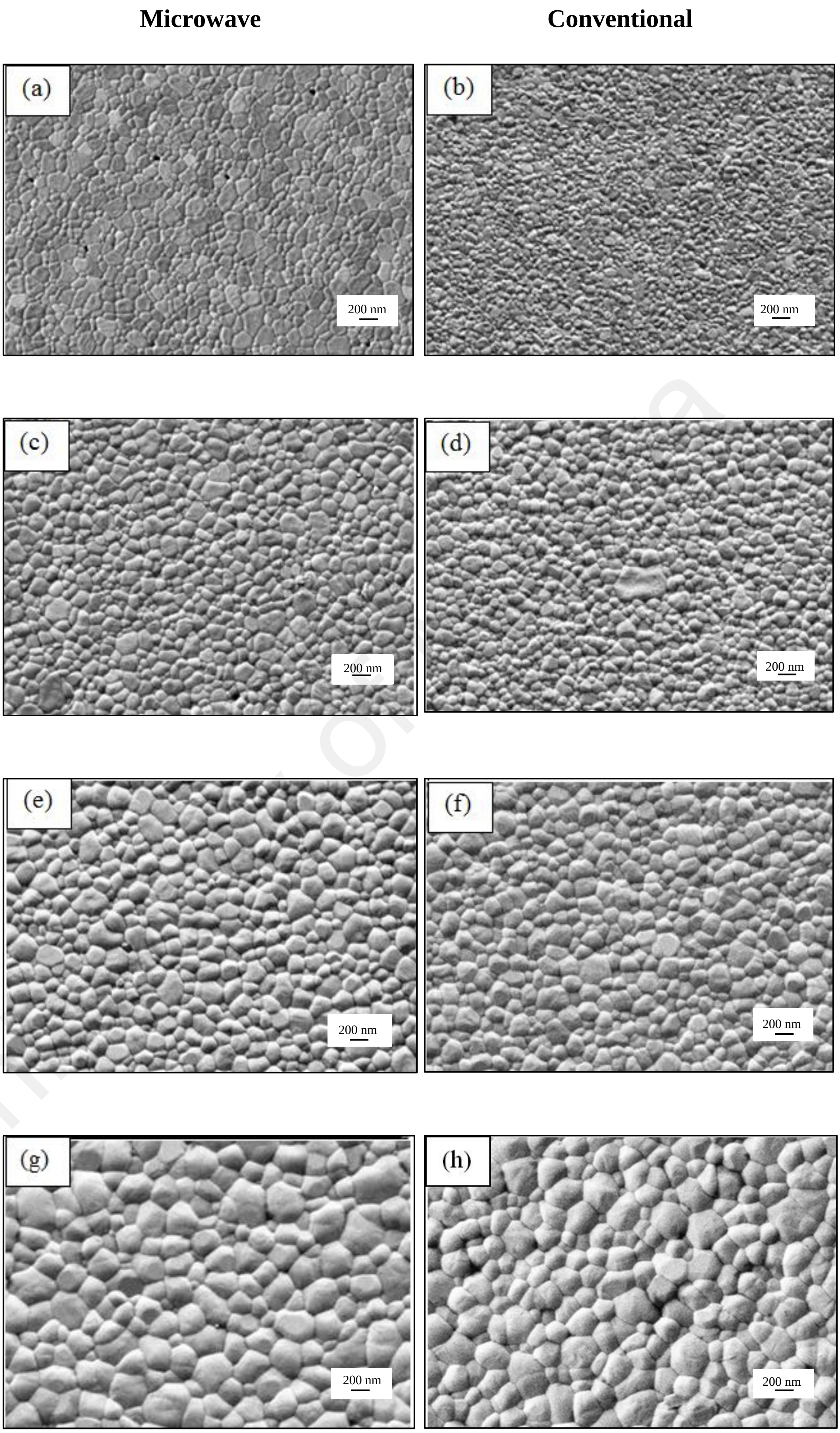

Microwave
Conventional
(a)
200 nm
(b)
200 nm
(c)
200 nm
(d)
200 nm
(e)
200 nm
(f)
200 nm
(g)
200 nm
(h)
200 nm

Figure 4.2: Difference in microstructural development of microwave and conventionally sintered KY 3ZF at 1200 ºC (a and b), 1300 ºC (c and d), 1400 ºC (e and f), and 1500 ºC (g and h).

Table 4.2: Average grain sizes of sintered zirconia

Temperature (ºC)	MW Sintering (μm)	CS Sintering (μm)
1200	0.16 ± 0.05	0.12 ± 0.07
1300	0.17 ± 0.03	0.18 ± 0.03
1400	0.22 ± 0.02	0.23 ± 0.01
1500	0.37 ± 0.02	0.36 ± 0.02

However, as the sintering temperature was increased to 1300 ºC, FESEM images in Figure 4.2 (c and d) show that both microwave and conventional sintered samples have undergone complete sintering as evident from the distinct appearance of grain boundaries. Moreover, the grains for both samples are round and smooth with minimal pores observed in the structure. From the images, the grain size for both samples is quite similar. These observations proved that conventionally sintered sample needs higher temperature to be sintered while microwave successfully sintered zirconia ceramics at 1200 ºC. Longer time is required to reach the higher temperature, thus grains have longer time for grain growth and completing the sintering process during conventional sintering. Apart from that, it can be observed that the grain size for both samples is quite similar. When the grain size is measured using Mendelson’s technique (Mendelson, 1969), it was proven that the grain size of conventionally sintered sample did not differ much with microwave sintered sample. Average grain size is shown in Table 4.2. The results indicated that there is a small difference between the grain sizes of conventional-sintered and microwave-sintered samples for samples sintered at 1300 °C and above. In general, the microwave sintering produces smaller grain than the conventionally sintered sample.

As the sintering temperature is further increased to 1400 ºC, the microstructures for both conventional and microwave sintered samples are quite similar. Complete sintering process has taken place. The grain sizes for both methods at each temperature are much alike. This shows that at higher temperatures, when densification has completed, grain coarsening proceeded regardless of sintering methods. This observation is in good agreement with the work reported by (Charmond et al., 2010).

Surprisingly, as the sintering temperature is increased to 1500 ºC, sample sintered using microwave has slightly larger grain size than sample sintered conventionally. However, the difference in grain size is not very significant suggesting that grain size is still strongly influenced by sintering temperature and holding time. Slightly larger grain for microwave sintered sample at this temperature might be due to grain coarsening process which occurs earlier during microwave sintering (densification process started at 1200 ºC). Therefore, microwave sintering would produce slightly larger grain compared to conventionally sintered ceramic that exhibited densification mechanism and grain coarsening process at 1300 ºC.

The results obtained proved that final sintering temperature strongly influenced the grain size regardless the sintering method. Since the ramping rate used in this work for microwave and conventional sintering process did not differ much, the results obtained is in agreement with the results reported by Charmond et al. (2010) where ceramics sintered at the same sintering temperature and ramping rate produced same microstructure regardless the sintering method. Sintering at high temperature means that the ceramics have longer time to be sintered, thus sintering mechanism can be activated for both methods. Despite having the same microstructure and almost similar grain size at the same sintering temperature, it can be highlighted here that microwave sintering required shorter processing time.

From previous literature (Borrell et al., 2012; Ivashutenko et al., 2016), it was reported that grain growth can be hindered at high temperature using microwave sintering. However, in this work, the grain size at high temperature is not very much different for both conventional and microwave techniques. This could be due to the ramp rate used during microwave sintering which is ~30 ºC/min. Other researchers (Mazaheri et al., 2008) reported very high ramping rate used during microwave sintering which is around 50 ºC/min to 200ºC/min. The authors explain that rapid heating during microwave sintering restrict the grain growth. Unfortunately, when using very high ramping rate, ceramics might not have enough time to be sintered especially at low temperatures (Xie et al., 1999). Such high ramp rates for MW is only advantageous for sintering at high sintering temperature (> 1300 °C) and will results in highly dense ceramics with fine grain size.

The current result is in contrast with previous literatures that reported MW sintering would significantly reduce the grain size of the sintered ceramics. Previous researchers (Benavente et al., 2014; Borrell et al., 2014; Presenda et al., 2017; Presenda et al., 2015; Xie et al., 1998) used longer holding time (1-3 hours) for conventional sintering while the holding time during microwave sintering is between 5-15 minutes.

The significant difference between the grain sizes was reported to be due to difference in sintering technique. However, it is debatable whether the finer grain observed for microwave sintered ceramics is due to microwave effect or shorter holding time used. From this study where same holding time was used, it was found that sintering method does not give significant effect on the grain size especially at higher temperatures where densification mechanism has been activated. In this study, it can be highlighted that microwave sintering only helps in reducing the energy consumption by lowering the sintering temperature and processing time.

4.4 Relative density

*Note that theoretical density of KZ 3YF is 6.07g/cm^3

Densification is the product of sintering where particles change shape to increase their contact area with neighbouring particles. This process leads to shrinkage of green body, thus reducing porosity through grain growth and boundary movement. From the results obtained, clear pattern for the relationship between density and temperature can be observed for both conventional and microwave sintering. High sintering temperature proved to promote densification where pores can be eliminated at the end of sintering process resulting in highly dense ceramics. Figure 4.3 shows the variation of relative density at various sintering temperature for microwave and conventionally sintered samples.

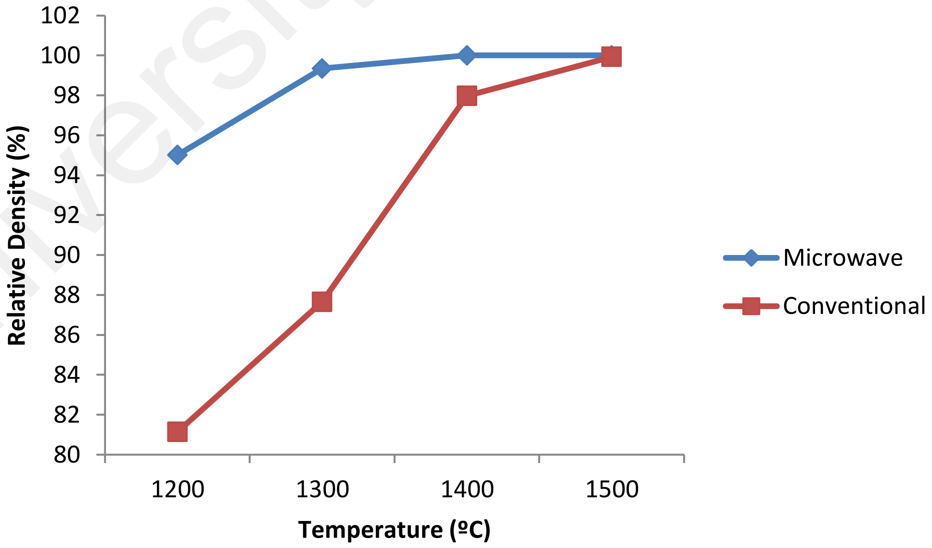


Figure 4.3: Relative densities at various temperatures for microwave and conventionally sintered zirconia.

At lower sintering temperature, remarkable difference in density of sintered zirconia can be observed between the two sintering methods. At 1200 ºC, density of conventionally sintered sample is relatively low compared to microwave sintered sample. Conventionally sintered sample only achieved 81% of its theoretical density while microwave sintered sample attained 95% of the theoretical density. Referring to the FESEM images, rough surface and absence of grain boundary indicate that the sintering process is incomplete when using conventional heating at low temperature. Incomplete sintering means that densification only occurs partially. Accompany with short holding time, grains did not have enough time to rearrange and grow during the sintering process. Therefore, pores are unable to be eliminated resulting in less dense ceramics. In contrast, highly dense sample is obtained during microwave heating indicates nearly complete densification process. Volumetric heating via microwave sintering helps in activating densification mechanism in a shorter time at low temperature since the heat is produced in the whole bulk of material. Apart from volumetric heating, enhancement in densification mechanism by microwave sintering is also due to reduction in activation energy as reported by Brosnan et al. (2003). Brosnan studied the activation energy during sintering of alumina tubes using microwave and conventional methods. From their studies, they revealed that the activation energy during conventional sintering was 520 kJ/mol while microwave sintering could lower the activation energy to only 85 kJ/mol.

From the results obtained, some pores can be observed for microwave sintered sample at 1200 ºC. Further heating at higher temperature is needed to eliminate the pores. At 1300 ºC, density of conventionally sintered sample is 87% while microwave sintered sample recorded value above 99% of the theoretical density. On the other hand, conventionally sintered zirconia can only achieved 99% of theoretical density once the sintering temperature reached 1500 ºC. As the temperature is increased to 1500 ºC, all sample achieved maximum density where sintering method does not affect the densification of ceramics. This temperature is high enough to activate the densification mechanism accompanied by longer time needed to achieve the high temperature, thus providing same chance of densification for all tested sample regardless the sintering mode.

4.5 Young's Modulus

Flexural-resonance frequency technique was used to determine Young's modulus, E, on bar samples of microwave and conventionally sintered zirconia. Figure 4.4 shows the Young's modulus of the sintered samples corresponds to the sintering temperature.

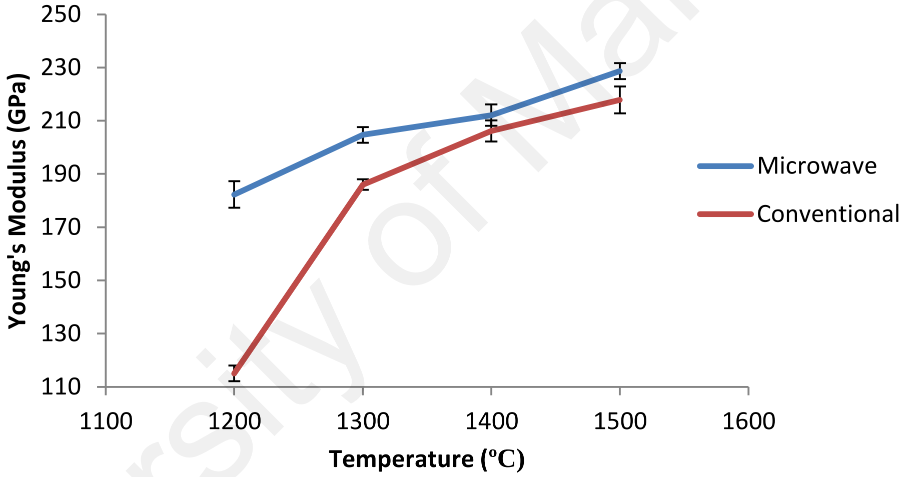


Figure 4.4: Effect of sintering temperatures on the matrix stiffness of the sintered zirconias.

The Young's modulus (E) of microwave and conventional sintered zirconia follows the density trends where the E values increased with sintering temperature as shown in Figure 4.4. It can be seen that the Young's modulus of microwave-sintered sample was always higher than the conventional-sintered samples at all temperatures. Significant improvement in matrix stiffness via microwave sintering can be seen, particularly at temperatures of 1200 ºC and 1300ºC.

At 1200 ºC, microwave sintered sample recorded E value of 182.27 ± 5 GPa compared to conventionally sintered sample that could only attain E value of 115.05 ± 3 GPa at the same sintering temperature. As the sintering temperature is increased above 1400 ºC, the E value at the same sintering temperature is comparable regardless the sintering mode. High E values might be attributed to their high densities. From the results, it can be inferred that density is an important parameter that determine the matrix stiffness of zirconia ceramics.

Previous studies also reported that Young's modulus is highly dependent on ceramics density (S Ramesh, Tan, Peralta, & Teng, 2007). Higher density would result in higher matrix stiffness. Since microwave sintering is proven to enhance densification process especially at low sintering temperature, indirectly this non-conventional sintering process is also beneficial in improving the matrix stiffness of zirconia ceramics. High E values can be attained at low sintering temperature, thus microwave can be considered as an effective sintering process which would help in reducing energy consumption and also processing time.

4.6 Vickers Hardness

The variation of average Vickers hardness at various sintering temperature for microwave and conventionally sintered zirconia is as shown in Figure 4.5.

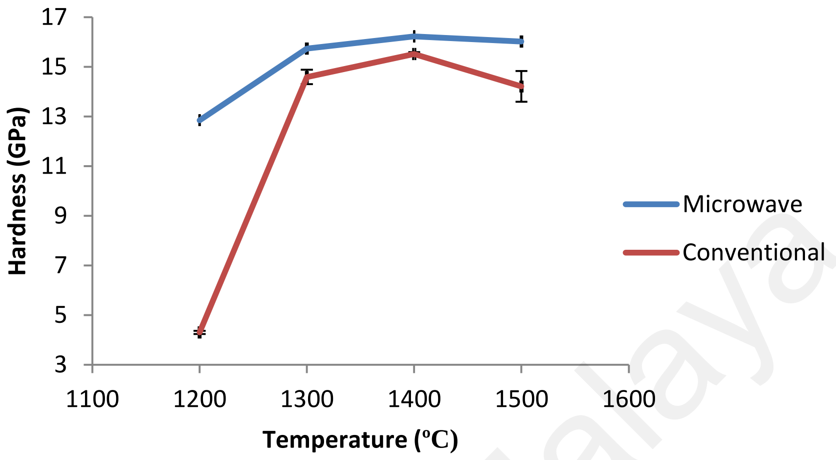


Figure 4.5: Variation of average Vickers hardness corresponds to the sintering temperature.

The results revealed that microwave sintering was beneficial in enhancing the hardness particularly when sintered at 1200 ºC. The hardness of conventional-sintered sample was only 4.3 GPa whereas the microwave-sintered sample achieved a high hardness of 12.8 GPa at the same sintering temperature. It was reported that there are two important factors affecting hardness of ceramics which are porosity and grain size.

Improvement in hardness for sample sintered via microwave might be linked with enhancement in densification mechanism especially at low sintering temperature. Volumetric heating and reduction of activation energy during microwave sintering results in the enhancement of densification mechanism. As a result, microwave sintering successfully produce highly dense ceramics at low sintering temperature, thus improving the hardness of ceramics.

As the sintering temperature increased, the hardness of both samples also increased and this is in good agreement with the increased in bulk density. From the results obtained, it was found that the maximum hardness of 16.2 GPa was obtained for sample sintered at 1400 ºC. As the sintering temperature is further increased to 1500ºC, there was a slight decrement in the hardness for both samples. This result is in good agreement with the observations made by other researchers (Hodgson, Cawley, & Clubley, 1999; S Ramesh et al., 2011; S Ramesh et al., 2016; Ran et al., 2010). This decreased in the hardness could be due to the larger grain size of the samples when sintered at 1500 ºC compared to the samples sintered at 1400 ºC. Previous researchers reported that hardness of ceramics is also influenced by grain size where fine grain microstructure was reported to improve the hardness (Yan, Gao, & Lu, 1996). Since the densities for samples heated at 1400 ºC and 1500 ºC are almost similar, grain size of the ceramics seems to be the determining factor for the decrement of hardness. Samples heated at 1500ºC have slightly larger grain size compared to samples heated at 1400ºC, hence explaining why the hardness decreased.

4.7 Fracture Toughness

The effect of microwave and conventional sintering on the fracture toughness (K_{Ic}) of zirconia is shown in Figure 4.6. The fracture toughness trend of the sintered samples was found to follow the hardness trend, wherein incremental of the toughness was observed with increasing sintering temperatures up to 1400ºC. A significant difference in the K_{Ic} values could be observed at 1200 ºC where the microwave sintering resulted in an enhanced toughness of the sintered body.

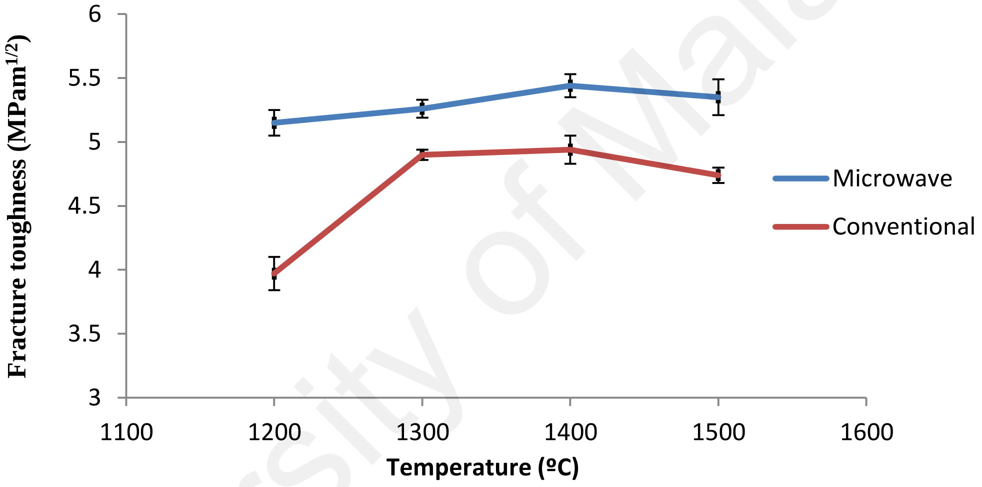


Figure 4.6: Variation of fracture toughness corresponds to sintering temperatures.

In general, a high value of above 5 MPam$^{1/2}$ was obtained for all the MW-sintered samples. In contrast, the maximum K_{Ic} obtained for the CS sample was 4.94 ± 0.11 MPam$^{1/2}$ when sintered at 1400 °C. The results show that, even at high sintering temperature, conventionally sintered sample could not achieve comparably high K_{IC} value as the values recorded via microwave sintering.

Lowest K_{IC} value was recorded by conventionally sintered sample at 1200ºC. At this temperature, sample sintered conventionally only attained K_{IC} value of 3.97 ± 0.13 $MPa^{1/2}$ while sample sintered via microwave achieved K_{IC} value of 5.15 ± 0.10 $MPa^{1/2}$.Highest K_{IC} value was attained by microwave sample at sintering temperature 1400 ºC (~5.44 $MPa^{1/2}$).

The fracture toughness of zirconia ceramics has been associated with the transformation toughening effect of the tetragonal grains. Simon Lawson (1995) reported that K_{IC} values are closely related to the stability of tetragonal grains in zirconia ceramics. Higher K_{Ic} value indicates that the tetragonal grains were in a metastable state and responded instantaneously to a propagating crack during the indentation test. In the present study, the highest K_{Ic} value was achieved at 1400 ºC for both microwave and conventional-sintered samples, thus indicating that besides the stability nature of the tetragonal structure, the grain size may also have played a role in governing the toughness of the zirconia. Further work would be required to elucidate this phenomenon.

4.8 Low Temperature Degradation (LTD) or Ageing

Samples sintered via microwave and conventional sintering were exposed to ageing environment in order to evaluate their degradation properties. Ageing experiment was conducted using autoclave consisting of superheated steam at 180 ºC and 10 bar pressure. Visual inspection and phase analysis were conducted after 1, 3, 9, 24, 48, 100 and 200 hours of ageing to evaluate the extent of phase transformation that has occurred. The results reveal that both microwave and conventionally sintered samples sintered at 1400 ºC were not aged after 200 hours of ageing. No further ageing was conducted since 200 hours of ageing in autoclave is equivalent to approximately 1000 years of ageing. It can be concluded that samples sintered at 1400 ºC with 5 minutes holding time are prone to ageing regardless the sintering method. The results might be linked with the grain size for both samples which is very fine and quite similar.

For samples sintered at 1500 ºC, phase transformation started after 1 hour of exposure for conventionally sintered zirconia while for sample sintered via microwave, phase transformation started after 9 hours of exposure to ageing environment. Results show that microwave sintering might delay the degradation process. The monoclinic content after 48 hours of ageing is less than 1% before it spike to 31% after 100 hours of exposure. However, further studies are needed to understand the mechanism behind the delay in phase transformation process via microwave sintering. The monoclinic content (V_m %) for microwave and conventionally sintered zirconia after certain ageing intervals is tabulated in Table 4.3.

Table 4.3: monoclinic content at different time intervals

Ageing time (hour)	Monoclinic content (%)	
	Microwave	Conventional
1	0	0.23
3	0	0.80
9	0.15	2.76
24	0.26	4.32
48	0.97	5.77
100	31.43	24.65

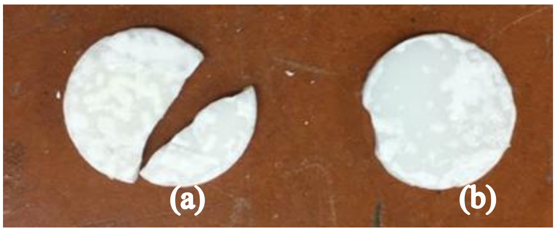


Figure 4.7: Physical inspection for (a) microwave and (b) conventional samples sintered at 1500 ºC after 100 hours of ageing.

From the physical inspection, both microwave and conventionally sintered zirconia failed after 100 hours of exposure to ageing environment. White spots are the transformed regions which are the results of phase transformation during ageing. The amount of white spots visible on the sample is in agreement with the monoclinic content determined via XRD analysis using relationship established by Toraya, Yoshimura, and Somiya (1984). Phase analysis using XRD revealed that sample sintered via microwave has better ageing resistance for the first 48 hours where the monoclinic content recorded was less than 1%. However, after 100 hours of exposure microwave sintered sample shows higher monoclinic content compared to sample sintered via conventional method. This result might be linked to the effect of grain size at prolonged ageing where microwave sintered sample sintered at 1500 ºC possessed larger grain size compared to sample sintered conventionally at the same sintering temperature. The result is in agreement with the results reported by previous researchers where ageing is strongly influenced by the grain size. Lange et al. (1986) proposed a thermodynamic approach to explain the effect of grain size on stability of tetragonal zirconia. Total energy change per unit volume (ΔG_{t-m}) that is required by zirconia grains for *t-m* phase transformation can be expressed as:

$$\Delta G_{t-m} = \Delta G_{CH} + \Delta G_{CE} + \Delta G_S$$

(4.1)

Where;

ΔG_{CH} is change of chemical free energy

ΔG_{CE} is the change of strain energy

ΔG_S is the change of surface energy

It was reported that smaller grain would increase the change is surface energy,ΔG_S, thus increase ΔG_{t-m} which is the total energy needed for phase transformation to take place. In other words, more energy is needed for phase transformation to take place for ceramics with smaller grain size. This explain why conventionally sintered sample at 1500 ºC has higher susceptibility to ageing compared to microwave sintered sample which has larger grain size. Results obtained also suggested that small difference in grain size (~18 nm) might give huge impact on degradation properties of zirconia. Nevertheless, further work is needed to be carried out to study the abnormal behaviour in ageing of microwave sintered ceramics and how it effectively controls ageing for the first 48 hours of exposure.

Visual inspection of the aged samples shows that the sample is made up of two regions; white spots and general regions. FESEM imaging was conducted to see the microstructure of the aged samples. Results show that ageing will cause surface roughening especially at white spots areas. Figure 4.8 (a), (b) and (c) show microstructures at white spots areas of microwave sintered sample that failed after 100 hours of exposure to ageing environment. From the images, it can be seen that the microstructure at white spot region is very rough with combination of two types of surfaces, around and inside craters. Crater is created when a part of the surface is pulled off. Around craters, the microstructure is made up of uneven surface which is a like a layer that coated sharp edges grains that lies underneath the layer. On the other hand, grains possessing sharp edges can be seen inside the craters.

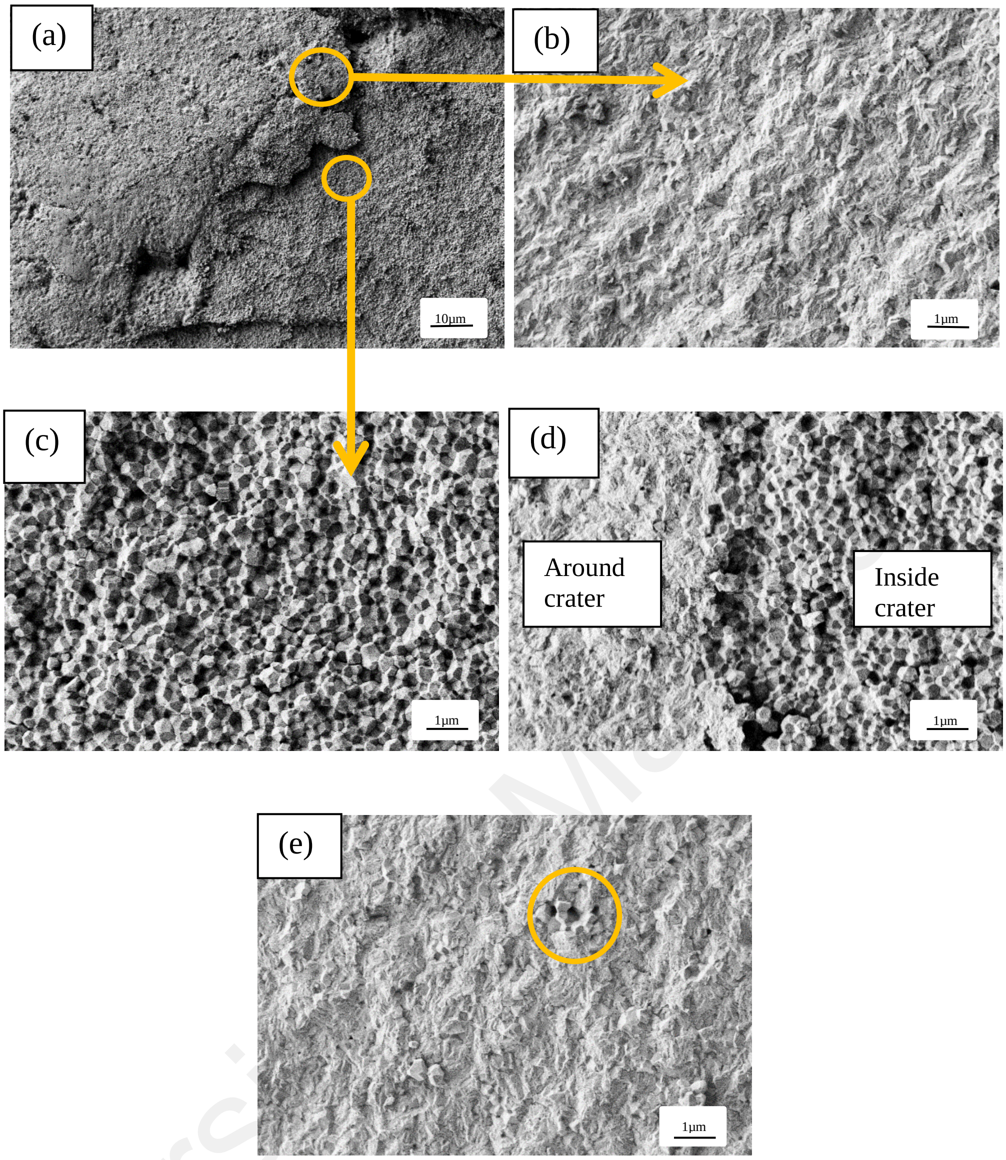


Figure 4.8: microstructures at white spots region of microwave-sintered sample after 100 hours ageing

(a) Overview of the surface at the white spot area of microwave sample sintered at 1500 ºC after 100 hours of ageing

(b) Microstructure of white spot around crater

(c) Microstructure inside crater (surface pull off create crater)

(d) Two types of microstructure at white spot regions

(e) Circle shows grains with sharp edges underneath layer-like structure.

The microstructure at general region is also rough, but smoother compared to microstructure at the white spots. Aside from that, the grain shape is rounder compared to the grains at white spot regions. Nevertheless, rough microstructure accompanied with formation of microcracks can also be seen in this region which indicates that this region has also undergone degradation process.

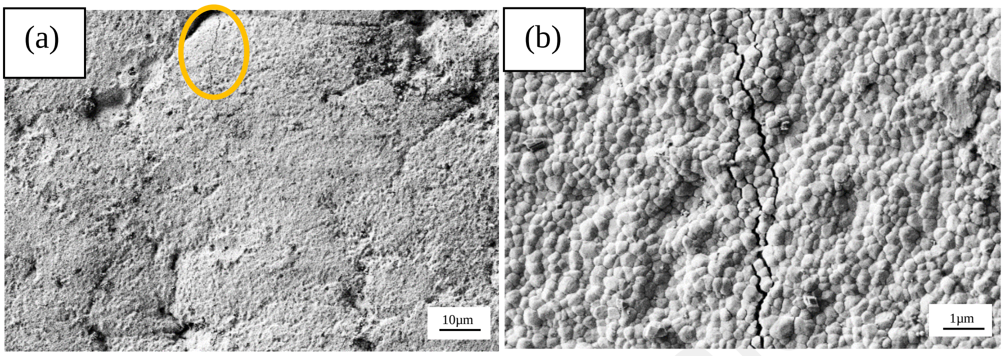


Figure 4.9: (a) overview of microstructure at general region. Circle shows the formation of microcracks on the surface (b) enlarged image for microcracks area.

Conventionally sintered sample also failed after 100 hours of ageing. Based on visual inspection, amount of white spot is less compared to microwave sintered sample. XRD analysis proved that the monoclinic content is also less showing that less phase transformation took place for this sample compared to sample sintered via microwave at the same sintering temperature (see Table 4.3). This indicates that conventionally sintered sample is more prone to degradation after 100 hours of ageing. As discussed earlier, this might be due to slightly smaller grain size possessed by conventionally sintered sample. FESEM imaging on the aged sample shows that white spots region is made up of grains with sharp edges.

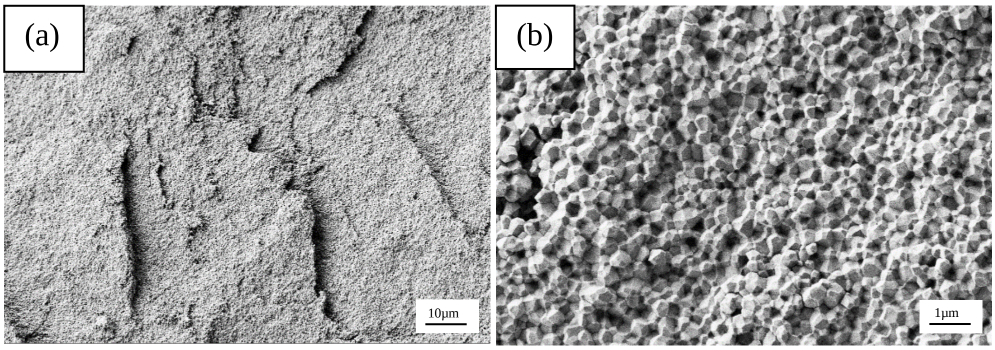


Figure 4.10: (a) overview of white spot of conventionally sintered zirconia after 100 hours of ageing (b) magnified microstructure of the region.

In contrast, the microstructure at general region is rough with combination of large and small grains. The large grain might be cubic grains, however, further analysis needed to be done for confirmation.

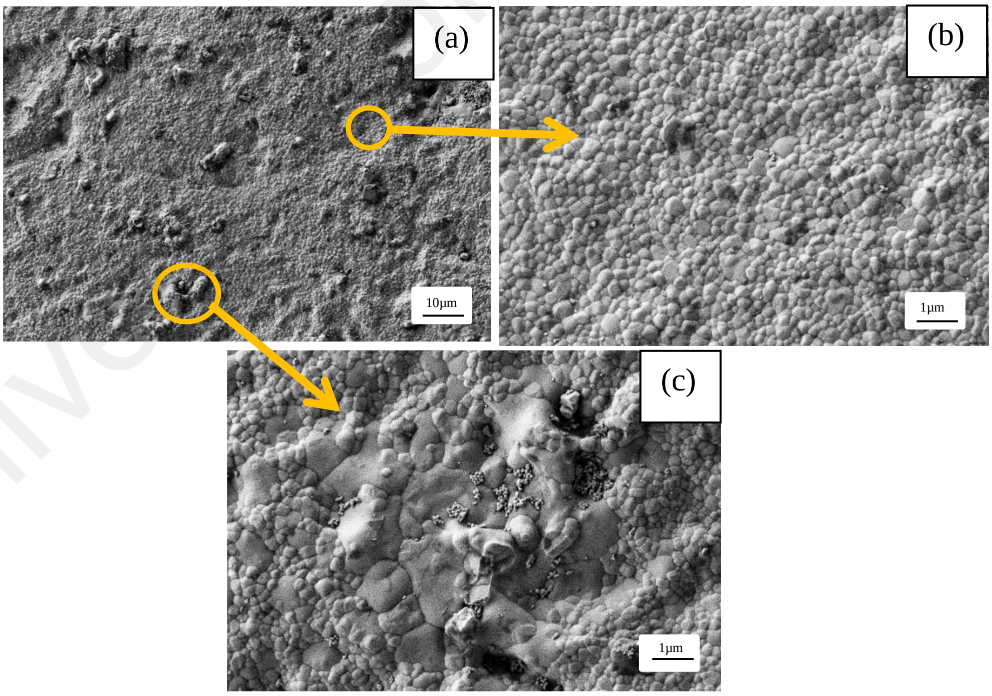


Figure 4.11: (a) overview of general region for conventionally sintered sample after 100 hour of ageing (b) magnified image at smooth region possessing small grains (c) magnified image at rough surface made up of large grains.

CHAPTER 5: CONCLUSIONS AND FUTURE WORKS

5.1 Conclusions

1. Microwave is advantageous in enhancing densification process of zirconia ceramics. Significant difference in microstructure development can be seen at 1200 ºC where complete grain growth was observed for microwave sintered sample while for conventionally sintered sample; there is no distinct grain boundary which indicates that sintering process was not completed using conventional sintering method at low sintering temperature.
2. Microwave sintering successfully reduced the sintering temperature. 99% of theoretical density can be achieved at 1300 ºC when using microwave sintering while conventional sintering needed higher temperature (1500 ºC) to attain the same density.
3. Since higher ramping rate is possible when using microwave sintering, the processing time has been reduced. For example, 239 minutes is needed to sinter the sample to 1200 ºC when using conventional sintering. In contrary, microwave sintering only needed 115 minutes to be sintered to the same temperature.
4. Mechanical properties were also improved via microwave sintering especially at low sintering temperatures.
5. However, as the sintering temperature is increased beyond 1400 ºC, mechanical properties and grain size are comparable for both microwave and conventional sintering. Results suggest that as the densification mechanism is activated, properties are strongly influenced by sintering temperature, not the sintering mode.
6. Interaction of microwave energy at atomic level might give effect on how zirconia reacts to the transformation process during ageing. However, further

study is needed to understand the exact interaction mechanism and how microwave sintering effectively controls the ageing resistance for the first 48 hours of ageing.

5.2 Future work

Some of the suggestions for future works are:

i. Conducting further studies on the effect of grain size in governing the toughness of zirconia.

ii. It would be interesting to study the effect of microwave processing of zirconia doped with alumina and manganese. From previous researches using conventional sintering, zirconia doped with alumina and manganese was reported to enhance the mechanical properties of zirconia.

iii. Further studies are required to elucidate abnormal degradation behavior of microwave-sintered zirconia. This study suggested that microwave sintering would delay the degradation process. Aside from that, this study also suggested that small difference in grain size would give huge impact on degradation properties of zirconia. Further work is needed to confirm this hypothesis.

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LIST OF PUBLICATION

1. Comparison between microwave and conventional sintering on the properties and microstructural evolution of tetragonal zirconia. *Ceramics International*, In press (2018). https://doi.org/10.1016/j.ceramint.2018.02.086