Comparative Sintering of Zirconia and Hydroxyapatite-Zirconia Composites

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This thesis is submitted in completion of the academic requirements of the degree of Doctor of Philosophy.
Declaration

This thesis is presented in fulfilment of the requirements for the degree of Doctor of Philosophy. It is entirely my own work and has not been submitted to any other university or higher education institution, or for any other academic award in this university. Where use has been made of the work of other people it has been fully acknowledged and fully referenced.

___________________________________________________

Colin Reidy.
Abstract

Hydroxyapatite [Ca_{10}(PO_{4})_{6}OH_{2}, HA] is the major constituent of the mineral phase of bone and exhibits desirable properties as a bone graft, such as biocompatibility, bioactivity, osteoconductivity and direct bonding to bone tissue. However, due to its limited mechanical properties, in particular low fracture toughness (K_{IC}) and tensile strength, HA is limited to non-load bearing applications and metal implant surface coatings. Zirconia (ZrO_{2}) based materials exhibit high fracture toughness due to the stress induced martensitic transformation of tetragonal to monoclinic ZrO_{2}. In theory, a composite material composed of HA and a reinforcing ZrO_{2} phase, combining the inherent bioactivity of HA with reinforcement from the ZrO_{2} is an attractive proposition in terms of load bearing bone replacement. The work contained herein attempts to improve the mechanical properties of HA through the addition of a ZrO_{2} phase and consolidation through two comparative sintering techniques, microwave and conventional sintering.

The first objective was to investigate the effect of microwave sintering on physical, mechanical and chemical properties of Y_{2}O_{3} (2-5 mol%) doped ZrO_{2} compositions compared with conventional sintering. Y_{2}O_{3} content was altered through the attrition milling of commercial undoped monoclinic ZrO_{2} powders with co-precipitated Y_{2}O_{3}-doped ZrO_{2} powders and these were characterized using X-ray diffraction (XRD), particle size analysis (PSA), transmission electron microscopy (TEM) and BET. Comparative sintering was performed at temperatures of 1100, 1200 and 1300°C. Post sintering characterization included phase analysis (XRD), microstructural analysis using scanning electron microscopy (SEM), density measurements and mechanical testing, which included Young’s modulus, biaxial flexural testing and microhardness. Compositions containing 2 mol% Y_{2}O_{3}, microwave sintered at a temperature of 1300°C exhibited the greatest improvement, due to retention of tetragonal ZrO_{2}, with a 5% increase in relative density compared with conventional sintering. Grain size analysis indicated that there was significant grain growth in microwave sintered samples (to d = 353nm) compared to their conventionally sintered counterparts (d = 200nm). Associated with this was a 22% increase in Young’s modulus to 220GPa, a 77% increase in Vicker’s Hardness up to 11.5GPa and a 165% increase in biaxial flexural strength up to 800MPa. Based on these observations, a reinforcing ZrO_{2} phase containing 2 and 3 mol % Y_{2}O_{3} was decided upon for addition to HA.

The second objective was to investigate the effect of microwave sintering on HA-ZrO_{2} composites containing a commercial HA powder and HA synthesized using a co-precipitation technique and ZrO_{2} with the optimum Y_{2}O_{3} content for Y-TZP found in the initial stage. HA was precipitated synthesized at temperatures of 25 and 45°C and characterized using XRD, X-ray fluorescence (XRF), TEM and BET. Commercial HA composites containing 0, 5, 10, 20 & 40wt % ZrO_{2} additions and synthesized HA (S-HA) composites containing 0, 5 and 10 wt% ZrO_{2} were comparatively sintered. The post sintering characterization was similar to the previous step. In terms of phase stability it was found that the decomposition of HA to α and/or β-TCP increased with increasing amounts of ZrO_{2} irrespective of the HA powder used. This decomposition increased with increasing temperature and was found to increase in microwave sintered samples at 1300°C. It was also found that CaO released through the decomposition of HA reacted with the ZrO_{2} reinforcing phase to form either a c-ZrO_{2} solid solution and/or CaZrO_{2} above temperatures of 1100°C. Microwave sintering resulted in increased densification at lower temperatures of 1000 & 1100°C. It was observed, however, that there was a reduction in the relative densities of ZrO_{2} composites compared to unfilled HA as the sintering temperatures increased to 1200°C. It was suggested that H_{2}O formed through the decomposition of HA led to formation of pores and lower densities. The increase in porosity was observed to be detrimental to the mechanical properties of the HA-ZrO_{2} composites. The highest stiffness, biaxial flexural strengths and microhardness of 112 GPa, 164MPa and 5.7GPa were observed in unfilled HA conventionally sintered at a temperature of 1300°C with a corresponding relative density of 96.7%. Comparative values of 109GPa, 138MPa and 4.9GPa were achieved in microwave sintered samples sintered at 1200°C. Subsequent increases in ZrO_{2} reduced the mechanical properties. The addition of 2.5 wt % CaF_{2} to microwave sintered synthesized HA-ZrO_{2} composites resulted in a significant increase in the relative density. The substitution of F for OH resulted in the partial formation of Fluoro-HA, increasing the thermal stability, limiting the formation of H_{2}O and thus increasing density. While the addition of CaF_{2} increased the density of composites, CaO formed in this case from the substitution of F for OH reacts with t-ZrO_{2} again forming CaZrO_{2} and/or c-ZrO_{2}. The increased density led to an increase in the Young’s modulus and the hardness. However, the biaxial flexural strengths of composites were not increased. While there was an increase in mechanical properties compared to HA-ZrO_{2} composites without CaF_{2}, the Young’s modulus and the hardness only exhibited values comparable to unfilled HA. The strengths were inferior to unfilled HA.

The biocompatibilities of HA-ZrO_{2} composites were determined using In vivo & In vitro evaluation. In vitro evaluation indicated that the materials induced a favourable response in rat osteosarcoma cells. In vivo evaluation indicated that the material was osteoconductive and biocompatible in the rat tibia model.
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“Perspective Pries upon once weighty eyes and it gives you wings”
Incubus
Nice to Know You
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1. Introduction

There is an ongoing search for appropriate implant materials to replace parts of the skeleton damaged as a result of accident, disease or defect. The intense research undertaken worldwide in more recent times has developed various advanced materials including ceramics, glass-ceramics and glasses, which can be manufactured into the required shapes and act as replacement parts in the human body with a variety of functionalities.

In the USA alone, approximately 6 million fractures occur per year, of which about 550,000 require some amount of bone grafting (Murugan and Ramakrishna 2005b). The turnover of the bone graft substitutes markets amounts to over 1 billion dollars a year with a yearly market growth of close to 10% (Bohner 2010).

The replacement of bone can be facilitated by traditional methods of autograft and allograft or through the use of a synthetic material. Autografts are the transplantation of bone tissue from one location on the body (typically the iliac crest) to another, in the same individual. Consequently, there is no immune response, excellent incorporation of tissue and low risk of transmitting disease. However there is a limited amount of tissue and the added complication of second site surgery to retrieve the donor tissue. Allografts are the transplantation of bone tissue from one individual to another. This method removes the need for the second site surgery and supplies a greater quantity of donor material. The disadvantages of this technique are the risks of rejection and the transmission of disease. The use of synthetic materials as replacement alternatives has gained significant attention due to increased availability, sterility and cost effectiveness and synthetic replacements now account for approximately 15% of all bone replacements (Murugan and Ramakrishna 2005b).

Calcium phosphate based ceramics, in particular hydroxyapatite [Ca_{10}(PO_4)_6(OH)_2, HA], have generated a significant amount of attention as replacements for hard tissue due to their similarity to the native mineral composition of bone. HA exhibits good properties as a bone graft, such as biocompatibility, bioactivity, osteoconductivity and direct bonding to bone tissue (Vallet-Regi and Gonzalez-Calbet 2004). However, HA is generally limited to non-load bearing applications and metal implant surface coatings
due to its limited mechanical properties, in particular low fracture toughness and tensile strength (Hench 1991). There have been numerous attempts to introduce a reinforcing phase into a HA/ceramic composite, the idea being to increase the mechanical properties of the HA while maintaining its bioactivity, thereby increasing the functionality to include load bearing applications (Li et al. 1995, Ramires et al. 2001, Rapacz-Kmita et al. 2006). Zirconia is of interest as a reinforcing phase due to its high mechanical properties.

Zirconia (ZrO$_2$) based materials exhibit high fracture toughness due to the stress induced martensitic transformation of tetragonal to monoclinic zirconia (Garvie et al. 1975, Evans and Heuer 1980, Hannink et al. 2000), generally known as transformation toughening. Yttria doped tetragonal zirconia polycrystals (Y-TZP) tend to be the most widely used zirconia ceramic for biomedical applications due to the retention of the “metastable” tetragonal phase, thus maximising the toughening mechanism. Studies on the formation of HA-ZrO$_2$ composites have generally found that creating composites is complicated by two main factors: (1) the addition of ZrO$_2$ can prevent the full densification of HA, and (2) at elevated temperatures the addition of large amounts of ZrO$_2$ can result in the decomposition of HA to tricalcium phosphate (TCP) and/or tetracalcium phosphate (TTCP) (Hae-Won et al. 2002, Ramachandra Rao and Kannan 2002, Heimann and Vu 1997). A proposed solution for this is to employ a different sintering regime to reduce the effective sintering temperature which can be achieved through microwave sintering.

Microwave sintering is fundamentally different from conventional sintering techniques as microwave energy is delivered directly to the material through molecular interaction with an electromagnetic field (Thostenson and Chou 1999), as opposed to heat being transferred from the surface to the bulk of the material. Considering both ZrO$_2$ and HA, microwave sintering has been shown to reduce both the sintering temperature and time needed to produce dense (>99% theoretical density) ceramics. In the case of HA-ZrO$_2$ composites it should be possible to microwave sinter a dense body, while maintaining a predominately HA phase and this is the basis for the current investigation.
There are two main objectives of the work contained herein. The first objective is to investigate the effect of microwave sintering on physical, mechanical and chemical properties of Y$_2$O$_3$ (2-5 mol%) doped ZrO$_2$ compositions compared with conventional sintering. The second objective is to investigate the effect of microwave sintering on HA-ZrO$_2$ composites using HA prepared in the laboratory and zirconia with the optimum Y$_2$O$_3$ content for Y-TZP found in stage 1. Again the mechanical, chemical and physical properties of the microwave and conventionally sintered composites are compared. Once an optimum HA-ZrO$_2$ composite composition was determined, microwave sintered samples were prepared for both in vivo and in vitro examination. In vivo evaluation of the composite was undertaken by implanting granules into rat femurs for four weeks. In vitro performance was evaluated using rat osteosarcoma cells cultivated with the materials for 48/72 hours. Cell viability and proliferation were determined by Alamar blue/DNA assays and SEM.

Following this introduction, Chapter 2 examines the relevant literature for this study. Chapter 3 discusses the materials & methods used in this study. Chapter 4 outlines the study of conventional and microwave sintering of yttria doped ZrO$_2$, while chapter 5 presents the investigation of conventional and microwave sintering of HA-ZrO$_2$ composites. In Chapter 6 the biological response to the HA-ZrO$_2$ composites is discussed. Chapter 7 presents conclusions of the overall study and recommendations for future work.
Chapter 2 Literature Review

Over the past four decades there has been significant advancement in the use of synthetic materials to replace diseased and damaged bone. Synthetic grafting is used in several different therapies including orthopaedic, cosmetic, oral, maxillofacial, and dental surgeries. Ceramics, in particular, have been used in a large number of applications pertaining to the replacement of bone. In bone graft applications the use of bioceramics tends to fall into two main categories: (1) bioinert ceramics and (2) bioactive ceramics. Bioinert oxide ceramics, including zirconia and alumina, illicit a limited host response within the body and typical applications include load bearing surfaces in hip prostheses while bioactive ceramics initiate a positive host tissue response and are used extensively as bone void fillers.

2.1 Bone

Bone is a living material composed of cells and blood supply incased in a strong interwoven composite structure. It is a complex, self sustaining organ and besides the obvious physical support supplied by the skeleton, bone also provides several important functions within the human body in terms of mechanical, synthetic and metabolic functions (Martini 2006). Bone exhibits a hierarchical structure from the nanoscale up to the macroscale that has a basic building block which composed of a mineralised collagen fiber matrix (Figure 2.1).

![Hierarchical structure of Bone](image)

**Figure 2.1.** Hierarchical structure of Bone (Rho et al. 1998).

2.1.1 Bone Matrix

The matrix composition of bone consists of 50-70% of an inorganic mineral phase, 20-40% of an organic phase and 5-10% of water. The average composition can vary depending on the age, anatomical location and health of the individual (Shea and Miller
Chapter 2 Literature Review

The inorganic phase contains approximately 85% hydroxyapatite (HA), 10% calcium carbonate and small amounts of magnesium, sodium, potassium, fluoride, carbonate and hydroxyl ions (Saladin 2001). Type I collagen accounts for the majority of the organic content. Cells account for approximately only 2% of the mass of a typical bone (Martini 2006). The HA in bone consists of very small plate like crystals with average lengths and widths of 50 x 20 nm and a thickness of 2-3 nm (Landis 1995, Ziv and Weiner 1994) and it imparts rigidity on bone. The HA crystals form small plates that are locked into the collagen fibers. This results in a collagen/HA composite with mechanical properties intermediate between both components.

2.1.2 Microstructure

The microstructure of both compact and cancellous bone consists of lamellae of mineralised collagen fibres stacked in either parallel or concentrically arranged layers. The thickness of individual lamellae ranges from 3-7μm wide and the orientation of the fibers in alternate lamellae differ, resulting in a plywood type structure (Weiner and Traub 1992). Approximately 80-85% of the total bone mass is cortical bone, while the remainder is trabecular (Shea and Miller 2005).

In compact bone, the lamellae are organised in concentric layers around a central canal to form what is known as an osteon or a haversion system (Saladin 2001). Each osteon is an elongated cylinder (approximately 200-250μm in diameter) which runs roughly parallel to the length of the diaphysis (Rho et al. 1998). The centre of each osteon houses the haversian canal which contains the blood supply, nerves and loose connective tissue. Osteocytes (mature bone cells) are nested between the lamellae in pockets called lacunae.
Cancellous bone consists of an interconnecting framework of plates known as trabeculae with the spaces filled by bone marrow (Shea and Miller 2005). Each trabeculae contains collagen fibres arranged in parallel lamellae. The trabeculae are oriented along stress lines and are extensively cross braced (Martini 2006). This type of structure, in addition to providing a large surface area for metabolic activities of bone, gives mechanical strength without increasing the weight.

2.1.3 Mechanical Properties of Bone

In general, bone, similar to all biological composites, is considered to be anisotropic i.e., its mechanical properties are dependent on the direction of loading (Turner et al. 1995). Bone is also a viscoelastic material (exhibiting time dependant strain). As bone is a composite material, the mechanical properties are dependent on the structural, as well as the material properties (Felsenberg and Boonen 2005). The structural properties of bone include its geometry (size and shape) as well as its microstructure (trabecular and cortical structure) (Follet et al. 2004, Cheng et al. 1997). Material properties of bone include the mineral and collagen content and orientation of the bone matrix as well as the localisation of micro-damage. The turnover (remodeling) rate will also have an effect on the mechanical properties. Table 2.1 indicates some of the mechanical properties of bone obtained from the literature. The anisotropy of cortical bone is visible in both the Young’s modules and tensile strength.
Table 2.1. Various mechanical properties of bone as reported in literature.

<table>
<thead>
<tr>
<th>Property</th>
<th>Bone Type</th>
<th>Load Direction</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>Cortical</td>
<td>Longitudinal</td>
<td>20-22</td>
</tr>
<tr>
<td></td>
<td>Cortical</td>
<td>Transverse</td>
<td>12-14</td>
</tr>
<tr>
<td></td>
<td>Trabecular</td>
<td></td>
<td>1-18</td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>Cortical</td>
<td></td>
<td>170-193</td>
</tr>
<tr>
<td></td>
<td>Trabecular</td>
<td></td>
<td>4-12</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>Cortical</td>
<td>Longitudinal</td>
<td>50-150</td>
</tr>
<tr>
<td></td>
<td>Cortical</td>
<td>Transverse</td>
<td>51</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
<td>Femur</td>
<td></td>
<td>190-209</td>
</tr>
<tr>
<td>Fracture Toughness (MPam(^{1/2}))</td>
<td>Cortical</td>
<td></td>
<td>2-8</td>
</tr>
</tbody>
</table>


2.2 Bioceramics

Ceramic materials can be defined as compounds consisting of metallic and non-metallic elements for which the interatomic bonding is predominantly ionic (Callister 2002). Ceramics used specifically for the repair and reconstruction of diseased or damaged tissues are referred to as Bioceramics (Hench 1991). Ceramic materials used in clinical applications include polycrystalline materials, glasses, glass-ceramics and ceramic filled bioactive composites, which can be manufactured either in porous or dense form, as granules or as coatings (Best et al. 2008). Applications within the body generally concern the replacement of hard tissue and include replacements for hips, knees, teeth, maxillofacial reconstruction, augmentation and stabilisation of the jaw bone, spinal fusion, and bone void fillers after tumour surgery (Hench 1991).

In order for a ceramic to be classified as a bioceramic the material must adhere to or exceed a specific number of desired properties of implantable materials (Billotte 2007). The bioceramic must be:
- Non-toxic
- Non-carcinogenic
- Non-allergic
- Non-inflammatory
- Biocompatible
- Biofunctional for its lifetime in the host.

While ceramics are suitable as implantable materials, the inherent brittle nature of ceramics can limit their scope in terms of biomedical applications. Two major characteristics of the brittle nature of ceramics are: (1) the fracture strength is far below the theoretical value and (2) it is more difficult to precisely predict failure strength in ceramics than in metals or polymers (Park 2008).

### 2.2.1 Classifications of Bioceramics for Hard Tissue Replacement

No material implanted in living tissue is inert; all materials elicit a response from the host tissue and as such bioceramics can be classified according to this response. In terms of material-host interactions, bioceramic implants are defined as being either bioinert (nearly inert), bioactive/surface reactive or bioresorbable (Billotte 2007). Figure 2.3 illustrates various types of bioceramic implants.

![Classification of bioceramics](image)

**Figure 2.3.** Classification of bioceramics according to their bioactivity; (a) bioinert, (alumina dental implant), (b) bioactive, hydroxyapatite (Ca_{10}(PO_{4})_{6}(OH)_{2}) coating on a metallic dental implant, (c) surface active, bioglass (d) bioresorbable tri-calcium phosphate implant [Ca_{3}(PO_{4})_{2}].

#### 2.2.1.1 Bioinert (nearly) inert

Bioinert materials do not elicit a negative response or release any toxic constituents but neither do they generate any positive interaction with living tissue. The host response to a bioinert ceramic is generally to form a non-adherent capsule of fibrous
connective tissue around the implant (Heimann 2002). The fixation of the implant into the body is made through a strong mechanical interlock, by tissue in-growth into undulating surfaces (Hayashi et al. 1992), by cementing the implant into the tissue or by press fitting into a defect (Hench 1998). Types of bioinert ceramics include Alumina ($\text{Al}_2\text{O}_3$) and Zirconia ($\text{ZrO}_2$).

### 2.2.1.2 Bioresorbable

Resorbable materials, (Table 2.1 type IV), are designed to degrade gradually over time, to be replaced with native host tissue (Hench 1991). Most resorbable bioceramics are based on calcium phosphates (De Aza et al. 2006). The two main limitations of resorbable bioceramics are (1) maintaining the strength of a resorbable bioceramic during the degradation and replacement with native tissue and (2) matching the resorption rate to the repair rate of the tissue (Hench 1998).

### 2.2.1.3 Bioactive (surface reactive)

Bioactive implants (Table 2.1 type III) are an intermediate between bioinert and bioresorbable implants. Bioactive materials are materials that elicit a specific biological response at the interface of the material which results in the formation of a bond between the tissues and the material and was first shown by (Hench et al. 1971). Types of bioactive ceramics include hydroxyapatite and bioactive glasses such as Bioglass®. With the exception of HA, which bonds directly to bone, bioactive materials bond to bone through a biologically active carbonate HA layer (CHA) (De Aza et al. 2006) (LeGeros and LeGeros 1993). In contrast to bioresorbable ceramics, the chemical reaction occurs only at the surface interface, leaving the rest of the implant stable (Hench and Wilson 1993).
Table 2.2. Classes of Bioceramics: Tissue Attachment and Classification (Hench 1998).

<table>
<thead>
<tr>
<th>Type</th>
<th>Type of Attachment</th>
<th>Example of Bioceramic</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Dense, nonporous, almost inert ceramics attach by bone growth into surface irregularities by cementing the device into the tissue, or by press fitting into a defect (morphological fixation)</td>
<td>Alumina Al₂O₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Zirconia ZrO₂</td>
</tr>
<tr>
<td>II</td>
<td>For porous implants, bone ingrowth occurs, which mechanically attaches the bone to the material (biological fixation)</td>
<td>Porous Hydroxyapatite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydroxyapatite coated metals</td>
</tr>
<tr>
<td>III</td>
<td>Surface-reactive ceramics, glasses and glass-ceramics attach directly by chemical bonding with the bone (bioactive fixation)</td>
<td>Bioactive glasses</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dense Hydroxyapatite</td>
</tr>
<tr>
<td>IV</td>
<td>Resorbable ceramics and glasses in bulk or powder form designed to be slowly replaced be bone</td>
<td>Calcium Sulfate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tricalcium phosphate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calcium phosphate salts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bioactive glasses</td>
</tr>
</tbody>
</table>

2.2.2 Mechanical Properties of Ceramics

Ceramics, both crystalline and non-crystalline, exhibit a brittle nature at room temperature and tend to fracture before any plastic deformation can occur.

2.2.2.1 Young’s Modulus (E)

The Young’s modulus or modulus of elasticity is a measure of the stiffness of a material. Brittle materials generally obey Hooke’s law:

\[ \sigma = E\varepsilon \] (2.1)

Where \( \sigma \) is the stress, force per unit area (F/A), \( \varepsilon \) is the strain which is the change in length divided by the original length and \( E \) is the modulus of elasticity. For an idealized bone graft material the stiffness of the material should be similar to that of the native bone (~20GPa). A mismatch between the implant and the bone (where \( E \) for the implant is much greater than \( E \) for the bone) can lead to “stress shielding” where the load on the transplant is not transmitted to the bone leading to a loss of cortical bone near the implant site (Heimann 2002). Moreover, the resultant stress gradient may cause fracture along the bone implant interface.
2.2.2.2 Fracture Toughness ($K_{IC}$)

The fracture of brittle materials tends to occur at much lower stresses than predicted by interatomic bonding forces. Griffith (1921) observed that this occurs because flaws within ceramic materials act as stress concentrators so that the stress located at a crack tip is much greater than the nominal stress on the specimen, resulting in failure of the material at applied stresses well below the calculated theoretical value. Irwin (1968) examined the crack propagation procedure from a critical stress intensity point of view and concluded that the criteria of crack propagation, the stress field intensity ($K$) of a crack tip should be larger than a critical stress intensity level ($K_c$) at which a given flaw starts to propagate. The strength of a brittle material ($\sigma_a$) is related to the critical stress intensity factor at a crack tip and can be calculated using the following equation:

$$K = Y\sigma_a\sqrt{c}$$

Where $c$ is the radius of the crack and $Y$ is a geometrical factor. The $I$ subscript for $K_{IC}$ denotes that this critical value for $K$ is for mode I crack displacement. An applied stress can operate on a material by one of three modes: Mode I - a tensile or opening mode, Mode II - a sliding mode, Mode III - a tearing mode. As brittle materials, such as ceramics, have very little ductility the value for $K_{IC}$ is generally low. The $K_{IC}$ value is a fundamental property that has one unique value for a particular material and it depends on many factors, with the most influential being the temperature, strain rate, and the microstructure (Callister 2007).

![Figure 2.4](image)

**Figure 2.4.** The different failure modes; (A) mode I tensile force, (B) mode II shear force and (C) mode III torsion force (Soderholm)

2.2.2.3 Porosity

Porosity has a significant influence on the mechanical properties of a ceramic as its presence tends to intensify stresses applied to the material (Park 2008). Porosity is deleterious to the flexural strength of a material for two reasons: (1) pores reduce the cross-sectional area of the material across which a load is applied and (2) pores act as stress raisers (i.e. for an isolated spherical pore, an applied tensile stress is amplified by
a factor of x2) (Callister 2002). The influence of porosity on the flexural strength of a ceramic is quite dramatic; increases in porosity of 10% can reduce mechanical properties by over 50% as can be seen for the hardness of HA in Figure 2.5. In the context of mechanical properties, the dependence of Young’s modulus, strength and hardness on porosity is generally well described by the following empirical exponential relationship (Rice 1998);

$$A = A_0 \exp(-b_A P)$$

(2.3)

where $A_0$ is the value of the property at zero porosity and $b_A$ is a measure of the rate of decrease in $A$ with increasing $P$. This equation tends to hold for low to intermediate values, ranging from zero porosity (theoretically fully dense ceramics) to a volume fraction porosity of roughly between 0.3 and 0.4 (Rice 2000b).

![Figure 2.5. The effect of volume fraction porosity on the hardness of hydroxyapatite. Squares represent samples uniaxially pressed and conventionally sintered. Circles represent samples cold isostatically pressed (CIP) and conventionally sintered. Triangles indicate samples Microwave sintered. The curve is the least-squares fit to the data ($H = H_0 \exp(-b_H P)$) (Hoepfner and Case 2003).](image)

### 2.2.3 Sintering

Ceramics are usually processed from an initial powder by forming a compact and then sintering at relatively high temperatures. Sintering is a thermal treatment for bonding particles into a coherent, predominantly solid structure via mass transport events that often occur on the atomic scale. This bonding leads to improved strength and lower system energy (German 1996). The driving force for all sintering systems is a reduction in surface free energy of the system consisting of a mass of consolidated particles (Rahaman 1995). This is accomplished by atomic diffusion mechanisms that
lead to either densification (reduction of the pore size) of the body or coarsening of the body (reorganization of the microstructure).

Prior to sintering, a green body or compact powder is formed which is composed of individual grains separated by between 25 to 60 volume percent porosity (Kingery et al. 1976). This is then fired at a temperature usually in excess of 0.5T_m, where T_m is the melting temperature. During the firing process, changes in grain size and shape as well as pore size and shape occur and bonding initiates between adjacent particles to form “grain boundaries”. Very high relative density and small grains of uniform size are desirable properties when trying to obtain a material with good mechanical properties. There are two main types of sintering that can occur: solid state sintering and liquid phase sintering.

### 2.2.3.1 Solid state sintering

Solid state sintering is the densification of a powder compact at a temperature below the melting temperature of any of the constituent phases present (Richerson 1982). The driving force is the difference in free energy between free surfaces of the particles and the points of contact. Material transport occurs by diffusion, which consists of the movement of atoms or vacancies along a surface, a grain boundary or through the bulk of a material to the interparticle neck region. There are six possible mechanisms of matter transport in polycrystalline materials during solid state sintering. All of these mechanisms lead to growth of necks between the particles which produce bonding between the particles. The six mechanisms are:

1. **Surface diffusion**: Material transport along the surface fills the neck region at an early stage.
2. **Lattice diffusion**: This is the movement of vacancies through the lattice of a material and results in the movement of material from a surface source to the neck region.
3. **Vapour transport**: Material is moved from the neighbourhood of a neck region via evaporation and deposited into the neck region by condensation.
4. **Boundary diffusion**: The defective nature of grain boundaries allows material transport along the boundary, driven by the high disorientation of atoms along the grain boundary.
5. *Lattice diffusion (grain boundaries):* Material is transported from the lattice along the grain boundary to the surface.

6. *Lattice diffusion (bulk):* Dislocations act as sources for vacancies which diffuse to the grain boundaries.

The first three mechanisms result in matter transport from the surface to the neck and do not result in shrinkage of the compact or reduction in porosity (densification). These mechanisms only cause a change of shape of the pores as material is being transported from one surface region to another. The last three mechanisms, on the other hand, result in transfer of matter from the particle volume or from the grain boundary between the particles which leads to shrinkage and pore elimination (densification). The level of coarsening and densification occurring during sintering will greatly affect the porosity of the ceramic. If coarsening is the predominant diffusion process the finished sample will have a highly porous microstructure. If densification dominates, the result is a highly dense body.

![Diagram of sintering mechanisms](image)

**Figure 2.6.** The six mechanisms of sintering. Non-densifying mechanisms: path 1, surface diffusion; path 2, bulk diffusion; and path 3, evaporation. Densifying mechanisms: path 4, grain boundary diffusion; path 5, bulk diffusion, grain boundaries as sources; and path 6, bulk diffusion, dislocations as sources (Föhl and Carstanjen 2002).

### 2.2.3.2 Stages of sintering

Although sintering is a continuous process, the microstructure of the consolidated powder alters considerably throughout the sintering process. Consequently it is convenient to consider sintering in several different stages depending on its microstructure at the time. Sintering is generally considered to occur in three stages, (i) the initial stage, (ii) the intermediate stage and (iii) the final stage (Rahaman 1995).
i. Initial stage: This is characterized by the initial bond between adjacent particles and consists of relatively rapid interparticle neck growth by diffusion, vapour transport, plastic flow, or viscous flow. The neck growth is small enough such that neighbouring necks grow independently of one another. The initial stage generally involves little grain growth.

ii. Intermediate stage: The intermediate stage is initiated when the grain necks begin to merge and the attention shifts to the interconnected pore structure surrounding the necks. This stage has significant effect on density with changes of relative density from 56% to 90%. Densification occurs as the pores shrink to reduce their cross section with the movement of vacancies away from the pore. This is associated with the movement of atoms into the pore, thus reducing the pore size. Eventually these pores become unstable and begin to pinch off, signifying the end of this stage.

iii. Final stage: This stage occurs when pores become isolated and grain boundaries form a continuous network. The energy for grain growth is provided by grain boundaries which are more numerous due to the reduction in the porosity during the previous stage (Warren and Lundberg 1992). This reduction of pores can increase the mobility of the grain boundaries, or at least leave the mobility unaffected (Barsoum 2003). If the mobility increases due to a reduction of pores in the material, then the rate of grain growth accelerates. One of the major problems with grain growth is that the grain boundaries can break away from the pores leaving them isolated within the grains. This type of pore is very difficult to eliminate as volume diffusion is the dominant matter transfer mechanism which is very limited in areas without grain boundaries (Stojanović et al. 1999). Residual porosity can be eliminated at this stage with increased sintering time or temperature; however the high temperatures and prolonged sintering time during this stage can lead to grain growth and coarsening (Wakai et al. 2005).
2.2.3.3 Grain growth.

During sintering both grain growth and densification processes are active, both leading to a decrease in the surface energy. Grain growth is a process in which the average grain size of a single-phase polycrystalline material increases as a function of time, driven by the reduction in the total grain-boundary energy (Chen 1995). Generally, as sintering continues the grain size substantially increases.

In the final stages of sintering, grain growth will be affected by the remaining pores that pin the grain boundaries and reduce the kinetic rate of grain growth. At this stage, isolated spherical pores are situated at the grain boundaries, and in particular at triple junctions. Pores in this case can be considered to be a secondary phase exhibiting an inhibitory force against grain boundary movement. At the beginning of the final stage of sintering, the boundary is at first dragged by the pore and the rate of grain growth is slow. However, as the densification increases the size and number of pores decreases. At a specific level of densification the boundary can separate away from the pore and grain growth will accelerate dramatically (Fang and Wang 2008).

The final grain size of the sintered ceramic, along with residual porosity, also has a relationship with the mechanical properties. The fracture stress of nanocrystalline materials with a grain size above 10nm generally exhibits a Hall-Petch relationship given by the following equation;
\[ \sigma = \sigma_o + kd^{1/2} \] (2.4)

Where \( \sigma \) is the fracture stress, \( d \) is the average grain size, \( k \) and \( \sigma_o \) are material constants (Pande and Cooper 2009). However in terms of ceramics, differing relationships with grain size have been observed. Rice, Wu and Boichelt (1994) reviewed the relationship between hardness and grain size for a range of both dense oxide and non-oxide ceramics. It was indicated that there were generally conflicting trends with either; (1) hardness exhibiting no grain dependence, (2) hardness decreasing from single crystals with decreasing grain size or (3) the generally accepted decrease in hardness with increasing grain size. In the case of \( \text{ZrO}_2 \), little dependence of Vickers Hardness (\( H_v \)) on grain size was observed over grain sizes of between 0.5 and 50\( \mu \)m. \( \text{Al}_2\text{O}_3 \), on the other hand, exhibited approximately a 10 % reduction in \( H_v \) with a 10 fold increase in grain size.

2.2.3.4 Factors affecting sintering.

The particle size, morphology, size distribution, presence of agglomerates and green packing density all effect the densification of a ceramics (Lu 2008). As the particle size of a ceramic green powder approaches the nano scale the surface area increases dramatically. Associated with this surface area is a high surface energy, thereby increasing the driving force for sintering. Powders with 10nm particles tend to sinter \( 10^6 \) to \( 10^8 \) times faster than micron sized powders (Barringer et al. 1984). The onset temperature of sintering of nanoscale powders is significantly lower than that of the micron scale powders as indicated in the left shift in Figure 2.8 (Fang and Wang 2008). Studies of \( \text{Y}_2\text{O}_3 \) doped \( \text{ZrO}_2 \) have shown that the sintering of nanocrystalline powders initiates at temperature 200°C lower than that of microcrystalline powders (Lee et al. 1992, Hahn 1993, Skandan 1995).
One of the issues associated with the high surface energy of nano-sized particles is the propensity of such powders to agglomerate. Particle agglomeration is undesirable as it consumes surface energy that would otherwise be expended during densification and the large inter-agglomerate pores have to be removed in order to achieve full densification (Lu 2008). Similarly, the presence of hard agglomerates in starting powders can result in heterogeneous density throughout a green compact. This in turn results in differential densification during sintering and stable residual pores (Chaim et al. 2008). Consequently, it can be nanoparticle agglomeration size rather than the individual nanoparticle size of a powder that governs the densification of the compacts. There is also a correlation between grain size and initial powder agglomeration. Mayo (1996) related this to the fact that higher temperatures are needed to eliminate large inter-agglomerate pores and at these temperatures the grain size can easily grow to the agglomerate size.

The particle size distribution can also affect the densification. It has been theorised that wide particle size distribution can enhance particle coarsening due to inhomogeneous dihedral angles between the nanoparticles (Cannon and Carter 1989). This appears to agree with experimental evidence for alumina; with both fine and uniform particle size being found to prolong the intermediate stage of sintering, with sintering proceeding with negligible grain growth (Shiau et al. 1998). On the other hand, when nano-particle size distributions are narrow, particle packing efficiency is low due
to the high frictional force between nano-particles and it can be difficult to achieve high green density, that are generally desired for sintering densification (Lu 2008).

Dry pressing (such as uniaxial pressing) is the most common method of forming powder compacts. However most of these methods can result in heterogeneous density within the green compact due to frictional forces between the particles (Chaim et al. 2008). It is possible to improve the homogeneity of the green compact by using cold isostatic pressing (CIP) (Van De Graaf et al. 1985).

To obtain a nearly theoretical dense compact with a fine grain size it is vital that the properties of the green powder and the green powder compact are optimised. The desired properties of the powder include nano-sized particles with narrow size distribution, free of hard agglomerates. The properties of the compact include a sufficient level of green density along with a homogenous density distribution.

2.2.3.5 Liquid state sintering

Liquid phase sintering differs from solid state sintering in that a liquid phase coexists with a particulate solid at the sintering temperature. This liquid phase usually enhances the rate of inter-particle bonding during sintering (German 1996) and significantly increase the densification rate (Kingery 1958). Liquid phase sintering, similar to solid state sintering, is often divided into three stages (Kingery 1958):

i. *particle rearrangement*: motion of solid particles due to capillary forces is responsible for the initial densification of the compact.

ii. *Solution reprecipitation*: different solubilities of the solid in the liquid are responsible for the transport of the material from the points of solid–solid contacts to the free surfaces of the particles,

iii. *coalescence*: permanent solid–solid contacts between particles form and liquid phase sintering ends.

2.3 Calcium Phosphate Ceramics

Calcium phosphate based ceramics are commonly used as bone graft materials due to their chemical stability and compositions similar to the mineral phase of natural bone (Kalita et al. 2007). Their ionic composition is similar to that of the natural minerals found in physiological environments, leading to significantly increased biocompatibility.
over inert ceramics such as alumina or zirconia. Figure 2.9 illustrates some of the commercial application of calcium phosphate base ceramics.

![Figure 2.9](image)

**Figure 2.9.** Commercial examples of calcium phosphate based bioceramics (Dorozhkin 2009).

There are several types of calcium phosphates which are shown in Table 2.3 along with their chemical formulae and Calcium to Phosphorous (Ca:P) ratios. These include hydroxyapatite (HA), alpha and beta tri-calcium phosphate (α-TCP, β-TCP) and tetra-calcium phosphate (TTCP). The behaviour of these phosphates *in vivo* is dependent on a variety of factors, including the Ca:P ratio, the crystallographic structure and the degree of porosity (Kalita et al. 2007). The stoichiometric ratio of Ca:P is of particular importance as it is related to the acidity and solubility of the material. For a Ca:P ratio less than 1, both acidity and solubility are very high, while both parameters decrease significantly for a ratio close to 1.667, which is the ratio of stoichiometric HA.

The two most important calcium phosphates, in terms of biomedical applications, are HA and β-TCP. Both materials are biocompatible and osteoconductive; however, they exhibit vastly different resorption rates. HA resorbs at a much slower rate than β-TCP (Knabe et al. 2000). Both materials are strong in compression but extremely susceptible to tensile and fatigue failure (Orlovskii et al. 2002a). HA is considered a more promising biomaterial than β-TCP, as it allows faster bony ingrowth into its macropores and is surrounded by less macrophages after implantation (Klein et al. 1983).
### Table 2.3. Calcium Phosphates: Ca:P ratios & solubility compiled from (Dorozhkin 2009, Sergey and Matthias 2002).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Ca/P</th>
<th>Solubility @37°C, -log(K_{sp})</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monocalcium phosphate monohydrate (MCPM)</td>
<td>Ca(H₂PO₄)H₂O</td>
<td>0.5</td>
<td>--</td>
<td>2.23</td>
</tr>
<tr>
<td>Monocalcium phosphate anhydrous (MCPA)</td>
<td>Ca(H₂PO₄)₂</td>
<td>0.5</td>
<td>--</td>
<td>2.58</td>
</tr>
<tr>
<td>Dicalcium phosphate dehydrate (DCPA)</td>
<td>CaHPO₄·2H₂O</td>
<td>1.0</td>
<td>6.63</td>
<td>2.32</td>
</tr>
<tr>
<td>Dicalcium phosphate anhydrous (DCPA)</td>
<td>CaHPO₄</td>
<td>1.0</td>
<td>7.02</td>
<td>2.89</td>
</tr>
<tr>
<td>Octacalcium phosphate (OCP)</td>
<td>Ca₉H₄(PO₄)₆·5H₂O</td>
<td>1.33</td>
<td>95.9</td>
<td>2.61</td>
</tr>
<tr>
<td>α–Tricalcium phosphate (α–TCP)</td>
<td>α–Ca₃(PO₄)₂</td>
<td>1.5</td>
<td>25.5</td>
<td>2.86</td>
</tr>
<tr>
<td>β–Tricalcium phosphate (β–TCP)</td>
<td>β–Ca₃(PO₄)₂</td>
<td>1.5</td>
<td>29.5</td>
<td>3.07</td>
</tr>
<tr>
<td>Hydroxyapatite (HA)</td>
<td>Ca₁₀(PO₄)₆(OH)₂</td>
<td>1.67</td>
<td>117.2</td>
<td>3.16</td>
</tr>
<tr>
<td>Fluorapatite (FAp)</td>
<td>Ca₅(PO₄)₃F</td>
<td>1.67</td>
<td>120</td>
<td>3.16</td>
</tr>
<tr>
<td>Tetracalcium phosphate (TTCP)</td>
<td>Ca₄(PO₄)₂O</td>
<td>2</td>
<td>37-42</td>
<td>3.05</td>
</tr>
</tbody>
</table>

#### 2.3.1 Hydroxyapatite

Hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] is the primary mineral content of bone and calcified tissues (Martin et al. 1998). HA is highly biocompatible, osteoconductive, non-toxic, non-inflammatory, and has a structural composition similar to that of native bone (Murugan and Ramakrishna 2004). The theoretical composition of HA is 39.68 wt% Ca and 18.45 wt% P, with a Ca/P ratio of 1.667. HA has a higher thermodynamic stability in aqueous media than other calcium phosphate ceramics and actively induces bonding, forming strong chemical bonds with the surrounding bone (Nath et al. 2006).

HA ceramics are currently used extensively in non-loading bearing bone replacements and as coatings on bioinert metallic implants as seen in Table 2.4. They are limited to non-load bearing applications due to poor mechanical properties, in particular low tensile strength and fracture toughness compared to bone.

<table>
<thead>
<tr>
<th>Type</th>
<th>Commercial products</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA ([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2])</td>
<td>Calcitite (Ceramed, CO)</td>
<td>Spinal Surgery</td>
</tr>
<tr>
<td></td>
<td>Osteograf (Ceramed, CO)</td>
<td>Bone Space fillers</td>
</tr>
<tr>
<td></td>
<td>Bioroc (Depuy-Bioland, France)</td>
<td>Periodontal augmentation</td>
</tr>
<tr>
<td>Coralline HA (derived from</td>
<td>Interpore, ProOsteon (Interpore, CA)</td>
<td>Alveolar ridge augmentation</td>
</tr>
<tr>
<td>coral)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biphasic calcium phosphates</td>
<td>MBCP (Biomatlante, France)</td>
<td>Adjuvant to the placement of metal implants</td>
</tr>
<tr>
<td>BCP (HA + (\beta)-TCP)</td>
<td>Triosite (Zimmer, IN)</td>
<td>Middle ear reconstruction</td>
</tr>
<tr>
<td></td>
<td>Osteosynt (Einco Ltd., Brazil)</td>
<td>Plasma-sprayed coatings for Dental and orthopedic implants</td>
</tr>
<tr>
<td></td>
<td>Tribone (Stryker, Europe)</td>
<td></td>
</tr>
<tr>
<td>Calcium deficient apatite</td>
<td>Osteogen (Impladent, NY)</td>
<td></td>
</tr>
<tr>
<td>(CDA)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3.1.1 Crystal Structure of Hydroxyapatite

HA displays an ionic character and its crystalline structure, with unit cell consisting of the formula \([\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]\), can be described as a compact hexagonal packing of oxygen atoms with metal ions occupying the tetrahedral and octahedral holes of the periodic network (De Aza et al. 2006). HA has a hexagonal structure with a \(P6_3/m\) space group and lattice parameters \(a = 0.942\text{nm}\) and \(c = 0.687\text{nm}\). \(\alpha = \beta = 90^\circ\) and \(\gamma = 120^\circ\). There are two independent Ca atoms in the unit cell, six atoms per unit cell are in position Ca 1 (Rho et al.) and four atoms are in position Ca 2. Ca 2 is located on the threefold axis and is coordinated by nine oxygens of phosphate groups. The Ca atoms form equilateral triangles. The OH groups reside in an off centre position (Orlovskii et al. 2002a).

![Crystal structure of HA](Vallet-Regi 2001)

Figure 2.10. Crystal structure of HA. (Vallet-Regi 2001)
The crystal structure of HA can accommodate substitutions of various other ions for the Ca\(^{2+}\), PO\(_{4}^{3-}\) and OH\(^{-}\) groups (Best et al. 2008). These substitutions can affect the lattice parameters, thermal stability, crystallinity, solubility and rate of dissolution of HA (De Aza et al. 2006). Cationic substitutions occur in sites occupied by the Ca\(^{2+}\) ions and include Na\(^{+}\), Mg\(^{2+}\) and Sr\(^{2+}\). Anionic substitutions can occur in either the PO\(_{4}^{3-}\) or the OH\(^{-}\) positions. Both fluorapatite and chlorapatite are common examples of anionically substituted hydroxapatite with F\(^{-}\) and Cl\(^{-}\) ions substituting for the OH\(^{-}\), respectively (Best et al. 2008).

### 2.3.1.2 Synthesis of Hydroxyapatite

HA can be synthesised using a variety of techniques including precipitation reactions, solid state reactions, hydrothermal reactions, sol-gel technique and mechanochemical synthesis. Figure 2.11 indicates the amount of calcium and phosphates and temperatures required to produce different apatites.

![Equilibrium phase diagram of different calcium phosphates](image)

**Figure 2.11.** Equilibrium phase diagram of different calcium phosphates (Manjubala and Sivakumar 2001).

**Precipitation technique:**

The most widely used technique for the synthesis of HA is the precipitation technique. The wide use of this technique is due to the ability to produce relatively large amounts of HA in the absence of organic solvents at a reasonable cost, along with the ability to strictly control the synthesis parameters (Yang 2004). The precipitation process can occur via a number of chemical routes. One of the first precipitation reactions was initially proposed by Yakai and Aoki (1965). Calcium hydroxide [Ca(OH)\(_{2}\)] and orthophosphoric acid [H\(_{3}\)PO\(_{4}\)] were used as starting powders in the following reaction:
10Ca(OH)$_2$ + 6H$_3$PO$_4$ → Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ + 18 H$_2$O \hspace{1cm} (2.5)

The size, shape and surface area of the HA particles obtained using this type of reaction are very sensitive to the orthophosphoric acid addition rate and reaction temperature. The addition rate is linked with the final pH obtained and the suspension stabilisation. The temperature affects the crystallinity of the HA, with low temperatures (<60°C) resulting in monocrystalline HA particles. In general, the reactants in all precipitation methods must be calcium and phosphate salts with ions that are unlikely to be incorporated into the apatite lattice. Jarcho, Bolen, Thomas, Bobick, Kay and Doremus (1976) proposed a similar method using calcium nitrate [Ca(NO$_3$)$_2$] and ammonium phosphate [(NH$_4$)$_2$HPO$_4$] since it has been claimed that NO$_3^-$ and NH$_4^+$ are not incorporated into crystalline apatites, or in the case of NH$_4^+$ presents a very limited incorporation. The reaction for this method is:

10Ca(NO$_3$)$_2$.4H$_2$O+6(NH$_4$)$_2$HPO$_4$+8NH$_4$OH→Ca$_{10}$(PO$_4$)$_6$(OH)$_2$+20NH$_4$NO$_3$+6H$_2$O \hspace{1cm} (2.6)

Apatites with different stoichiometry, crystallinity and morphology can be prepared by varying the synthesis parameters of the reaction and the effects of synthesis temperature, aging time, pH and the atmosphere on synthesised HA have all been studied. Pang and Bao (2003) similar to Bouyer et al previously, found that increases in the sintering temperature from 15°C to 99°C lead to an increase in the crystallinity. The temperature has also been shown to affect the particle size and morphology. Pang et al. (2003) also found that at low temperatures the HA exhibits a small needle like morphology, with lengths ranging from 20 to 40nm, while increases in the synthesis temperature morphology changed to a more regular thicker shape (Figure 2.12). Both Towler (1997) and Bernache-Assollant, Ababou, Champion and Heughebaert (2003) observed different effects, with high temperatures leading to a more elongated, rod shaped morphology.
The ageing time of the synthesis can affect the morphology, crystallinity and Ca:P ratio. Silva and Domingues (1997) suggested that by agitating a precipitated solution for 7 hours and ageing the solution for a further 17 hours at room temperature, time is allowed for the solution to stabilise and attain a Ca:P ratio closer to 1.667. Similarly, Pang et al. (2003) found that an increase in ageing time allows for a greater purity to be obtained due to the stabilisation of the HA structure via a possible recrystallisation process. As with temperature, increases in the aging time also tend to increase the HA crystallinity (Pang and Bao 2003).

The pH of the reaction has also been found to influence the synthesis of HA. In the reaction proposed by Jarcho et al., (1976), a pH of 10-12 was used; however, a variety of different pH values have been investigated from 8.5 to 12 (Tsutsumi, Lu, & Yuboa) (Raynaud et al. 2002a). Raynaud et al. (2002a) indicated that a pH greater than 8 was required to allow a full reaction of the calcium and phosphate species (i.e. pH > 8 is needed before the Ca:P ratio of the initial Ca and P sources is similar to the Ca:P ratio of the final powder).

The atmosphere in which the precipitation reaction takes place can result in negative effects on the HA powder. When HA is synthesised under normal atmospheric conditions, it is possible that CO₂ is incorporated into the apatite structure in place of the \( \text{PO}_4^{3-} \) creating a drain on the Ca as it is bound up in carbonates (\( \text{CO}_3^{2-} \)), resulting in
a calcium deficient HA (Elliott 1994). As the reagents in the co-precipitation method are mixed over a period of time, carbonates would have more time to form, reducing the Ca/P ratio of the synthesized HA.

**Solid state:**

In solid state reactions the calcium and phosphate precursor powders are mixed thoroughly and sintered above 900°C. HA can be prepared by mixing Ca$_3$(PO$_4$)$_2$ and CaCO$_3$, CaP$_2$O$_7$ and CaCO$_3$ or CaHPO$_4$.2H$_2$O and CaO between 900 and 1300°C in the presence of water vapour. While the solid state techniques can produce stoichiometric HA, it requires significant amounts of energy and time. Moreover the products of such processes typically large heterogeneity and suffer from large grain sizes (Orlovskii et al. 2002b).

**Sol gel:**

Sol gel synthesis offers an alternative technique to precipitation synthesis and solid state reactions, particularly in the context of thin film HA coatings. The coating of titanium implants with HA generally requires the use of either electrochemical deposition or thermal spraying, the latter being associated with a number of undesirable side effects, including HA decomposition due to the high temperatures involved and phase changes of the metal substrate (Li et al. 2001). Sol gel synthesis can be achieved at lower temperatures addressing some of these issues. HA has been synthesised using a sol-gel technique at temperatures as low as 350°C using calcium nitrate and triethylphosphate (PO(OEt)$_3$) in an ethanol based solution (Li et al. 2001). There have been several studies that examined HA synthesised in a temperature range of 300-500°C that generally found the crystallinity of the HA to be low (Lopatin et al. 1998, Brendel et al. 1992). Generally, the HA requires post synthesis thermal treatment to increase the crystallinity of the HA. While the sol-gel technique is an attractive alternative for producing bioactive coatings on metal substrates, it is limited in terms of producing large quantities of HA compared to precipitation or solid state techniques.

**Other techniques:**

There are numerous other synthesis techniques based on the general starting point of using a calcium source and a phosphorus source mixed to attain a ratio of ~1.667. Hydrothermal synthesis of HA involves reactions of Ca and PO$_4$ precursors at high temperatures and pressures and requires the use of expensive equipment. Generally the reagents are similar to those used in solid state reactions, except under steam pressure of
Mechanochemical synthesis triggers the formation of a HA phase by high energy mechanical activation using an alumina vial with stainless steel milling media to react a dry mixture of anhydrous calcium phosphate (CaHPO$_4$) and calcium oxide (CaO) (Yeong et al. 2001). Microwave synthesis has been achieved using a 2.45 GHz microwave to form HA from Ca(NO$_3$)$_2$ and Na$_2$HPO$_4$ solutions (Kalita and Verma 2010). HA has also been synthesised by irradiating calcium and phosphate solutions with acoustic waves. Each technique requires a mixed solution of a Ca and P source and a form of energy to produce a reaction, be it heat, acid/base, impact or wave energy. A summary of some of the synthesis techniques of HA is presented in Table 2.1.

Table 2.5. Synthesis techniques of HA & properties (Murugan and Ramakrishna 2005b).

<table>
<thead>
<tr>
<th>Technique</th>
<th>Grain size (nm)</th>
<th>General Remarks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid State</td>
<td>500</td>
<td>Inhomogeneous, large grain size, irregular shapes, reaction conditions 900-1300°C</td>
<td>(Yoshio et al. 1998)</td>
</tr>
<tr>
<td>Wet Chemical/Precipitation</td>
<td>20-200</td>
<td>Nanograin size, low crystallinity, homogenous reaction conditions: room temperature to 100°C</td>
<td>(Murugan and Ramakrishna 2005a)</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>10-80</td>
<td>Homogenous, fine crystals, high temperatures and high pressure atmosphere</td>
<td>(Ioku et al. 2002)</td>
</tr>
<tr>
<td>Mechanochemical</td>
<td>20-100</td>
<td>Easy production, semi-crystalline, ultra fine crystals, room temperature processing</td>
<td>(Nakamura et al. 2001)</td>
</tr>
<tr>
<td>pH shock wave</td>
<td>20-100</td>
<td>High-energy dispersing, nonporous, monocristalline particles with Ca/P molar ratio 1.43-1.66</td>
<td>(Koumoulidis et al. 2001)</td>
</tr>
<tr>
<td>Microwave</td>
<td>100-300</td>
<td>Uniform, nanosize particles, time and energy saving</td>
<td>(Yang et al. 2002)</td>
</tr>
</tbody>
</table>

2.3.1.3 Sintering of Dense HA

The mechanical properties of HA, like other brittle ceramics, are predominantly related to its final density and the presence of processing flaws. As such, the method of sintering and the individual parameters (i.e. heating rate, hold time & atmosphere) have a significant effect on the mechanical properties. The densification of HA, as a function of the sintering temperature, has a sigmoidal relationship with a plateau in maximum densification levels between 1100-1300°C (Ruys et al. 1995b). This temperature and the associated densification level depend predominately on the surface area of the starting
powder (Best et al. 1989, Ruys et al. 1995a) and to a lesser extent the Ca/P ratio (Raynaud et al. 2002b) of the HA powder.

A decrease in the initial particle size (increase in surface area) leads to a decrease in the shrinkage onset temperature (Orlovskii et al. 2002b). In terms of the calcium to phosphorus ratio, it has been shown that lower Ca:P ratios are detrimental to the final density of the sintered bodies (Raynaud et al. 2002b) as can be seen in Figure 2.13. The Ca/P ratio was varied through the addition of TCP to HA starting powders. A sintering temperature of 1250°C was used for all compositions. The final density increased as the calcium / phosphorus ratio increased to a maximum approaching that of stoichiometric HA (1.667), beyond which the final density decreased. Mostafa (2005) found similar results with calcium deficient HA, again having significantly lower final density than stoichiometric HA.

![Figure 2.13. Densification of calcium phosphates with varying Ca/P ratios sintered at 1250°C (Raynaud et al. 2002b).](image)

The densification is further complicated by the loss of the OH⁻ radical (Orlovskii et al. 2002b) and the fact that HA is a hydrated phase that decomposes to anhydrous calcium phosphates such as tri-calcium phosphate (TCP) and tetra-calcium phosphate (TTCP) at temperatures between approximately 1200-1450°C (Ruys et al. 1992). It is important that this decomposition is avoided as, in the context of hard tissue replacements, these calcium phosphates have greater dissolution rates in vitro (Ducheyne et al. 1990). HA reversibly dehydroxylates at temperatures above approximately 800°C. Despite the dehydroxylation, HA can maintain its crystal structure and upon cooling the HA can rehydrate (Ruys et al. 1995a). Equation 2.7
indicates the dehydroxylation process (where $0 < x < 1$) and Equation 2.8 indicates the decomposition of HA.

$$\text{Ca}_{10}\text{(PO}_4\text{)}_6(\text{OH})_2 = \text{Ca}_{10}\text{(PO}_4\text{)}_6(\text{OH})_2 \cdot 2x\text{O}_x \square + x\text{H}_2\text{O} \quad (2.7)$$

$$\text{Ca}_{10}\text{(PO}_4\text{)}_6(\text{OH})_2 = 2\alpha\text{-Ca}_3\text{(PO}_4\text{)}_2 + \text{Ca}_4\text{P}_2\text{O}_9 + \text{H}_2\text{O} \quad (2.8)$$

There have been several studies examining the effects of sintering temperature on the mechanical and chemical properties of commercially available HA; one examined the temperature range of 1000-1450°C sintered in air using a ramp rate of 2°C/min and a hold time of 2 hrs (Ruys et al. 1995a) and another sintered HA in a temperature range of 900-1400°C, under a pressurized argon atmosphere (1MPa) using a heating rate of 3.3°C/min and a hold time of 1hr (Muralithran and Ramesh 2000). Ruys et al. (1995a) summarized their results in terms of both the dehydroxylation behavior and the microstructural development. Below 800°C there was a small loss of the hydroxyl ions which accelerated between 800 and 1350°C. At 1350°C a critical point was reached where irreversible dehydroxylation and decomposition occurred. In terms of microstructure, the majority of densification occurred between 900-1150°C, a plateau was reached between 1150-1200°C beyond which a large number of blowholes started to form and the density decreased significantly. Similar blowhole formation was observed in studies by (Peelen et al. 1978) and (Royer et al. 1993).

Muralithran et al. (2000) observed similar results in terms of the densification plateau and decomposition of HA. An optimum temperature of 1250°C was identified in terms of maximum density (>99%), beyond which there was a reduction in the density and decomposition of the HA occurred at 1350°C. There was no evidence of the formation of blowholes above 1250°C; however, excessive grain growth did occur at higher temperatures (2.03µm at 1250°C to 12.26µm at 1400°C).

The effect of hot-pressing on the thermal stability of HA during the sintering processes has also been investigated (Rapacz-Kmita et al. 2006). HA synthesized by the wet process was sintered from 1150-1300°C in an argon atmosphere for 0.5hrs. These were then compared to HA sintered by conventional means at similar temperatures, in terms of phase composition and dehydroxylation. There was no significant phase
decomposition observed in either technique, within the temperature range studied. This was attributed to the high thermal stability of the starting powders. There was a significant difference found, in terms of dehydroxylation, between the two techniques. There was no evidence of dehydroxylation in the hot-pressed samples at all, while there was a significant degree observed at 1300°C in conventionally sintered samples.

Spark Plasma Sintering has also been used to sinter dense HA ceramics (Gu et al. 2002). HA powder was sintered in a graphite die at sintering temperatures between 850-1100°C under a constant load of 30MPa at a rate of 50°C/min and a hold time of 5 mins. A maximum relative density of 99.6% was achieved at a sintering temperature of 950°C. At temperatures above 1000°C there was a slight decrease in the density due to the decomposition of HA to tri-calcium phosphate. There was a significant decrease in sintering temperature and time using the SPS method, which the authors attributed to a combination of electrical discharge, resistance heating and pressure application effects. Whilst similar densities were achieved at lower temperatures than conventional sintering a similar trend was observed in terms of decomposition of HA and corresponding reductions of density, albeit at approximately 200-300°C lower.

The consolidation of dense HA through microwave sintering has also been examined (Ramesh et al. 2008). Using a frequency of 2.45GHz, HA compacts were sandwiched between two SiC susceptors and sintered between temperatures of 1000-1300°C for a duration of 30mins. Maximum relative densities of 96 and 98% were achieved at 1100°C and 1300°C, respectively. However there was significant grain growth between these temperatures from 0.25µm to 2µm. There was no observation of HA decomposition, even at the higher temperature range of 1300°C. A similar study (Ramesh et al. 2007) directly compared conventional sintering of HA (prepared by chemical precipitation method) to microwave sintered samples using a similar sintering regime of 1000-1300°C. XRD phase analysis indicated that neither method caused decomposition of the HA in the temperature ranges studied. However there was significant grain growth observed in conventional samples compared to microwave sintered samples, particularly at temperatures over 1200°C.

A further study by Yang, Ong and Tian (2002) compared conventional sintering of HA at 1100°C for 1hr to microwave sintered samples in a 10kW, 2.45GHz furnace heated at 1050-1100°C for 5/10 mins. Grain size measurements obtained from SEM
imaging of the fracture surface indicated that the microwave sintered samples had much finer grain size (0.3-0.5µm) than their conventional counterparts (3-5µm) and also greater densities. The authors attributed this to the higher efficiency of microwave sintering. The effects of temperature on the final grain size can be seen in Figure 2.15.

![Figure 2.15](image)

**Figure 2.14.** Temperature effects on the relative density of HA from Literature: conventionally sintered (CS), spark plasma sintered (SPS) and microwave sintered (MWS).

In summary, the sintering of dense HA bodies is a complicated procedure. The final density and thus, structural properties are dependent on a significant number of factors. These include Ca:P ratio, particle size and surface area, sintering technique and the type of atmosphere used. In the case of conventionally sintered samples the optimum temperature of sintering appears to be in the range of 1200-1300°C. Beyond these temperatures, there are significant amounts of decomposition, grain growth and reduction in density. The SPS method exhibited a similar trend; however equivalent densities and decomposition occurred at temperatures 200-300°C lower, as seen in Figure 2.14. Interestingly, in the case of microwave sintering of HA, there was no indication of decomposition, even at temperatures of 1300°C. Also, the final grain size after sintering was smaller than those observed using of conventional techniques with similar densities.
2.3.1.4 Mechanical Properties of Dense HA

There have been numerous studies on the mechanical properties of dense HA ceramics. The literature reveals significant variations in the mechanical properties of HA as indicated in Table 2.6. The large variation in properties is thought to arise from several factors including different sintering regimes, decomposition of HA, random strength variations, effects of residual porosity, grain size, impurities, differing synthesis techniques and the Ca:P ratio (Metsger et al. 1999, Orlovskii et al. 2002b). The strength tends to increase as the Ca:P ratio increases, reaching a maximum at 1.67 and sharply decreasing as the ratio exceeds 1.67 (Suchanek and Yoshimura 1998). This may be related to the fact that a deviation from the stoichiometric ratio leads to a reduction in final density and hence an increase in residual porosity, seen previously in Figure 2.13. In general, significant amounts of porosity post sintering will have deleterious effects on the mechanical properties of HA ceramics, as discussed previously (2.2.2.3 Porosity).

The Young’s modulus of dense HA varies from 40~120 GPa, approximately 2 to 6 times that of cortical bone (~20GPa), depending on residual porosity post sintering. The elastic modulus tends to increase linearly with an increase in the relative density (de With et al. 1981). The compressive strengths are greater than the flexural strengths with ranges varying from 500~913 and 60~120 MPa respectively. The strength tends to decrease almost exponentially with increases in porosity (Tancret et al. 2006, Bouler et al. 1996). The hardness of HA ranges from 4 to 7.4 GPa. Ramesh et al. (2008) indicated that the hardness increases with increasing grain size to a critical point, where any further increases in grain size lead to a decrease in hardness.
The $K_{IC}$ of HA varies from approximately 0.9 to 1.5 MPa.m$^{1/2}$, significantly lower than human bone (2~8 MPa.m$^{1/2}$). It decreases almost linearly with an increase in porosity. The fracture also exhibits a dependence on grain size. Halouani et al., (1994) investigated the $K_{IC}$ of hot pressed HA with grain sizes in the range 0.2~1.2μm. Two distinct patterns were observed. Initially, the $K_{IC}$ increased with decreasing grain size to a maximum of 1.2 MPa.m$^{1/2}$ at 0.4μm. Subsequently, any further reduction in grain size led to a decrease in the toughness. It is worth noting that the majority of recent studies determined the fracture toughness using indentation techniques, the validity of which has been called into question (George and Richard 2007). The Weibull modulus of HA tends to reside in the range of 5~12 in wet environments, typical of brittle ceramics (Suchanek and Yoshimura 1998). This indicates low reliability, particularly in the case of load bearing applications.

In conclusion, whilst there has been a significant amount of research into producing HA compacts with near theoretical densities, small grain size and stoichiometric Ca:P ratios, the resultant mechanical properties, in particular flexural strength and fracture toughness, are still low compared to those of natural bone. Consequently this has lead researchers to attempt to add a reinforcing phase to the HA.
Table 2.6. Comparison of the mechanical properties of dense HA in literature.

<table>
<thead>
<tr>
<th>Author</th>
<th>Temp (°C)</th>
<th>E (GPa)</th>
<th>Hardness (Gpa)</th>
<th>$K_{IC}$ (MPa.m$^{1/2}$)</th>
<th>Compressive Strength (MPa)</th>
<th>Flexural Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Rapacz-Kmita et al. 2006)</td>
<td>1150-1300</td>
<td>119</td>
<td>5.7~6.6</td>
<td>0.9~1.1</td>
<td>-</td>
<td>84~101</td>
</tr>
<tr>
<td>(de With et al. 1981)</td>
<td>1250</td>
<td>110</td>
<td>-</td>
<td>0.93~1.3</td>
<td>800</td>
<td>115</td>
</tr>
<tr>
<td>(Lu et al. 1998)</td>
<td>1100-1350</td>
<td>-</td>
<td>5.6~7.4</td>
<td>-</td>
<td>-</td>
<td>90~110</td>
</tr>
<tr>
<td>(Gu et al. 2002)</td>
<td>850-1100$^{1}$</td>
<td>75~110</td>
<td>4~5.5</td>
<td>1.15~1.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Muralithran and Ramesh 2000)</td>
<td>1250</td>
<td>-</td>
<td>6.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Ruys et al. 1995b)</td>
<td>1150</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>(Jarcho et al. 1976)</td>
<td>1100</td>
<td>-</td>
<td>4.8</td>
<td>-</td>
<td>917</td>
<td>-</td>
</tr>
<tr>
<td>(Akao et al. 1981)</td>
<td>1300</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>509</td>
<td>113</td>
</tr>
<tr>
<td>(Ramesh et al. 2008)</td>
<td>1000-1300$^{2}$</td>
<td>-</td>
<td>5.5~7.25</td>
<td>1~1.45</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Thangamani et al. 2002)</td>
<td>1200</td>
<td>-</td>
<td>6</td>
<td>0.9</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>(Ramesh et al. 2007)</td>
<td>1150$^{2}$</td>
<td>-</td>
<td>6.38</td>
<td>1.45</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2.3.2 Zirconia

Zirconia (ZrO$_2$) exhibits three distinct crystallographic phases with increasing temperature at normal atmospheric pressure: a monoclinic phase, stable from ambient temperatures to 1170°C, a tetragonal phase, stable from 1170 to 2370°C and a cubic phase, stable above 2400°C (Basu et al. 2004b, Jin 2005). The high temperature cubic phase exhibits a face centered cubic (FCC) fluorite structure, while the tetragonal and monoclinic polymorphs are distorted versions of this structure (Ruhle and Heuer 1984). At higher pressures two distinguishable orthorhombic structures have been observed in partially stabilised zirconia (Shukla and Seal 2005).

The transformation from tetragonal to monoclinic at 950°C is an athermal, martensitic transformation which is associated with a volume expansion of 4-5% and a shear strain of approximately 14-15% (Hannink et al. 2000, Basu 2005). This leads to detrimental fracture and crumbling of sintered pure zirconia ceramics. The addition of oxide dopants such as ceria, magnesia, calcia, yttria etc. are needed to stabilise the high temperature tetragonal and/or cubic phases (Din and Kaleem 1998, Evans and Cannon 1986). The solid solution of the zirconia + oxide dopant eliminates the detrimental monoclinic phase transformation during heating and cooling.

2.3.2.1 Crystal Structure

Cubic:

The cubic (c-ZrO$_2$) phase has a FCC fluorite type structure, in which each zirconium atom is coordinated by eight equidistant oxygen atoms and each oxygen atom is tetrahedrally coordinated by four zirconium atoms.

Tetragonal:

The tetragonal phase (t-ZrO$_2$) exhibits a similar structure to that of the cubic form except that it is elongated along the crystallographic c-axis.

Monoclinic:

The monoclinic phase (m-ZrO$_2$) has a seven fold coordination of zirconium atoms with a range of bond lengths and bond angles. The strong covalent nature of the Zr-O bond favours this seven fold coordination and, as a result, it is thermodynamically stable at lower temperatures.
2.3.2.2 Stabilisation of Zirconia

Stabilisation of zirconia refers to the retention of the high temperature tetragonal/cubic phases at room temperature through the addition of oxide dopants. In undoped zirconia, lattice oxygen ion vacancy concentration increases at higher temperatures and is primarily responsible for the stabilisation of both the tetragonal phase (requiring a small concentration of vacancies) and the cubic phase (requiring a large proportion of vacancies), due to the association of oxygen ion vacancies with $\text{Zr}^{4+}$ cations (Shukla and Seal 2005). Aliovalent cation dopants (ions with a different valency to the ones they replace) can be used to stabilise tetragonal/cubic phases at room temperature. It is generally considered that the dopant cations can substitute for a Zr ion (Ping Li 1994), creating oxygen vacancies in the process. Using Kroger-Vink notation the defect reaction of zirconia doped with yttria can be written as,

$$Y_2O_3 \rightarrow 2Y_{Zr}^\cdot + 3O_{o}^{\cdot} + V_{o}^{-}$$  \hspace{0.5cm} (2.9)

where $Y_{Zr}$ indicates a yttrium atom occupying a zirconium lattice site, $O_{o}^{\cdot}$ is an oxygen atom occupying a normal lattice site and $V_{o}^{-}$ is a vacancy at an oxygen lattice site. The increase in oxygen vacancies, caused by the dopant addition, increases the disorder in the system, thus increasing the stability of the tetragonal phase (Basu 2005).
The size, charge and concentration of the dopant cations are all considered to be important factors that influence stabilisation (Subbarao et al. 1974). The valency and size (with respect to Zr) of dopant cations were both found to affect the stabilisation of zirconia (Ping Li 1994). It has been suggested that the particle size of nanocrystalline ZrO$_2$ can also affect the oxygen ion vacancies, (Shukla and Seal 2005) with ion vacancy concentration of the nanocrystalline ZrO$_2$ increasing with decreasing nanocrystallite size (Shukla and Seal 2005).

Yoshimura (1988) examined the phase stability of high temperature zirconia phases both in terms of thermodynamics and kinetics. From a thermodynamic point of view the tetragonal phase can be stabilised by the addition of dopants because its free energy decreases with increasing amounts of dopant. In contrast to this, due to kinetic reasons, an unstable tetragonal phase can be retained metastably, if insufficient activation energy is provided at lower temperatures.

### 2.3.2.3 Transformation toughening.

Transformation toughening is a mechanism by which the fracture toughness of a material increases as a direct result of a phase transformation occurring due to the stress field ahead of the tip of an advancing crack in a material (Kelly and Francis Rose 2002). The tetragonal to monoclinic (T$_{t-m}$) phase change that is detrimental to the structural integrity of undoped zirconia is the same phenomenon that increases the toughness of doped zirconia. Transformation toughening of zirconia was first discovered by Garvie, Hannink and Pascoe (Garvie et al. 1975), who demonstrated that the T$_{(t-m)}$ phase transformation in partially stabilised zirconia (PSZ) improved the mechanical strength and toughness of zirconia ceramics. It was observed that regions of metastable tetragonal phase finely dispersed in a cubic phase matrix were able to transform to a monoclinic phase if the matrix constraint exerted on them was relieved, i.e. in the case of a propagating crack in the material.
Toughening occurs through the development of a zone of transformed material ("process zone") around the crack tip (Figure 2.17) (Piconi and Maccauro 1999). This process zone is the source of stress and displacement disturbance that tends to shield the crack tip from the applied stress (Evans and Heuer 1980). The 4-5% volume expansion characteristic of the $T_{t-m}$ martensitic-like transformation introduces a net compressive stress in the process zone around the crack tip (Jin 2005). This reduces the local crack tip stress intensity factor, therefore reducing the driving force for crack propagation, effectively increasing the toughness of the zirconia ceramic.

2.3.2.4 Types of Zirconia

Zirconia containing ceramics are generally classified into four categories: tetragonal zirconia polycrystalline (TZP), partially stabilized zirconia (PSZ), fully stabilised zirconia (FSZ) and zirconia toughened/dispersed ceramics (ZTC/ZTD) (Basu 2005). TZP consists of a room temperature stabilised tetragonal single phase ceramic, stabilised by yttria and/or ceria additions. These ceramics are often prefixed with a Ce- or Y- to denote, respectively, ceria or yttria as the stabilising oxide. For example 3Y-TZP represents zirconia doped with 3 mol% yttria. Commercial Y-TZP products are prepared with typical compositions in the range 1.75-3.5 mol% yttria content (Hannink et al. 2000) sintered in the region of 1300 to 1500°C to form a stabilised tetragonal phase.

The PSZ microstructure contains dispersed particles of metastable tetragonal phase in a stable cubic matrix (Hannink et al. 2000). PSZ ceramics are also prefixed with
chemical symbols in order to indicate the stabilising dopant. For example, Mg-PSZ and Ca-PSZ indicate that magnesia (MgO) and calcia (CaO), respectively, are the stabilising dopants. There is typically a higher temperature and yttria dopant content needed to form Y-PSZ than to form TZP as highlighted in the phase diagram (Figure 2.18).

![Figure 2.18 Zircona-Yttria phase diagram (Piconi and Maccardo 1999).](image)

Zirconia Toughened ceramic (ZTC) materials are characterized by the dispersion of 5-30% tetragonal or unstabilised zirconia in a ceramic matrix (Basu 2005). The most common ZTC material is zirconia toughened alumina (ZTA), as it combines the inherent hardness of alumina with the superior toughness of zirconia (Basu et al. 2004a). ZTA composites have shown superior fracture toughness than that of the monolithic materials (De Aza et al. 2006).

2.3.2.5 Mechanical Properties of ZrO₂

The mechanical properties of ZrO₂ are dependent on a number of factors including density, dopant type, the phase(s) retained and final grain size. Like all ceramics residual porosity severely affects the mechanical properties. In terms of phase retention, maintaining a majority of tetragonal phase will result in maximizing the transformation toughening effect, thus enhancing the strength and fracture toughness of the material. In Table 2.7 the mechanical properties of Y₂O₃ and MgO doped ZrO₂ are compared. Y-
TZP tends to exhibit better mechanical properties than Mg-PSZ. This is due to the retention of the tetragonal phase and the associated toughening mechanisms.

Table 2.7. Mechanical properties of Mg-PSZ (De Aza et al. 2006) & Y-TZP (Heimann 2002) ceramics used for biomedical applications.

<table>
<thead>
<tr>
<th>Property</th>
<th>Mg-PSZ</th>
<th>Y-TZP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconia content (mol %)</td>
<td>96-97</td>
<td>95-97</td>
</tr>
<tr>
<td>Yttria/Magnesia content (mol %)</td>
<td>3-4</td>
<td>3-5</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>5.72</td>
<td>6.05-6.09</td>
</tr>
<tr>
<td>Average grain size (μm)</td>
<td>0.42</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>E (GPa)</td>
<td>208</td>
<td>150-210</td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>1850</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>KIC (MPa.m¹/²)</td>
<td>~8</td>
<td>7-9</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
<td>800</td>
<td>900-1300</td>
</tr>
<tr>
<td>Vickers Hardness (GPa)</td>
<td>11.2</td>
<td>12-13</td>
</tr>
</tbody>
</table>

2.3.2.6 Clinical Applications of Zirconia

Ceramic materials demonstrate a lower coefficient of friction than metals when articulating with polyethylene (Masonis et al. 2004) and this lead to the use of alumina as ball heads. Zirconia was considered as an alternative to alumina due to its superior fracture toughness and wear properties (Kim et al. 2001). Interest in using zirconia as a biomaterial is due to several of its inherent properties, including chemical and dimensional stability, mechanical strength and toughness, coupled with a Young’s modulus of the same order of magnitude as stainless steel (Piconi and Maccauro 1999). The primary biomedical use of zirconia is as a bearing surface in total hip replacement prostheses (THR).
Zirconia ball heads used in THR (Piconi and Maccauro 1999) & knee replacement.

Yttria doped TZP are the primary compositions used in ceramic femoral heads and as of 2005, more than 600,000 zirconia femoral heads have been implanted worldwide, primarily in Europe and the US (Chevalier 2006). There are concerns of low temperature degradation (LTD) occurring with Y-TZP. LTD is the progressive transformation of stabilised tetragonal zirconia to monoclinic during ageing at relatively low temperatures, typically between 100 and 300°C, in an aqueous medium (Roebben et al. 2003). This phenomenon, along with a change in sintering methods, has been associated with roughening of implants after steam sterilisation and the failure of Prozyr® THR ball heads (Chevalier 2006). Consequently, as of 2001, zirconia has been removed from THR in France and the USA.

2.3.2.7 Biocompatibility of Zirconia

There have been numerous in vivo and in vitro studies into the effects of zirconia on biological tissues. When considering a material to be used in a composite for hard tissue replacement, it is necessary to determine any negative effects of zirconia both on the living cells in bone and bone tissue as a whole.

Biocompatibility on Osteoblasts

There have been numerous in vitro studies on the effects of zirconia on osteoblast cells. The in vitro effects of zirconia and alumina on human osteoblast cells in terms of cell viability and proliferation indicated that zirconia did not illicit any cytotoxic effect and was able to interact with osteoblast by intimate contacts (Josset et al. 1999). Similar results were reported with zirconia powders in direct contact with rat osteoblast cells (Toricelli et al. 2001) with an absence of any toxic effects. Lohmann, Dean, Köster, Casasola, Buchhorn, Fink, Schwartz and Boyan (2002) demonstrated similar results
with osteoblast like cells demonstrating a lower reduction of osteoblasts in the presence of zirconia compared to alumina.

**Biocompatibility in Hard Tissue**

The first *in vivo* examination of the biocompatibility of zirconia in hard tissue was performed by Helmer and Driskell (1969). Pellets of 6 mol% Y₂O₃ stabilised ZrO₂ were implanted into monkey femurs and no adverse reactions to zirconia were reported. However an apparent ingrowth was detected. Mg-PSZ has been evaluated using a rabbit femur model and reported no significant bone reaction (Garvie et al. 1984). The literature is generally in agreement that in terms of biocompatibility, zirconia ceramics are considered to be bioinert. *In vivo* tests of various types of zirconia (Hulbert et al. 1972, Garvie et al. 1984, Maccauro et al. 1992) indicate that there are generally no local or systemic adverse reactions correlated with zirconia implants or cytotoxic effects associated with zirconia (Piconi and Maccauro 1999).

### 2.4 HA Composites

While HA is strong in compression, it is extremely susceptible to tensile and fatigue failure (de Groot 1980). In order to expand the functionality of HA to include load bearing applications the strength and toughness of these ceramics need to be increased. This has lead to research into the production of a composite material that can address some of the mechanical limitations of HA while maintaining its bioactivity. In any composite material, there are two major constituents: (a) a matrix (continuous phase) and (b) the dispersed phase(s) (Choi and Awaji 2005). The matrix is responsible for filling the volume and surrounding/supporting the dispersed phase by maintaining their relative positions. The purpose of the dispersed phase is usually to reinforce/enhance the mechanical properties of the matrix. In terms of HA composites, polymers, metals and ceramics have all been examined as reinforcing phases.

In the context of a HA/ceramic composite, the reinforcing phase serves to impede crack growth. There are several methods by which this can occur, including deflecting crack tips, forming bridges across crack phases, absorbing energy during pullout and causing a redistribution of stresses in regions adjacent to crack tips (Niihara 1991). The transformation toughening phenomenon associated with zirconia combined with its biocompatibility result in a promising candidate for a reinforcing phase in HA. In practice, however, the formation of HA-ZrO₂ is complicated by several factors.
2.4.1 HA-ZrO$_2$ Composites

HA-ZrO$_2$ composites can be produced via a variety of methods, reagents grades and mixing conditions. The most common approach typically consists of ball milling both constituent phases, followed by pressing and consolidation by some form of heat treatment. There has been a wide range of studies into the formation of HA-ZrO$_2$ composites examining several different aspects of the composite including synthesis techniques, variations in the amount of reinforcing phase, variations in the type of ZrO$_2$ used and different sintering regimes and techniques (Ramachandra Rao and Kannan 2002, Evis 2007, Silva and Lameiras 2000) (Edward et al. 2005)(Miao, Chen, Guo and Khor, 2004) (Kumar et al. 2005).

2.4.2 Sintering Techniques

A range of different sintering techniques have been examined in the production of dense HA-ZrO$_2$ composites including pressureless sintering (Inuzuka et al. 2004) (Towler and Gibson 2001), hot isostatic pressing (HIP) (Edward et al. 2005), spark plasma sintering SPS (Miao, Chen, Guo and Khor, 2004) (Kumar et al. 2005) and high frequency induction heat sintering (HFIHS) (Khalil et al. 2007). The sintering technique generally has significant effects on the final density and constituent phases of the composite.

There have been several studies on conventionally sintered HA-ZrO$_2$ composites dating back more than 20 years and the reoccurring issue is the reaction that can occur between the matrix and the reinforcing phase. A study by (Wu and Yeh 1988) found that, while HA generally remains stable at a sintering temperature up to 1400°C, the addition of ZrO$_2$ (3 mol% Y$_2$O$_3$) led to phase transformations at lower temperatures that increased as the temperature increased. At 1150°C the HA decomposed to β-TCP and the ZrO$_2$ transformed from a cubic to a tetragonal form. As the temperature increased, further decomposition of the HA led to greater amounts of CaO reacting with the ZrO$_2$ to form CaZrO$_3$. At the maximum sintering temperature of 1400°C both β-TCP and CaZrO$_3$ had formed at the expense of HA and t-ZrO$_2$. (Heimann and Vu 1997) observed similar results. As seen previously, HA decomposes to α-TCP and TTCP by the first two equations below, without the presence of ZrO$_2$:

$$\text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 \rightarrow \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 - 2x\text{O}_2 \text{x} + x\text{H}_2\text{O}$$

$$\text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 \rightarrow 2\alpha\text{-Ca}_3 (\text{PO}_4)_2 + \text{Ca}_4 [\text{O}(\text{PO}_4)_2] + \text{H}_2\text{O}$$
Heimann et al., (1997) observed an absence of TTCP in XRD patterns with ZrO₂ additions and suggested that CaO released from either TTCP or HA reacts to form calcia stabilised t-ZrO₂ or CaZrO₃ according to the following equations:

\[
\text{Ca}_4[\text{O(PO}_4)_2] + m\text{-ZrO}_2 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + \text{Ca-doped t-ZrO}_2
\]

\[
2.12
\]

\[
\text{Ca}_4[\text{O(PO}_4)_2] + \text{Ca-doped t-ZrO}_2 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + \text{CaZrO}_3
\]

\[
2.13
\]

or

\[
\text{Ca}_{10}(\text{PO}_4)_{6}(\text{OH})_2 + m\text{-ZrO}_2 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + \text{CaZrO}_3/t\text{-ZrO}_2 + \text{H}_2\text{O}
\]

\[
2.14
\]

Thus it was proposed that ZrO₂ additions significantly accelerate the transformation of TTCP into TCP. Similar observations have subsequently been reported in other studies (Ramachandra Rao and Kannan 2002, Evis 2007, Silva and Lameiras 2000). Consequently, it appears that the decomposition of HA in the presence of ZrO₂ is interrelated to the exchange of CaO and ZrO₂. As CaO forms a solid solution with ZrO₂, the HA reduces with a corresponding increase in TCP. The rate of this reaction increases with temperature, until all the HA has decomposed and t/m-ZrO₂ has reacted to form CaZrO₃.

HIP has been used in several studies as an alternative to consolidating HA-ZrO₂ composites. Adolfsson, Alberius-Henning and Hermansson (2000) compared HIP with conventional sintering in air. Composites containing 20-85 vol% ZrO₂ (3 mol% Y₂O₃) were HIPed at 1200°C under a pressure of 160MPa for 1hr and compared to composites which had been conventionally sintered, also for 1hr. The HA decomposed in the presence of ZrO₂ at temperatures greater than 950°C in samples sintered in air. In contrast, the HIPed samples remained thermally stable at temperatures up to 1200°C, with no indication of HA decomposition as indicated by XRD phase analysis. The authors suggested that the decomposition was primarily related to vacancies created by the release of the hydroxyl ions and not the temperature. By using a closed system (HIP), the loss of the water from the apatite was limited and thus a higher temperature stability was achieved. Rapacz-Kmita, Slósarczyk, Paszkiewicz and Paluszkiewicz (2004) reported similar findings. In composites containing up to 20 wt% pure ZrO₂
additions, hot pressed at temperatures in the range 1150-1300°C, there was no indication of decomposition of the HA phase as shown by either FTIR or XRD analysis. Again it was suggested that the isolated environment played a role in the thermal stability. While both studies examined the effect on phases present, no mechanical properties or composite densities were reported. Evis and Doremus (2007b) did however report mechanical results achieved via HIPing of composites containing 10-40 wt% undoped ZrO₂. In this study the HA phase remained stable at 1100°C but an increase in the temperature to 1200°C resulted in the formation of α-TCP and CaZrO₃. The 40 wt% zirconia composite resulted in increases in diametral strength and fracture toughness over pure HA and densities of over 90% of theoretical density were achieved in each of the composites.

SPS has also been examined in the densification of HA-ZrO₂ composites. Miao, Chen, Guo and Khor (2004) sintered composites containing 40 wt% percent ZrO₂ (3 mol% Y₂O₃) using SPS and reported that the HA phase remained stable until 1150°C, above which it started to decompose to α-TCP. The tetragonal ZrO₂ remained stable, even at temperatures of 1150°C. A relative density of 93% was achieved and SEM imaging revealed a homogenous dispersion of t-ZrO₂ in the HA matrix and limited amounts of porosity (Figure 2.20). Bending strength and Young’s modulus of 200MPa and 160GPa, respectively, were observed, almost double those values for pure HA sintered using SPS. Shen, Adolfsson, Nygren et al. (2001) sintered composites containing 50-90 vol% ZrO₂ (3 mol%Y₂O₃) using SPS at 1150°C. Tetragonal ZrO₂ and HA were the only phases present, as determined by XRD analysis. It was proposed that limiting the formation of vacancies in the hydroxyapatite structure suppressed the decomposition reactions. High flexural strengths of 439 MPa were observed in the 50 vol% ZrO₂ compositions, between 4-5 times greater than mono-phasic hydroxyapatite. While the results of this study are promising, it is worth noting that at these levels of additions, ZrO₂ is the primary phase, not a reinforcing one.
A novel method employing the use of high frequency induction heating sintering (HFIHS) has also been used to consolidate HA-ZrO₂ composites (Khalil et al. 2007) A composite mixture containing 20 vol% ZrO₂ (3 mol% Y₂O₃) was surrounded by a coil of wire through which a high frequency, high power ac current was passed, causing the densification. Decomposition of the HA phase to TCP was only observed in samples heated at 1200°C. A decrease in the hardness and toughness was observed at 1200°C compared to 1150°C, which corresponds with the decomposition of HA.

2.4.3 Density of Composites

It has been observed that the addition of ZrO₂ to HA results in a decrease in the relative densities of composites which decreases as the amount of ZrO₂ additive increases (Figure 2.21). Contrary to this, two studies reported small density increases with low levels of ZrO₂ (< 5wt%), followed by a decrease with further additions (Towler and Gibson 2001, Yougojoti et al. 2008a). Both studies also observed corresponding increases in mechanical properties of samples with low zirconia additions compared with pure HA. It has been suggested that the increase in porosity is related to the increased release of water from the decomposition reaction between HA and ZrO₂ (Evis 2007).

The difficulty in achieving near theoretical densities is a significant limitation to the composites. Residual porosity is, in general, detrimental to mechanical properties. The use of SPS and HIP sintering techniques have both increased the relative densities of the composites, reportedly due to the closed environment limiting hydroxyl ion loss in HA.
(Adolfsson et al. 2000, Shen et al. 2001). However, even using these techniques, achieving relative densities greater than 95% remains difficult, particularly when large volume fractions of a ZrO₂ reinforcing phase are added. Limiting the quantity of ZrO₂ phase to small amounts appears to be the optimum approach to achieve sufficiently high final densities.

![Figure 2.21. Effect of ZrO₂ additions on the relative density of HA-ZrO₂ composites.](image)

### 2.4.4 Mechanical Properties

In general there is a wide variation in the reported mechanical properties of HA-ZrO₂ composites. This is most likely due to the large number of variables involved in the formation of the composites including synthesis techniques, amount of ZrO₂, type of ZrO₂ (t/c/m), sintering technique and sintering temperature involved. The mechanical properties of several studies on HA-ZrO₂ composites are reported in Table 2.8.
### Table 2.8. Mechanical Properties of HA-ZrO₂ Composites.

<table>
<thead>
<tr>
<th>Author</th>
<th>Composition</th>
<th>Temp (°C)</th>
<th>E (GPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Compressive Strength (MPa)</th>
<th>K&lt;sub&gt;IC&lt;/sub&gt; (Mpa.m&lt;sup&gt;1/2&lt;/sup&gt;)</th>
<th>Hardness (GPa)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Inuzuka et al. 2004)</td>
<td>ZrO₂ (3mol% Y₂O₃) +1-10 wt % HA</td>
<td>1400</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.16-9.45</td>
<td></td>
<td>Porosity and β-TCP increase with increase in HA</td>
</tr>
<tr>
<td>(Yougojoti et al. 2008b)</td>
<td>HA + 2-10 wt % ZrO₂ (2.5mol% Y₂O₃)</td>
<td>1150-1250</td>
<td>72-36</td>
<td>34-13</td>
<td>-</td>
<td>-</td>
<td></td>
<td>Increase in strength with 2 wt% ZrO₂, only HA &amp; t-ZrO₂ phases present. Decrease in mech properties after 2 % with increase in ZrO₂. Increase in α-TCP &amp; CaZrO₃ with increase in ZrO₂.</td>
</tr>
<tr>
<td>(Khalil et al. 2007)</td>
<td>HA + 20 wt % ZrO₂ (3mol% Y₂O₃)</td>
<td>1200°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.7-7</td>
<td>5.6-7</td>
<td>Higher K&lt;sub&gt;IC&lt;/sub&gt; and hardness that HA alone.</td>
</tr>
<tr>
<td>(Kumar et al. 2005)</td>
<td>HA + 20 wt % ZrO₂</td>
<td>1050°-1100°</td>
<td>133</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
<td>5</td>
<td>Evidence of TCP, t-&amp;c-ZrO₂ &amp; CaZrO₃</td>
</tr>
<tr>
<td>(Rapacz-Knita et al. 2004)</td>
<td>HA + 20 wt % ZrO₂</td>
<td>1150-1300°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>ZrO₂ did not accelerate dehydroxylation or decomposition of HA when hot pressed.</td>
</tr>
<tr>
<td>(Erik et al. 2000) (Adolfsson et al. 2000)</td>
<td>HA + 85-20 vol% ZrO₂ (3mol% Y₂O₃)</td>
<td>1200°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>No detectable decomposition of HA.</td>
</tr>
<tr>
<td>(Evis and Doremus 2007b)</td>
<td>HA + 10-40 wt% m-ZrO₂</td>
<td>1100-1200°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.6-2.25</td>
<td>5-6.5</td>
<td>Porosity and HA decomposition increased with increasing amounts of ZrO₂ and temp. Mech properties increased with increase in ZrO₂. Additions of ZrO₂ above 2.5% led to decrease in density. Mech properties increased up 2.5% ZrO₂ and decreased with additional amounts.</td>
</tr>
<tr>
<td>(Towler and Gibson 2001)</td>
<td>HA + 1.5-20 wt % ZrO₂</td>
<td>1220</td>
<td>43-20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3-3.3</td>
<td>MgF₂ suppressed decomposition of HA, led to lower porosity and higher mech properties. Increase in mechanical properties with 1.5wt % ZrO₂, decreased with added ZrO₂.</td>
</tr>
<tr>
<td>(Evis and Doremus 2007a)</td>
<td>HA + 25 wt % ZrO₂ + 5 wt % MgF₂</td>
<td>1100-1200°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.8-2</td>
<td>6.25-6.5</td>
<td>Addion of 5 CaF₂, reduced the porosity &amp; increased mech properties.</td>
</tr>
<tr>
<td>(Edward et al. 2005)</td>
<td>HA + 1.5-15 wt % ZrO₂</td>
<td>1000°</td>
<td>243</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.3</td>
<td>Partial decomposition of the HA phase in TCP and TTCP become more intense as the sintering temperature increased.</td>
</tr>
<tr>
<td>(Hae-Won et al. 2002)</td>
<td>HA + 20wt% ZrO₂ +0-10wt% CaF₂</td>
<td>1300</td>
<td>132</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>Addition of 5 CaF₂, reduced the porosity &amp; increased mech properties</td>
</tr>
<tr>
<td>(Silva et al. 2001)</td>
<td>HA + 40-60wt% ZrO₂ (Ca-PSZ)</td>
<td>1200-1500</td>
<td>80-110</td>
<td>-</td>
<td>300-750</td>
<td>-</td>
<td>4.4-7.8</td>
<td>Partial decomposition of the HA phase in TCP and TTCP became more intense as the sintering temperature increased.</td>
</tr>
<tr>
<td>(Miao et al. 2004)</td>
<td>HA + 40wt% ZrO₂ (3mol% Y₂O₃)</td>
<td>1100-1250°</td>
<td>120-160</td>
<td>140-200</td>
<td>-</td>
<td>-</td>
<td>5.5-9</td>
<td>Above 1150 HA started to decompose to α-TCP. t-ZrO₂ phase remained throughout.</td>
</tr>
</tbody>
</table>

2.5 Microwave Sintering

In conventional thermal processing i.e. sintering, energy is transferred to the material via the transmission of heat from the surface to the bulk of the material. Microwave heating is fundamentally different, with microwave energy being delivered directly to the material through molecular interaction with an electromagnetic field (Thostenson and Chou 1999). The transfer of heat from the surface to the core, in conventional firing, results in high temperature gradients and stresses. However, in microwave heating, electromagnetic energy is converted directly to heat energy and is energy conversion rather than heat transfer. This difference results in several advantages associated with microwave sintering including, volumetric and rapid heating, inverse temperature profiles, reduced processing cost, reduced time, low power requirements, more uniform specimens and improved properties (Ramesh et al. 1999, Thostenson and Chou 1999, Clark and Sutton 1996).

2.5.1 Phenomenological Aspects of Microwaves

Microwaves are electromagnetic waves with a frequency range of ~300 MHz to ~300Ghz and an associated wavelength of ~1mm to ~1m. Microwaves can be transmitted, reflected and/or absorbed. Absorbed microwave energy is converted into heat within materials, resulting in an increase in temperature.

![Electromagnetic Spectrum and Microwave Range](image)

**Figure 2.22:** The electromagnetic spectrum and the microwave range. The most commonly used frequency is 2.45GHz with a wavelength of 12.2cm (Clark and Folz 2006).

The Federal Communications Commission (FCC) reserved two specific frequencies, 0.915 and 2.45GHz (Thostenson and Chou 1999, Clark and Sutton 1996)
for industrial, scientific and medical (ISM) purposes, of which 2.45GHz is most commonly used. At room temperature, most ceramics do not absorb appreciable amounts of microwaves at 2.45GHz. However, it is possible to increase their absorption by increasing the temperature, adding absorbing constituents (e.g. SiC, carbon, binders), altering the microstructure and defect structure, by changing their form (e.g. bulk versus powder), or by changing the frequency of the microwaves.

2.5.1 Ceramic Interactions with Microwaves

There are two ways in which materials can interact with microwaves: Polarisation and ionic conduction. Polarisation involves the short range displacement of charge centres through the formation and rotation of electric dipoles while conduction involves the long range transport of charge (Clark and Sutton 1996). Microwave processing of ceramics primarily involves the former. Interactions of microwaves with molecular dipoles results in the rotation of the dipoles and energy is dissipated as heat from the internal resistance to the rotation (Thostenson and Chou 1999).

![Diagram of dielectric properties](image)

**Figure 2.23.** The two absorption mechanisms that contribute to dielectric loss: ionic conduction and dipole rotation. The absorption curves for both mechanisms shift to higher frequencies when the temperature is increased. This can mean that a material can be poor absorber at room temperature (RT) and a high absorber of microwaves at (HT). Terms: x=distance, A=amplitude of the electric field, \(\varepsilon''_{\text{eff}}\) = effective dielectric constant (Clark and Folz 2006).

The degree of interaction and heating of ceramics in a microwave field is dependent on its dielectric properties, the relative dielectric constant (\(\varepsilon'\)) and the loss
factor ($\varepsilon''$) which are both frequency and temperature dependant (Clark and Folz 2006). The dielectric constant is a measure of the electrical polarisability of a given material e.g. the ability of dipoles and changes in the materials to respond to the microwave field (Siores and Rego 1995). The dielectric loss factor is a measure of the absorption losses (due to ionic conduction or rotation of dipoles), which is dissipated as heat (Clark and Folz 2006). The dielectric properties are commonly expressed in terms of the complex dielectric constant ($\varepsilon^*$) given by:

$$\varepsilon^* = \varepsilon' - i \varepsilon''$$ (2.15)

The dielectric response can also be expressed in terms of the loss tangent:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$ (2.16)

Loss tangent values are indicative of whether a material will be transparent (low loss), a good absorber (medium value), or a reflector (very high loss) of microwaves (Upadhyaya et al. 2001b). The rate at which a material can absorb energy is expressed in terms of the power absorbed per unit volume and is expressed as:

$$P = 2\pi f \varepsilon^* E^2$$ (2.17)

where $f$ is the frequency of the microwave radiation and $E$ is the amplitude of the field (Thostenson and Chou 1999). As the microwave energy is absorbed by the material, the microwave field decreases as a function of the distance from the surface of the material. The penetration depth ($D$) is defined as the distance from the surface at which the incident power is reduced by $e^{-1}$ (approximately 37%) of its surface value (Metaxas and Meredith 1983) and is expressed as:

$$D = \frac{3\lambda_0}{8.686\pi \tan \delta \left(\varepsilon'_0 \right)^\frac{3}{2}}$$ (2.18)

Where $\lambda_0$ is the incident wavelength ($\lambda_0 = 12.2$cm for 2.45GHz). From Equation 2.18 it can be seen that the loss tangent and the dielectric constant play a significant role in ability of microwaves to penetrate a given material. The higher the
dielectric properties the smaller the penetration depth will be at a given wave length. The penetration depth is of considerable importance when considering the processing of thick materials. If the penetration depth is much less than the thickness of the sample only the surface layers will be heated, with the rest of the sample being heated through conduction (Thostenson and Chou 1999) leading to non uniform specimens.

Ceramics tend to exhibit an abrupt increase in $\varepsilon''$ with respect to increasing temperature. The temperature at which this change occurs is known as the critical temperature ($T_c$). Below $T_c$, at a given frequency, the ceramic is a poor absorber and needs to be heated by an external source. Above $T_c$ the ceramic absorbs the microwaves. There is no equation that relates temperature to fundamental material properties; hence $T_c$ values must be measured (Clark and Folz 2006). The $T_c$ can pose some issues in the relation to the processing of complex and large samples. Unless heated uniformly by an external source, localised hot spots can develop in the material. These spots begin to absorb the microwaves before the rest of the material in a process known as “thermal runaway”. This can lead to the fracture and/or warping of samples. Thermal runaway can be limited by using uniform external heating and a homogeneous microwave field.

2.5.2 Microwave Sintering of Zirconia

Zirconia exhibits a dielectric loss factor different from those of other oxide and non oxide ceramics and does not couple with microwaves with a frequency of 2.45GHZ at room temperature. The loss factor ($\varepsilon''$) of Y-TZP at room temperature is similar to microwave transparent materials ($\varepsilon''_{TZP} \sim 0.04$) (Goldstein et al. 1999). However, since the dielectric loss increases with temperature ($\varepsilon''\sim 100$ at 1000°C), zirconia can be made absorptive by raising the temperature. There are two main methods used to achieve this:

1. A susceptor, generally silicon carbide (SiC), surrounds the specimen interacting with the microwave field at room temperature and heats the specimen through conventional thermal radiation to a critical temperature where the specimen interacts with the microwave field and the susceptor becomes transparent to the same field. This appears to be the more commonly used approach in literature (Goldstein et al. 1999, Upadhyaya et al. 2001b, Nightingale et al. 1997, Wilson and Kunz 1988).
2. Employ conventional resistive elements to initial heat the zirconia until a critical temperature is reached and the zirconia interacts with the microwave field of its own accord (Zhang et al. 2001).

In general, it is observed from literature that microwave sintering of zirconia can achieve comparable mechanical properties and densities to those of conventionally sintered samples, at lower temperatures and shorter duration (García-Gañán et al. 2006, Wilson and Kunz 1988, Upadhyaya et al. 2001a, Nightingale et al. 1997).

2.5.3 Microwave Sintering of HA

The microwave sintering of HA has been examined in the literature. (Nath et al. 2006) found that microwave sintered samples of HA exhibited higher densities than conventionally sintered samples, when sintered at the same temperatures. However, microwave samples sintered at 1000°C and 1100°C (with densities of 99% T.D.) tended to crack. Vijayan and Varma (2002) reported similar results. HA sintered at 1000°C for 5 minutes achieved theoretical densities of 95%. The authors again suggested that the major issue with microwave sintering was the densification of large samples without cracking.

In general, the literature agrees that microwave sintering of HA can produce samples with higher density and finer grain sizes at a fraction of the energy and time of conventional sintering. (Ramesh et al. 2007, Yang et al. 2002). Yang et al. (2002) also observed that microwave sintered samples exhibited no detrimental effect on the development of cell morphology. Table 2.9 indicates reported densities and mechanical properties of microwave processed HA. Densities of greater than 95% are achievable for microwave sintering times of 30 minutes.

<table>
<thead>
<tr>
<th>Property</th>
<th>Author</th>
<th>Value</th>
<th>Temperature</th>
<th>Sintering time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Density (%)</td>
<td>(Ramesh et al. 2007)</td>
<td>96</td>
<td>1100°C</td>
<td>30 mins</td>
</tr>
<tr>
<td></td>
<td>(Nath et al. 2006)</td>
<td>99</td>
<td>1000°C/1100°C</td>
<td>30 mins</td>
</tr>
<tr>
<td></td>
<td>(Vijayan and Varma 2002)</td>
<td>95</td>
<td>1000°C</td>
<td>5 mins</td>
</tr>
<tr>
<td>K\text{IC}</td>
<td>(Ramesh et al. 2007)</td>
<td>1.45</td>
<td>1050°C</td>
<td>30 mins</td>
</tr>
<tr>
<td>Hardness (GPa)</td>
<td>(Ramesh et al. 2007)</td>
<td>6.38</td>
<td>1150°C</td>
<td>30 mins</td>
</tr>
</tbody>
</table>
2.6 Rationale

The objective of this research is to examine an all ceramic bone filler material based on HA with increased strength and bioactivity, which can be tailored to a range of complex shapes for use in load-bearing skeletal (maxillofacial, orthopedic and vertebral) applications.

The first objective was to investigate the effect of microwave sintering on physical, mechanical and chemical properties of \( Y_2O_3 \) (2-5 mol\%) doped \( ZrO_2 \) compositions compared with conventional sintering. \( Y_2O_3 \) content was altered through the attrition milling of commercial undoped monoclinic \( ZrO_2 \) powders with co-precipitated \( Y_2O_3 \)-doped \( ZrO_2 \) powders and these were characterized using X-ray diffraction (XRD), particle size analysis (PSA), transmission electron microscopy (TEM) and BET. Comparative sintering was performed at temperatures of 1100, 1200 and 1300°C. Post sintering characterization consisted phase analysis (XRD), microstructural analysis using scanning electron microscopy (SEM), density measurements and mechanical testing, which included Young’s modulus, biaxial flexural testing and microhardness.

The second objective was to investigate the effect of microwave sintering on HA-\( ZrO_2 \) composites containing a commercial HA powder and HA synthesized using a co-precipitation technique and \( ZrO_2 \) with the optimum \( Y_2O_3 \) content for Y-TZP found in the initial stage. HA was initially synthesized at temperatures of 25 and 45°C and characterized using XRD, X-ray fluorescence (XRF), TEM and BET. Commercial HA composites containing 0, 5, 10, 20 & 40 wt % \( ZrO_2 \) additions and synthesized HA composites containing 0, 5 and 10 wt% \( ZrO_2 \) were comparatively sintered. Post sintering characterization again consisted of phase analysis (XRD), microstructural analysis using scanning electron microscopy (SEM), density measurements and mechanical testing, which included Young’s modulus, biaxial flexural testing and microhardness. Composites containing similar level of S-HA and \( ZrO_2 \) but also containing \( CaF_2 \) were also examined using similar techniques. The biocompatibility of HA-\( ZrO_2 \) composites were determined using \textit{In vivo} & \textit{In vitro} evaluation.
3. Experimental Procedure

Initially, ZrO₂ compositions with varying Y₂O₃ additions were examined in the regions where both a purely tetragonal phase and a combination of cubic/tetragonal phase (2~5 mol% Y₂O₃) would be expected. The powder compositions were characterised, compacts pressed and microwave and conventionally sintered to identify an optimum ZrO₂-Y₂O₃ composition. Hydroxyapatite composites were then produced from a combination of laboratory synthesised or commercial HA using a variety of ZrO₂ contents and Y₂O₃ dopants. The composites were pressed and microwave and conventionally sintered. The sintered composites were then characterised in terms of phase composition and microstructure and mechanical properties were tested.

3.1 Materials

3.1.1 Y₂O₃ doped ZrO₂ Compositions

Commercial co-precipitated 3 & 8 mol% Y₂O₃ ZrO₂ (Tosoh TZ-3Y & TZ-8Y, Tosoh Corporation, Tokyo) powders were mixed with a Y₂O₃ free monoclinic powder (Tosoh TZ-0, Tosoh Corporation, Tokyo) to obtain mixtures containing 2, 3, 4 & 5 mol% Y₂O₃ (Table 3.3.1). The powder mixtures were attrition milled for one hour using distilled water as a medium, in a Netzsch Molinex attrition mill with 3mm diameter ZrO₂ beads and a silicon carbide pot and stirrer. The attrition milling ensures the powders are thoroughly mixed and the particle size is reduced and regulated. The use of ZrO₂ grinding media limits the amount of contamination to the powder.

Table 3.3.1: Powder mixtures

<table>
<thead>
<tr>
<th>Tosoh Starting Powders</th>
<th>Mol% Y₂O₃</th>
<th>Milled Mixtures</th>
<th>Resultant mol% Y₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>TZ-0Y</td>
<td>0</td>
<td>TZ-0Y + TZ-3Y</td>
<td>2</td>
</tr>
<tr>
<td>TZ-3Y</td>
<td>3</td>
<td>TZ-3Y</td>
<td>3</td>
</tr>
<tr>
<td>TZ-8Y</td>
<td>8</td>
<td>TZ-0Y + TZ-8Y</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TZ-0Y + TZ-8Y</td>
<td>5</td>
</tr>
</tbody>
</table>

3.1.2 Freeze Drying & Pressing (ZrO₂)

The attrition milled slurry was frozen rapidly using a shell freezer and the powder was then recovered using a freeze dryer. The rapidly frozen suspension of solids ensures that no sedimentation occurs thus maintaining the homogenous distribution of the attrition milled powders. Freeze drying exploits the triple point property of water to remove the liquid via sublimation. The freeze dryer consists of an evacuated
refrigeration unit to which the flasks, containing the attrition milled slurry, can be attached. Following freezing of the mixture, by lowering the pressure in the flasks below the triple point of water it should be possible for the ice to thaw, but if there is not enough pressure for a liquid to form, it becomes a gas. This is drawn through the vacuum system where it condenses and forms ice on the walls of the refrigeration unit.

The freeze dried powders were then sieved through a 90 micron sieve to remove agglomerates. The powdered mixtures were then uni-axially pressed using a 20mm diameter stainless steel die under a pressure of 80MPa. These pellets were subsequently isostatically pressed in a Stansted Fluid Power isostatic press to a pressure of approximately 150 MPa to remove density gradients introduced by the wall of the die used with the uni-axial pressing. The formed pellets weigh approximately 3g with dimensions approximately 3mm thick and 19mm in diameter.

3.1.3 HA Synthesis

Samples of pure HA were produced by a simple precipitation method based on that of Jarcho et al. (1976). Production temperatures of 25°C and 45 °C were investigated. HA was synthesised by the drop-wise addition of laboratory reagent grade di-ammonium hydrogen orthophosphate \([\text{NH}_4\text{HPO}_4]\) (Fisher Scientific Ltd, Leicestershire, UK) into laboratory reagent grade calcium nitrate hydrated \([\text{Ca(NO}_3)_2.4\text{H}_2\text{O}]\) (Fisher Scientific Ltd, Leicestershire, UK). The solution was kept basic above a pH of 10.0 by the addition of laboratory reagent grade ammonium hydroxide \([\text{NH}_4\text{OH}]\) (Sigma Aldrich).

3.1.4 Precipitation synthesis of HA

78.72g (0.3335 mol) of \(\text{Ca(NO}_3)_2.4\text{H}_2\text{O}\) in 600ml of water was made basic through the addition of 10ml of \(\text{NH}_4\text{OH}\). 26.41g (0.200 mol) of \((\text{NH}_4)_2\text{HPO}_4\) was made basic in 1066ml of water through the addition of 25ml of \(\text{NH}_4\text{OH}\). The \(\text{Ca(NO}_3)_2.4\text{H}_2\text{O}\) and \((\text{NH}_4)_2\text{HPO}_4\) solutions were stirred vigorously to ensure the powders were completely dissolved. Both solutions were brought to the desired synthesis temperature, while still under continuous vigorous stirring, and the \((\text{NH}_4)_2\text{HPO}_4\) was added dropwise from a glass funnel into the \(\text{Ca(NO}_3)_2.4\text{H}_2\text{O}\) solution over an interval of 60 minutes. Throughout the synthesis the pH was kept above 10.0 by the addition of \(\text{NH}_4\text{OH}\) at constant intervals to avoid “shock to the system”, i.e. a sudden large pH increase of ± 0.5. Once drop-wise addition was completed, the solution was kept at the synthesis temperature for one hour under the same stirring conditions. The sample was then left to
stand for 24 hrs at room temperature. The supernatant was removed and replaced with fresh distilled water, re-stirred for one hour and left to stand again for 24 hours. This procedure was undertaken three times to remove any unwanted residue from the precipitate. Before filtering the solution under vacuum, a sample of the precipitate suspension was taken as this was used for particle size analysis (PSA), transmission electron microscopy (TEM) and Energy dispersive X-ray spectroscopy (EDX). Once the suspension sample was obtained, the supernatant was removed a final time and replaced with distilled water and spun for 15 minutes. The suspension was then filtered under vacuum, using a Buchner filter and distilled water until the ammonia was removed. The filter cake was then removed from the filter and placed into a beaker and dried in a fan assisted oven at 85°C for 20 hours. The synthesis of HA was performed at production temperatures of 25°C and 45°C.
Figure 3.1. Flow chart of the precipitation process of HA.
3.1.5 HA Powder Preparation

The filter cake was dried in an oven at 85°C for 20 hours, ground using a pestle and mortar and then sieved in a 90 micron sieve. Powder preparation is similar for each of the composites.

3.1.6 Hydroxyapatite-Zirconia (HA-ZrO₂)

Two types of HA in the HA-ZrO₂ composites were examined, one containing commercial HA and 3mol % Y₂O₃ in ratios of 95:5, 90:10, 80:20 & 60:40 wt% and the second composition consisting of synthesised HA with 95:5 and 90:10 wt% ZrO₂ additions of differing Y₂O₃ content. The method of mixing the composites was identical in both cases. The ZrO₂ was added to containers in amounts ranging from 5 to 40 wt% of the weight of the HA into HDPE containers. The HA-ZrO₂ containers were then ball milled using twelve alumina balls as milling medium for 6 hours. 1.3g of the resultant powder was pressed in a 20mm diameter die, under a pressure of approximately 80MPa tons and left for 30 seconds. Each sample set contained 9 pellets.

3.2 Green Powder Characterisation

The characterisation of both ZrO₂, HA and HA-ZrO₂ composites was carried out in a similar fashion.

3.2.6 Phase Analysis by X-ray Diffraction (XRD)

The ZrO₂ & HA powders were pressed into ethyl-cellulose pellets using a 32mm stainless steel die. These were then placed in an X-ray Diffractometer (Philips X’Pert), using Cu-Kα as the radiation source, for an initial scan covering a range of 10° to 70°, with a step size of 0.083° and a step time of 120.015 seconds. The XRD patterns were then matched to patterns in the JCPDS database, using the X’Pert software, to determine the phases present. Analysis of the obtained spectra was also performed in Origin Pro 8 (OriginLab Corporation, Massachusetts, USA).

3.2.4 Transmission electron microscopy (TEM)

Images of the powders were obtained using a JOEL JEM-2011 electron microscope with STEM attachment (Tokyo, Japan). Using a syringe, one drop of suspension solution was dropped onto a 3mm circular copper grid and was examined under a microscope to ensure that the precipitate solution coated the copper grid. The sample was then placed into the column of the TEM under vacuum, running at 200KV, and viewed under magnifications allowing resolutions ranging from 0.5 μm to 100 nm.
Selected-Area Electron Diffraction (SAED) was then performed on various particulate samples.

### 3.2.2 Particle Size Analysis

Particle size analysis was performed on both original and attrition milled zirconia powders and both HA powders using a Malvern Mastersizer 2000 (Worcestershire, UK), attached to a personal computer running Mastersizer software. Dispersant was added to approximately 5ml of a suspension of the powders in distilled water. The suspension was agitated for 1 minute using ultrasound to disperse the particles throughout the water. The suspension fluid was then added to the Malvern Mastersizer along with de-ionised water where it was continuously agitated by stirring and ultrasound. The particle size distribution profile, the median particle size ($D_{0.5}$) and the particle diameter values at 10% and 90% ($D_{0.1}$ and $D_{0.9}$, respectively) on the cumulative frequency curve were recorded.

### 3.2.3 Surface Area Measurement

The surface area of both the HA and Zirconia powders was determined using the BET method. (micrometrics ASAP 2010, USA) utilising nitrogen as the adsorbate. Approximately 0.5~1g of powder was weighed to an accuracy of 0.0001g and was degassed overnight at a temperature of 120°C in a vacuum. The degassed sample was removed and weighed again to determine the degassed weight. The sample was then attached to the ASAP and the programme was run. The surface area of the powder was then used to estimate an average particle size using the following relationship:

$$D_{(BET)} = \frac{6000}{(\rho S_{(BET)})}$$  \hspace{1cm} (3.1)

Where $D_{(BET)}$ is the average particle size, $S_{(BET)}$ is the surface area and $\rho$ is the density (g/cm$^3$).

### 3.2.5 X-ray Fluorescence (XRF)

XRF is used to determine the chemical composition of the HA powder synthesised at 25°C. The testing of the powders was sourced out to Ceram (Stoke-on-Trent, UK). A full report of the chemical analysis was received along with the calcium to phosphorous ratio (Ca:P).
3.3 Sintering

3.3.1 Dilatometry

The sintering shrinkage was determined using a Netzsch Dil 402 C (Stoke-on-Trent, UK) dilatometer. It consists of a moveable furnace, sample holder and a push rod. The sample is placed in the sample holder and is held in place by a minute force exerted by the push rod, the furnace is slid shut with the sample contained inside and it runs through a programmed cycle. As the sample expands/contracts the push rod measures this change in dimension and relates the information back to the computer. This allows a graph of temperature versus change in sample length to be plotted indicating the onset temperature of sintering. For green sample dilatometry, cylindrical shaped compacts approximately 7.5mm in length and 8mm in diameter were placed into the dilatometer which was programmed with a heating profile of ambient temperature to 1400°C at a heating rate of 5°C/min. These results were corrected against an alumina standard of approximately the same dimensions as the samples to compensate for the expansion of the sample holder and the push rod. The densification of a compact powder during the intermediate stage of sintering can be described by

\[
\frac{\left( \frac{\Delta l}{l_0} \right)}{T} = \text{const} \times \exp \left( \frac{-nE_A}{RT} \right)
\] (3.2)

where \( T \) is the temperature, \( n \) is a constant that describes the path for material transport (\( n = 1 \) = viscous diffusion, \( n = 0.5 \) = volume diffusion and \( n = 0.33 \) = grain boundary diffusion), \( E_A \) is the activation energy and \( R \) is the universal gas constant.

By plotting \( \ln \left( \frac{\Delta l}{l_0} \right) \) vs. \( \frac{1}{T} \) a straight line with slope \( \frac{-nE_A}{R} \) is obtained when only one single mechanism is operative (Theunissen et al. 1993, Young and Cutler 1970).
3.3.2 Microwave & Conventional Sintering

Samples were microwave sintered (MS) using a microwave furnace with a cavity of 33 cm x 22 cm x 31 cm lined with an alumino-silicate fibreboard insulating material (Fiberfrax Duraboard™, Unifrax LLC, USA). Power is provided by a 1.45kW magnetron (I.B.F. Electronic, Germany), which is regulated by a programmable process controller (Eurotherm 3214, Eurotherm Ltd, UK). Temperature is measured using an optical pyrometer (Land Instruments, UK) focused directly onto the samples which does not influence or interfere with the microwave field distribution within the cavity. Traditional metal thermocouples can interfere with the microwave field within the cavity preventing accurate measurements from being made. The pyrometer was calibrated at several temperature points using a type B Pt-Rh thermocouple placed in contact with the samples when the magnetron was deactivated. The small thickness of the samples ensures that axial temperature gradients are small. In the case of ZrO$_2$ samples a constant power output of ~700, 650 & 600W was employed to sinter the samples at 1300, 1200 and 1100°C respectively. This system was further optimised for the HA-ZrO$_2$ composites by increasing the maximum power output of the magnetron and by directly connecting the pyrometer to the controller allowing for a more precise control of the power output and hence heating rate.

The homogeneity of the field within the cavity was tested by lining the floor of the furnace with sample vials containing 2ml of distilled water, running the magnetron for a short time and measuring the temperature of the individual vials using an electronic thermometer probe (Accumet®, Fisher Scientific Ireland Ltd, Ireland).

A hybrid heating method for sintering the ceramic samples utilized a nested crucible assembly with a surrounding silicon carbide (SiC) layer into which the green zirconia bodies to be fired were inserted (n=9 per firing). This method minimizes thermal gradients within the individual samples and homogenizes the temperature within the crucible itself through mutual heating, whilst providing the ability to conventionally heat them to a critical temperature beyond which they heat solely due to microwave radiation absorption (Ramesh et al. 1999). Figure 3.2 indicates the temperature profile of microwave sintered samples. Between~ 1100-1200°C onwards, the energy absorption is almost completely balanced by thermal losses from the system and the heating rate decreases markedly.
Chapter 3 Experimental Procedure

Figure 3.2. Microwave sintering heating profile of ZrO₂ Compositions.

The conventional sintering (CS) of composites was carried out in an elite furnace (Elite thermal systems) which approximated the heating rates observed in the microwave furnace as seen in Figure 3.3.

Figure 3.3. Conventional furnace heating profile.

Figure 3.4 plots the temperature profile of the microwave sintered HA-ZrO₂ composites. A constant maximum microwave voltage was maintained until a temperature of 663°C was reached. The time taken to reach this temperature was found to be approximately 32 minutes upon which a 10°C/min ramp rate was employed to the given temperature. The composites were fired at four temperatures between 1000-1300°C with a hold time of 1 hour and comparatively sintered using a similar heating profile in an elite furnace.
3.4 Characterisation of Sintered Materials

Characterisation of the ZrO₂, HA and HA-ZrO₂ composites was carried out on each in a similar manner. Phase analysis was performed using XRD. Density and porosity measurements were determined using an Archimedes technique. Young’s modulus was determined using an ultrasound technique. The flexural strength and hardness were determined using standard tests. SEM analysis was performed on the fracture surfaces.

3.4.1 Phase Analysis by XRD

The sintered pellets were loaded into the X-ray Diffractometer (Philips X’Pert) carrousel, using Cu-Kα as the radiation source and scanned with the same set-up as Section 3.2.6. The XRD patterns were then matched to patterns in the JCPDS database using the X’Pert software to determine the phases present. The volume fraction of m-ZrO₂ was calculated from the relative intensities of the principle m-ZrO₂ and t/c-ZrO₂ peaks in the range 28-32° 2θ (Yoshimura 1988).

\[
V_m = \frac{1.311X_m}{1+0.311X_m} \tag{3.3}
\]

\[
X_m = \frac{I_{(111)m} + I_{(111)c}}{I_{(111)c} + I_{(111)m} + I_{(111)m}} \tag{3.4}
\]
where $V_m$ is the monoclinic volume and $X_m$ is the relative intensity of the monoclinic peaks. Quantitative phase analysis was performed on HA-ZrO$_2$ composites by analyzing the XRD traces of composites using X’pert Highscore software suite (Panalytical, Netherlands) in order to identify the amounts of HA, ZrO$_2$ and possible degradation phases present in the CS and MS sintered HA-ZrO$_2$ composites. Inorganic Crystal Structure Database (ICSD) files were matched to phases in the samples by X’Pert Highscore and converted to CIF files to perform Rietveld analysis.

### 3.4.2 Density & Porosity

The relative (bulk) densities and open porosities of the sintered bodies were measured using an immersion method on a Sartorius YDK-01 balance kit. Samples were weighed in air and then placed in a chamber under a high vacuum for 1 hour. Water was introduced into the chamber without breaking the vacuum. The samples were left for 2 hours under vacuum to allow the water to penetrate the pores. The samples were then removed from the vacuum and excess water was absorbed from the surface using absorbent paper. The samples were then weighed in air and subsequently in water. The density was calculated using the following equation:

$$\rho = \left[ \frac{W_a \rho_f - 0.0012}{0.99983 W_a - W_f} \right] - 0.0012$$

(3.5)

where $W_a$ is the weight of the saturated sample in air, $W_f$ is the weight of the body when submerged in a fluid, $\rho_f$ is the density of the fluid, which is dependent on the temperature of the water, (0.0012) is a correction due to the density of air and (0.99983) is a correction due to the buoyancy of the sample holder. The theoretical density of HA-ZrO$_2$ composites were calculated using the following equation:

$$Composite_{TD} = \rho / \rho_{th}$$

(3.6)

where $\rho$ is the measured density of the sample and $\rho_{th} = \sum x_i \rho_i$ and $x_i$ is the weight fraction of each phase (HA, $\alpha$-TCP, $\beta$-TCP, c-, t- and m-ZrO$_2$) and $\rho_i$ is the theoretical density of each phase.
3.4.3 Microhardness

Samples were mounted in epoxy and finely polished to a mirrored surface using a 20μm grinding wheel and 9μm and 3μm diamond slurries on polishing cloths using a Buehler Motopol 2000 wheel. The Vickers hardness was measured using a Leco M-400-G1 tester by applying either a 1kg load (ZrO₂) or a 100g load (HA samples) through a diamond tip to form an indentation, measuring the diagonals of the indent, and applying the following formula:

\[ H_V = \frac{2PS\sin{\theta}}{d^2} \]  

(3.7)

where \( H_V \) is Vickers’s hardness, \( P \) is the applied load, \( \theta \) is the apex angle of the diamond tip and \( d \) is the mean of the measured indentor diagonals.

3.4.4 Elastic Modulus (E)

The elastic moduli of sintered Y₂O₃ doped ZrO₂ and ZrO₂-HA composites were obtained using ultrasound measurements. The method used was an adaptation of ASTM C1198-01 (Diaz et al. 2005) which requires samples with uniform rectangular/cylindrical cross sections, of between 3 and 5mm long and also to have parallel end faces to which the transducers are attached. The test method employs the use of two transducers, one which generates a transverse wave and the other which generates a longitudinal wave. One transducer is attached, at a time, to one end of the sample with a sonically conductive medium. An ultrasonic pulse with a frequency of 5 kHz is generated by the transducer and propagates through the sample. This pulse is reflected off the opposite side of the sample and picked up by the transducer, which displays the echo on an oscilloscope. The time between subsequent echoes measures a time of flight (t.o.f), the time taken for the pulse to propagate through the sample and return. Measurements for both longitudinal and transverse waves are taken. For the longitudinal pulse a vegetable oil medium is employed, while the transverse pulse uses honey. Three measurements of time are made between the successive echoes using a digital oscilloscope and the results are averaged. The time of flight and the thickness of the sample are used to calculate the velocity of sound through the medium using the following equation:

\[ V_i = \frac{2L}{(t.o.f.)_i} \]  

(3.8)
where \( V_i \) is the velocity (where \( i \) indicates “l” for longitudinal and “t” for transverse) (m/s), t.o.f. is the time of flight (sec) and \( L \) is the thickness of sample (m). The Young’s modulus can then be calculated using the following equation:

\[
E = \frac{\rho[3V_l^2 - AV_t^2]}{\frac{V_l^2}{V_i^2} - 1}
\]

(3.9)

where \( E \) is the Young’s modulus (GPa), \( \rho \) is the density of the sample (g/cm\(^3\)), \( V_l \) is the longitudinal sound velocity calculated for the sample (m/s) and \( V_t \) is the transverse sound velocity calculated for the sample (m/s). The shear modulus \( (G) \), bulk modulus \( (B) \) and Poisson’s ratio \( (v) \) of the material can also be calculated from the acoustic test using the following relations (Ori Yeheskel 1999):

\[
G = \rho V_l^2
\]

(3.10)

\[
B = \frac{EG}{3(3G - E)}
\]

(3.11)

\[
v = \frac{E}{2G} - 1
\]

(3.12)

3.4.5 Biaxial flexural Strength

3.4.5.1. Yttria-doped Zirconia (Y\(_2\)O\(_3\)-ZrO\(_2\))

Disc shaped sintered Y\(_2\)O\(_3\)-ZrO\(_2\) samples were ground to a thickness of approximately 2mm. The circular faces were then polished to a mirror finish before flexural testing. A biaxial flexural strength rig with a base containing three 2mm diameter ball bearings sitting 120 degrees apart at the circumference of a circle with diameter of 8mm. The disc shaped samples sit on the ball bearings. A load was applied perpendicular to the face at the centre of the sample using a hardened steel pin of diameter 1.58mm with a thin layer of plastic to cushion the pin and distribute the load evenly over its cross section. The jig is placed in a load frame attached to a 5kN load cell and then loaded at a rate of 0.1mm/min. The load/displacement and the load at
fracture are then recorded. The biaxial flexural strength is then calculated from the load at fracture using the following equation:

\[ s = -0.2387 \frac{P(X - Y)}{d^2} \]  

(3.13)

X and Y are calculated using the following relationships:

\[ X = (1 + \nu) \ln \left( \frac{B}{C} \right)^2 + \left( \frac{1 - \nu}{2} \right) \left( \frac{B}{C} \right)^2 \]  

(3.14)

\[ Y = (1 + \nu) \left[ 1 + \ln \left( \frac{A}{C} \right)^2 \right] + (1 - \nu) \left( \frac{A}{C} \right)^2 \]  

(3.15)

where \( \nu \) is Poisson’s ratio, \( A \) is the radius of the support circle, \( B \) is the radius of the sample and \( C \) is the radius of the loaded area (1.58mm).

3.4.5.2 Hydroxyapatite-Zirconia (HA-ZrO₂) Composites

The biaxial flexural strengths of the HA-ZrO₂ composites were determined using a method similar to that of Williams (2001) using a three support bearing on the test rig. The test jig was fixed to an Instron universal testing machine using a load cell of 1kN at a crosshead speed of 1 mm.min⁻¹. Sample thickness was measured at the point of fracture using a digital vernier calliper. The biaxial flexural strength (SS) was calculated according to the formula:

\[ SS(MPa) = \frac{Load(N)}{t^2} \left[ (1 + \nu) \{0.485 \ln(\frac{a}{t}) + 0.52\} + 0.48 \right] \]  

(3.16)

where \( SS \) is the biaxial flexural strength, \( \nu \) is Poisson’s ratio (calculated using the ultrasound technique), \( a \) is the radius of the support diameter (mm) and \( t \) is the thickness of the specimen.

3.4.6 Scanning Electron Microscopy (SEM) of Fracture Surfaces

Scanning electron microscopy and energy dispersive X-Ray analysis (SU70 FE-SEM, Hitachi high technologies Europe, Krefelel, Germany) were performed on the fracture surface of the biaxial flexural tested samples. The average grain size of samples was determined using the mean linear intercept method of polished and etched surfaces proposed by Wurst and Nelson (1972), using the following relationship:
where $D$ is the average grain size, $C$ is the total length of the line used, $N$ is the number of grain boundary intercepts on the line and $M$ is the magnification of the micrograph. In the case of ZrO$_2$ compositions this equation was used on SEM images of the fracture surface and not polished and etched surfaces. In HA-ZrO$_2$ composites polished and etched fracture surfaces were examined.
4. Zirconia (Reinforcing Phase)

4.1 Green powder characterisation

4.1.1 Phase Analysis by X-ray Diffraction (XRD)

The phase analysis of the as-received bulk Tosoh powders are shown in Figure 4.1. The major peaks were identified using X'Pert Highscore and a search match of known ICSD patterns. In the case of the TZ-0Y, the closest match found is Baddeleyite or monoclinic ZrO$_2$ (86-1451). The presence of peaks at 28.2° and 31.5° 2θ and the absence of a peak at 30° 2θ in TZ-0Y confirm that the powder is entirely monoclinic.

The closest match to the TZ-3Y powder is tetragonal Zirconium Yttrium Oxide (ICSD 01-078-1808). A search match of the TZ-8Y revealed a closest match with cubic Zirconium Yttrium Oxide (ICSD 01-077-2114). It is difficult to distinguish between the cubic and tetragonal forms of ZrO$_2$ due to similarities in the major peaks; however, the increase in Y$_2$O$_3$ between TZ-3Y and TZ-8Y results in the convergence of the tetragonal (002) and (110) peaks at 34.6° and 35.1° 2θ, respectively, into one cubic (200) peak at 34.4° 2θ and, similarly, the convergence of the t(103) and t(211) peaks at 59.3° and 60° 2θ, respectively, into one c(311) peak at 58.7° 2θ. The minor peaks in the TZ-3Y powder at 28.2° and 31.5° 2θ indicate that there is a residual amount of monoclinic phase present. The amount of monoclinic phase can be obtained from the relative intensities of these peaks compared to the major peak at 30° 2θ. In the case of TZ-3Y, 22 volume % monoclinic phase is observed.

![Figure 4.1. XRD phase analysis of the as received ZrO$_2$ powders.](Image)
The XRD phase analysis of the attrition milled powders is shown in Figure 4.2. Monoclinic ZrO$_2$ phase is present in all of the samples, which is consistent with the fact that monoclinic powders were added to the co-precipitated powders to alter the Y$_2$O$_3$ content. While it is difficult to distinguish between the cubic and tetragonal phases in these powders, the samples with 2 and 3 mol % Y$_2$O$_3$ both exhibit peaks at 34.6° and 35.1° 2θ, which is indicative of a tetragonal ZrO$_2$ phase. The 4 and 5 mol % Y$_2$O$_3$ compositions exhibit one major peak at approximately 34° 2θ indicating a primarily cubic phase.

![Figure 4.2. XRD phase analysis of the attrition milled powders.](image)

The volume % monoclinic ZrO$_2$ content of the bulk and attrition milled powders determined from the relative intensities of the monoclinic and the tetragonal/cubic phase are reported in Table 4.1. The Y$_2$O$_3$ free powder is entirely monoclinic, while the 8 mol % Y$_2$O$_3$ powder contains no monoclinic phase. The attrition milled powders all contain a similar level of monoclinic phase of between 21~25% which is consistent with the fact that Y$_2$O$_3$ free ZrO$_2$ monoclinic powders were added to the co-precipitated Y$_2$O$_3$ doped ZrO$_2$ powders.

**Table 4.1.** Monoclinic phase present in the bulk and the attrition ZrO$_2$ powders.

<table>
<thead>
<tr>
<th>As received powders</th>
<th>Attrition milled powders</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mol % Y$_2$O$_3$</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>21</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.1.2 Particle Size Analysis (PSA)

The particle size analyses using laser diffraction of the as received bulk powders and the attrition milled powders are shown in Figure 4.3 and Figure 4.4. There is a bimodal particle size distribution evident in the as received powders, with particles ranging in size from 0.04 µm to approximately 20 µm. The PSA analysis indicates that 10% of the particles \( d_{(10)} \) are less than 0.102 µm, 50% of the particles \( d_{(50)} \) are less than 0.888 µm and 90% of the particles \( d_{(90)} \) are less than 4.169 µm.

The attrition milling of the power has considerable effects on the particle size and distribution. There is a significant reduction in the \( d_{(10)} \), \( d_{(50)} \) and \( d_{(90)} \) of the powder to 0.073 µm, 0.170 µm and 1.158 µm respectively. There is a decrease in the peak in the 1-2 µm range from 4.5 volume % to 3 volume % and a corresponding increase in the peak in the range of 0.1-0.2 µm from 3.8 volume % to 8 volume %, indicative of the significant reduction in the size of the particles. While the mean particle size is reduced from a micron to a submicron size, the bimodal distribution is not entirely eliminated.

Table 4.2 indicates the particle size of the as received powders and the mixed compositions. The attrition milled powders exhibit similar particle size distributions.
irrespective of the amount of Y$_2$O$_3$ doping. The $d_{(10)}$ of the powders varied from 71 to 73 nm, the $d_{(50)}$ varied from 146 to 170 nm and the $d_{(90)}$ varied from 1.185 to 1.158 μm. The attrition milling for 1 hr reduces the particle size of the powders; however it could not fully remove the bimodal distribution of particles. In the case of a narrow nano-particle distribution it can be difficult to obtain a high green density, desirable for optimum densification, due to high frictional forces between nano-particles (Lu 2008). With a bimodal size distribution, the smaller particles may fill the interstices between the larger particles and increase the green density. However, it is also possible that small amounts of larger particles will not increase the packing density but instead act as seeds for abnormal grain growth during sintering (Lu 2008).

Table 4.2. Particle size of the bulk and attrition milled powders.

<table>
<thead>
<tr>
<th>As received powders</th>
<th>Attrition milled powders</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mol % Y$_2$O$_3$</td>
</tr>
<tr>
<td>0</td>
<td>0.072</td>
</tr>
<tr>
<td>3</td>
<td>0.102</td>
</tr>
<tr>
<td>8</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>5</td>
</tr>
</tbody>
</table>
4.1.3 Transmission Electron Microscopy (TEM)

The transmission electron micrographs of the attrition milled ZrO₂ powders are shown in Figure 4.5. The particle morphology of the powders is generally similar for all the Y₂O₃ doped compositions. The particles are spherical in shape with an approximate size in the range 40-70nm but are agglomerated into larger structures several hundred nanometres in size. The particles size observed in the TEM images are lower than those observed using the laser diffraction technique. This may be because the laser diffraction technique will measure agglomerates as particles whereas TEM gives direct observation and measurement.

Figure 4.5. TEM image of attrition milled ZrO₂ powders; (a) 2 mol% Y₂O₃ (b) 3 mol% Y₂O₃ (c) 4 mol% Y₂O₃ and (d) 5 mol% Y₂O₃. Scale bar = 100nm.
4.1.4 Accelerated Surface Area & Porosimetry using Brunauer Emet and Teller method (ASAP BET)

The specific surface area (S\textsubscript{BET}) and equivalent spherical diameter (ESD\textsubscript{BET}) results are shown in Table 4.2 along with the mean particle size (d\textsubscript{50}) determined using laser diffraction. The surface area varied between 23.4 and 15.4 m\textsuperscript{2}/g. There is no correlation between increasing Y\textsubscript{2}O\textsubscript{3} content and the specific surface area. The highest S\textsubscript{BET} is observed in the 2 mol\% Y\textsubscript{2}O\textsubscript{3} doped ZrO\textsubscript{2} and the lowest was observed in the 4 mol \% Y\textsubscript{2}O\textsubscript{3} composition. Similar values for Tosoh 3Y-TZP of 16.1 and 14.52 m\textsuperscript{2}/g have been reported in literature by Seidensticker, Mayo and Osseo-Asare (1993) and Hasanuzzaman, Rafferty, Olabi and Prescott (2008).

Table 4.3. BET surface area and average particle size determined using ASAP and PSA.

<table>
<thead>
<tr>
<th>Mol % Y\textsubscript{2}O\textsubscript{3}</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>S\textsubscript{BET} (m\textsuperscript{2}/g)</td>
<td>23.4</td>
<td>17.4</td>
<td>15.4</td>
<td>18.8</td>
</tr>
<tr>
<td>ESD\textsubscript{BET} (nm)</td>
<td>42</td>
<td>57</td>
<td>65</td>
<td>53</td>
</tr>
<tr>
<td>d\textsubscript{50} (nm)</td>
<td>146</td>
<td>170</td>
<td>163</td>
<td>160</td>
</tr>
<tr>
<td>TEM (nm)</td>
<td>40-70</td>
<td>40-70</td>
<td>40-70</td>
<td>40-70</td>
</tr>
</tbody>
</table>
4.3 Sintering

4.3.1 Dilatometry

The green powders were pressed uniaxially into cylindrical green compacts 8mm in diameter and approximately 9.5mm in length and subjected to non-isothermal dilatometric analysis to identify the optimum sintering temperature and the effect of the Y$_2$O$_3$ dopant on the sintering temperature. Samples were heated at a rate of 5°C/min to a maximum temperature of 1400°C. Figure 4.6 shows the shrinkage curves (black line) for the zirconia compositions with 2-5 mol% Y$_2$O$_3$ along with the 1st derivative of the shrinkage curve (red line) indicating the densification rate.

Initially all compacts exhibited a small level of thermal expansion which was arrested on the onset of sintering between approximately 1000-1100°C. The maximum densification rate for zirconia with both 2 and 3 mol% Y$_2$O$_3$ occurs at similar temperatures of 1230 and 1222°C, respectively, while higher temperatures of 1298 and 1296°C are observed, respectively, in the case of zirconia with 4 and 5 mol% Y$_2$O$_3$. This suggests that the higher mol% Y$_2$O$_3$ compositions lead to increases in the optimal sintering temperature.

![Figure 4.6](image_url)

**Figure 4.6.** Shrinkage (black line) and densification rate (red line) of ZrO$_2$ doped with 2 to 5 mol% Y$_2$O$_3$ measured using dilatometry with a constant heating rate of 5°C/min.
The densification of a powder compact during the initial stages of sintering has previously been described in Section 3.3.1. On plotting the $-\ln[(\Delta l/l_0)/T]$ versus $1/T$ determined using the dilatometry shrinkage curve from a change of length of between 1 and 10 percent (Figure 4.7), the slope of the line obtained is equal to $nE_A/R$ when only one densification mechanism is present. Assuming that either grain boundary diffusion ($n=0.33$) or volume diffusion ($n=0.5$) are the major densification mechanism, the apparent activation energy for densification for each powder was determined (Theunissen et al. 1993).

![Figure 4.7. Arrhenius plot of $-\ln[(\Delta l/l_0)/T]$ versus $1/T$ reciprocal of temperature for the initial sintering stage of $Y_2O_3$ doped $ZrO_2$. The slope of each line was used to determine the apparent activation energy for densification $E_A$.](image)

In Table 4.4 the onset temperature, the temperature at maximum densification and the activation energies of densification, calculated using the slopes in Figure 4.8, of all $Y_2O_3$ doped $ZrO_2$ compositions are presented. The lower temperatures of onset and maximum densification in the case of $ZrO_2$ with 2 and 3 mol % $Y_2O_3$ are consistent with the lower activation energies observed.

<table>
<thead>
<tr>
<th>Mol % $Y_2O_3$</th>
<th>Onset Temp (°C)</th>
<th>Maximum densification rate (°C)</th>
<th>Activation Energy (kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$n = 0.5$</td>
</tr>
<tr>
<td>2</td>
<td>1072</td>
<td>1230</td>
<td>346</td>
</tr>
<tr>
<td>3</td>
<td>1064</td>
<td>1222</td>
<td>338</td>
</tr>
<tr>
<td>4</td>
<td>1102</td>
<td>1298</td>
<td>428</td>
</tr>
<tr>
<td>5</td>
<td>1095</td>
<td>1296</td>
<td>432</td>
</tr>
</tbody>
</table>
4.3.2 Relative density

The relative densities of all Y₂O₃ doped ZrO₂ compositions, both microwave and conventionally sintered at 1100, 1200 and 1300°C, are shown in Figure 4.8. For both CS and MS compositions the relative density increases as the sintering temperature increases. Relative density either increases slightly or remains similar as Y₂O₃ content increases from 2 to 3 mol% and then decreases slightly with further increase in Y₂O₃ content except at 1300°C, where a slight increase in density is observed for MS samples from 4 to 5 mol% Y₂O₃ and for the CS samples, a general increase is observed with Y₂O₃ content.

At 1100°C there is a significant difference between the relative densities of MS and CS compositions. The relative density of MS samples ranges from 87.3% (±5.3) for the 3 mol % Y₂O₃ composition, which has the highest density, down to 82.9% (±5.55) for the 5 mol % Y₂O₃ composition (lowest density). The trends for the CS samples are the same but densification is much lower resulting in relative densities of between 65.6% (±0.7) for the 3 mol % Y₂O₃ composition (highest density for CS) and 61.3% (±0.3) for the 5 mol % Y₂O₃ composition (lowest density). At this lower temperature, while there is greater densification in the case of the microwave sintered samples, the standard deviations of densities of the microwave processed samples are much greater than the conventionally sintered samples.

![Figure 4.8](image.png)

**Figure 4.8.** Relative density of Y₂O₃ doped ZrO₂ compositions microwave (MS) and conventionally (CS) sintered at temperatures of 1100 to 1300°C.

At 1200°C the differences between MS and CS samples are much less pronounced. Whilst the MS samples exhibit greater densities than CS samples, the difference is only significant (~5% difference) in the case of the ZrO₂ with 2 mol % Y₂O₃. The relative
densities of the MS samples vary from 90.2% (±4.6) for the 3 mol % Y$_2$O$_3$ composition (highest density) to 85.2% (±3.3) for the 5 mol % Y$_2$O$_3$ composition (lowest density). The CS samples range from 84.7% (±0.7) to 87.5% (±0.4) for the 5 and 3 mol % Y$_2$O$_3$ compositions, respectively. Again the standard deviation in densities is considerably larger in the MS samples.

At 1300°C, higher relative densities of 96.8% (±0.5) and 96.3% (±0.9) are observed in the MS ZrO$_2$ with 2 and 3 mol % Y$_2$O$_3$, respectively, compared to their CS counterparts with relative densities of 90.5% (±2.4) and 92.5% (±0.5), respectively. Relative density decreases slightly for the MS samples as more Y$_2$O$_3$ dopant is added so that there is no difference in density between the MS and CS ZrO$_2$ with 4 and 5 mol % Y$_2$O$_3$. Even at the maximum temperature of 1300°C it was not possible to reach a relative density greater than 97%, most likely due to the short duration of the sintering.

Overall, microwave sintering gave higher densities than conventional sintering, particularly for ZrO$_2$ with 2 and 3 mol % Y$_2$O$_3$.

### 4.3.3 Phase Analysis of sintered zirconia

The X-ray diffraction patterns of both microwave (MS) and conventionally sintered (CS) Y$_2$O$_3$ doped ZrO$_2$ samples sintered at 1100°C together with the identification of major peaks are shown in Figure 4.9.

![Figure 4.9](image)

Figure 4.9. XRD traces of conventionally sintered (CS) and microwave sintered (MS) 2-5 mol % Y$_2$O$_3$ doped ZrO$_2$ samples at 1100°C.

Both the CS and MS 2 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions show significant peaks at 28.2° and 31.5° 2θ which is indicative of a monoclinic ZrO$_2$ phase. Using the
relative intensities of these peaks to the peak at 30° 2θ it was determined that the CS and MS samples contained 93.1% 66.6% monoclinic respectively. There is no evidence of monoclinic ZrO$_2$ in any of the compositions containing greater than 2 mol % Y$_2$O$_3$, irrespective of the sintering technique and despite considerable amounts of monoclinic ZrO$_2$ in the green powders. In both MS and CS samples, a similar trend in phase assemblages is observed as the Y$_2$O$_3$ content is increased. The 3 mol % Y$_2$O$_3$ compositions contain two peaks at 34.6° and 35.1° 2θ, two at 50.2° and 50.6° 2θ and another two peaks at 59.3° and 60° 2θ, indicating that the tetragonal phase is prevalent. In the 4 mol % compositions, while there are peaks evident at 34.6°, 35.1°, 59.3° and 60° 2θ, they are beginning to converge and there is only one peak observed at 50° 2θ. This suggests that there is an increase in the amount of cubic phase at the expense of tetragonal ZrO$_2$. In the case of the samples containing 5 mol % Y$_2$O$_3$, single peaks at 34°, 50° and 58.7 suggest that the cubic form of ZrO$_2$ has now entirely formed in the place of the tetragonal phase.

In Figure 4.10 the XRD patterns of both MS and CS compositions sintered at 1200°C are shown. The CS 2 mol % Y$_2$O$_3$ composition again consists almost entirely of a monoclinic phase (88.6%). The MS 2 mol % Y$_2$O$_3$ sample also shows a large amount of monoclinic ZrO$_2$ (45.3%). Samples containing 3-5 mol % Y$_2$O$_3$ have been stabilised as either tetragonal/cubic ZrO$_2$ with no trace of a monoclinic phase. Increases in Y$_2$O$_3$ again lead to increasing amounts of cubic phase at the expense of tetragonal ZrO$_2$.

![Figure 4.10. XRD traces of conventionally sintered (CS) and microwave sintered (MS) 2-5 mol % Y$_2$O$_3$ doped ZrO$_2$ samples at 1200°C.](image)

The XRD patterns of both MS and CS compositions sintered at 1300°C are shown in Figure 4.11. The CS 2 mol % Y$_2$O$_3$ composition again consists primarily of a
monoclinic phase, with only 13.3% tetragonal phase stabilized. The MS 2 mol % Y₂O₃ sample, however, has been almost entirely stabilized into a tetragonal phase, with only 5.5% monoclinic phase present. Similar to the lower temperatures, samples containing 3-5 mol % Y₂O₃ have been stabilised as either tetragonal/cubic ZrO₂ with no trace of a monoclinic phase. Increases in Y₂O₃ again lead to increasing amounts of cubic phase at the expense of tetragonal ZrO₂.

**Figure 4.11.** XRD traces of conventionally sintered (CS) and microwave sintered (MS) 2-5 mol % Y₂O₃ doped ZrO₂ samples at 1300°C.

At all temperatures, the 2 mol % Y₂O₃ doped ZrO₂ samples are the only compositions that show mainly a monoclinic ZrO₂ structure. In Figure 4.12 the effect of temperature on the phases present in conventionally sintered samples is shown. As the sintering temperature increases from 1100 to 1300°C, there is a small increase in the amount of tetragonal phase present, indicated by the small growth of the peak at 30° 2θ. However the major peak remains at high intensity representing 86.7 % monoclinic ZrO₂ at 1300°C.

**Figure 4.12.** XRD traces of ZrO₂ doped with 2 mol % Y₂O₃ conventionally sintered at 1100, 1200 and 1300°C.
Figure 4.13 shows the evolution of the tetragonal and monoclinic phases present in the case of the samples microwave sintered in the range 1100-1300°C. There is an increase in the intensity of the tetragonal peak at 30° 2θ and a corresponding reduction in the monoclinic peaks at 28.2° and 31.5° 2θ to very low intensity as the microwave sintering temperature is increased to 1300°C.

Figure 4.13. XRD traces of ZrO$_2$ doped with 2 mol % Y$_2$O$_3$ microwave sintered at 1100, 1200 and 1300°C.

The volume % monoclinic phase present in the CS and MS 2 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions sintered in the range 1100-1300°C is shown in Table 4.1. At a sintering temperature of 1100°C, the major phase in both CS and MS samples is monoclinic ZrO$_2$, irrespective of the sintering technique, although the amount present in the MS samples is much less at 66.6% compared with 93.1% for CS samples. As temperature increases, the amount of monoclinic in CS samples only reduces slightly whereas in the MS samples, the amount of monoclinic ZrO$_2$ reduces to a very low level (5.5%) with the formation of tetragonal ZrO$_2$.

Table 4.5. Volume % monoclinic phase present in samples containing 2 mol % Y$_2$O$_3$. The remaining phase in each case is t-ZrO$_2$.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Volume % Monoclinic phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CS</td>
</tr>
<tr>
<td>1100</td>
<td>93.1</td>
</tr>
<tr>
<td>1200</td>
<td>88.6</td>
</tr>
<tr>
<td>1300</td>
<td>86.7</td>
</tr>
</tbody>
</table>
4.3.4 Elastic Moduli

4.3.4.1 Young’s Modulus

The Young’s modulus of both MS and CS Y$_2$O$_3$ doped ZrO$_2$ compositions are shown in Figure 4.14. The stiffness exhibits a similar trend to the relative density in that values of modulus increase slightly or remain similar as Y$_2$O$_3$ content increases from 2 to 3 mol% and then decrease slightly with further increase in Y$_2$O$_3$ content except at 1300°C, where for both MS and CS samples, values for 2 and 3 mol% Y$_2$O$_3$ are similar and then a slight increase is observed at higher Y$_2$O$_3$ contents. At a sintering temperature of 1100°C, MS compositions exhibit 2~3 times greater modulus than their CS counterparts depending on the Y$_2$O$_3$ dopant content. In the case of MS samples the modulus ranges from 165 GPa (±39) to 116 GPa (±45) for the 3 and 5 mol % Y$_2$O$_3$ compositions, respectively. The CS modulus values range from 48.5 GPa (±3.8) to 40 GPa (±5) for the 2 and 5 mol % Y$_2$O$_3$ compositions, respectively. The standard deviations of modulus values are also significantly larger in the MS samples. At 1200°C MS samples exhibit higher Young’s moduli than their CS counterparts and are all significantly different with the exception of the 5 mol % Y$_2$O$_3$ composition.

![Figure 4.14](image_url)  
Figure 4.14. Young’s modulus of ZrO$_2$ compositions microwave (MS) and conventionally (CS) sintered at temperatures of 1100 to 1300°C.

At a sintering temperature of 1300°C, the MS samples also exhibit slightly higher moduli than their CS counterparts, with the exception of the CS ZrO$_2$ with 5 mol % Y$_2$O$_3$ which exhibits the highest Young’s modulus with a value of 206 GPa (±2.5); the
MS 5 mol % Y\textsubscript{2}O\textsubscript{3} composition exhibits a similarly high Young’s modulus with a value of 204 GPa (±3). The MS ZrO\textsubscript{2} with 2 mol% Y\textsubscript{2}O\textsubscript{3} has a significantly higher modulus than its CS counterpart with values of 196 GPa (±5) and 183GPa (±6), respectively. The increase in Young’s modulus in the MS samples, particularly at the lower temperatures, is primarily due to the increased density achieved using the microwave sintering. As the sintering temperature is increased the differences in property values between samples from both sintering techniques is reduced considerably.

### 4.3.4.2 Shear Modulus

Figure 4.15 illustrates the shear modulus of MS and CS Y\textsubscript{2}O\textsubscript{3} doped ZrO\textsubscript{2} samples sintered at temperatures of 1100, 1200 and 1300°C. For all samples, as for Young’s modulus, an increase in temperature leads to an increase in the shear modulus and the effect of Y\textsubscript{2}O\textsubscript{3} content generally also follows similar trends to those for Young’s modulus. This is primarily due to the increase in the density achieved with higher sintering temperatures. MS samples exhibit higher values of shear modulus than their CS counterparts at a temperature of 1100°C, with values for MS samples ranging from a maximum of 53GPa (±23) for 5 mol % Y\textsubscript{2}O\textsubscript{3} and ~45GPa (±14) for 2 and 3 mol % Y\textsubscript{2}O\textsubscript{3} compared with values in the range 16-20GPa (±1.6) for the CS compositions.

![Shear modulus graph](image)

**Figure 4.15.** Shear modulus of 2-5 mol % Y\textsubscript{2}O\textsubscript{3} doped ZrO\textsubscript{2} compositions microwave (MS) and conventionally (CS) sintered at temperatures of 1100 to 1300°C.

At 1200°C, MS 2 and 3 mol % Y\textsubscript{2}O\textsubscript{3} samples exhibit higher values of shear modulus than their CS counterparts, ranging from 71.6GPa (±5.1) for 3 mol % Y\textsubscript{2}O\textsubscript{3} and 70.9GPa (±5.1) compared with values of 57-60GPa (±2.3) for the CS compositions.
The 2 mol % Y₂O₃ compositions are the only samples that are statistically greater that their conventionally sintered counterparts at a sintering temperature of 1300°C.

### 4.3.4.3 Bulk Modulus

The bulk modulus of MS and CS Y₂O₃ doped ZrO₂ samples sintered at temperatures of 1100-1300°C is shown in Figure 4.16. Both the MS and CS samples exhibit an increase in the bulk modulus as the sintering temperature is increased and at all temperatures, greater values of modulus are observed in MS samples over CS samples, irrespective of the mol % Y₂O₃ dopant. However, at 1300°C, both CS and MS 4 and 5 mol % Y₂O₃ compositions have similar bulk moduli. The standard deviations observed in MS sintered samples are generally larger than those observed in CS samples. The maximum bulk modulus observed was 185GPa (±8.8) in the case of MS 2 mol % Y₂O₃ doped ZrO₂. The bulk modulus appears to be predominantly dependant on the relative density achieved.

![Figure 4.16. Bulk modulus of 2-5 mol % Y₂O₃ doped ZrO₂ compositions microwave (MS) and conventionally (CS) sintered at temperatures of 1100 to 1300°C.](image)

### 4.3.4.4 Poisson’s ratio

The Poisson’s ratio of Y₂O₃ doped ZrO₂ compositions microwave and conventionally sintered from 1100°C to 1300°C is shown in Figure 4.31. The Poisson’s ratio varies from approximately 0.2 to 0.31 depending on the sintering temperature and mol % Y₂O₃ dopant used. A similar trend to that for Young’s modulus is observed, with an increase in the sintering temperature leading to an increase in the Poisson’s ratio in both the MS and CS samples. With a sintering temperature of 1100°C microwave
sintered samples exhibit higher average values of Poisson’s ratio compared with the CS samples. However, this is only statistically different in samples containing 2 and 5 mol % Y₂O₃. At sintering temperatures of 1200°C and higher, there is no statistical difference between the Poisson’s ratio of CS and MS sintered compositions. The standard deviation in values of Poisson’s ratio is again greater in the MS samples than for their CS counterparts.

Figure 4.17. Poisson’s ratio of 2-5 mol % Y₂O₃ doped ZrO₂ compositions microwave (MS) and conventionally (CS) sintered at temperatures of 1100 to 1300°C.

4.3.5 Biaxial Flexural Strength

The biaxial flexural strengths of both CS and MS Y₂O₃ doped ZrO₂ compositions are shown in Figure 4.18. The strengths of both MS and CS samples increase as the sintering temperature is increased. At a sintering temperature of 1100°C the MS samples exhibit higher strengths on the order of 3~4 times greater than their CS counterparts. The strengths of MS Y₂O₃ doped ZrO₂ range from ~294 MPa (±170) and 303 MPa (±39) for the 2 and 3 mol % Y₂O₃ compositions to 146 MPa (±31) for the 5 mol % Y₂O₃ composition. The strengths of CS compositions, by comparison, range from 90 MPa (±22) for 2 mol % Y₂O₃ doped ZrO₂ to 40 MPa (±5) in the case of the 5 mol % Y₂O₃ composition. The higher strengths for MS samples are more likely due to the higher relative densities observed compared with the CS samples.
Figure 4.18. Biaxial flexural strength of 2-5 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions microwave (MS) and conventionally (CS) sintered at temperatures of 1100 to 1300°C.

At a temperature of 1200°C, the MS compositions exhibit greater strengths than their conventionally sintered counterparts; however the wide variation of standard deviations suggests that there is no statistical difference between the MS and CS samples. The highest strength was observed for the MS 3 mol % Y$_2$O$_3$ composition with a value 462 MPa (±124), close to the MS 2 mol % Y$_2$O$_3$ composition with a value 440 MPa (±203). For both MS and CS samples, strength decreases as Y$_2$O$_3$ dopant increases from 3 to 5 mol %. The lowest strength was observed for the CS 5 mol % Y$_2$O$_3$ composition with a value of 237 MPa (±33) which compares with ~334 MPa (±118) for its MS counterpart. At 1300°C there is no statistical difference between the strengths of MS and CS compositions with the exception of the 2 mol % Y$_2$O$_3$ composition which exhibits a much greater strength of 807 MPa (±83) which is almost 300 MPa higher than the strength of the next nearest composition, with 3 mol % Y$_2$O$_3$, with a value of 540 MPa (±51), despite these compositions having similar relative densities of 96.8 and 96.3%, respectively.

4.3.6 Vickers Hardness

The Vickers Hardness of both microwave and conventionally sintered Y$_2$O$_3$ doped ZrO$_2$ samples is shown in Figure 4.19. A similar trend to both the biaxial flexural strength and Young’s modulus is observed in that, values of hardness increase as Y$_2$O$_3$ content increases from 2 to 3 mol% and then decrease as Y$_2$O$_3$ content increases further, except at 1300°C where, values for the MS samples increase at 5 mol% Y$_2$O$_3$ and for the CS samples, hardness values increase from 2 to 5 mol% Y$_2$O$_3$ content. This
indicates that hardness is, as before, primarily dependant on the final density achieved. The hardness of MS compositions at 1100°C is significantly higher than their CS counterparts; however the deviation in the values for the MS samples is greater than those observed in the CS samples. The highest value observed at a sintering temperature of 1100°C is the MS 3 mol % Y₂O₃ sample with a value of 6.3GPa (±3.7) and the lowest value observed is that of the CS 5 mol % Y₂O₃ with a value of 0.9GPa (±0.05).

![Figure 4.19. Vickers Hardness of 2-5 mol % Y₂O₃ doped ZrO₂ compositions microwave (MS) and conventionally (CS) sintered at temperatures of 1100 to 1300°C.](image)

At the sintering temperature of 1200°C the MS samples again exhibit higher hardness values than the CS samples; however only the 3 mol % Y₂O₃ composition is significantly different with a value of 9.8 GPa (±1.4) for the MS samples compared to 7.4 GPa (±0.6) for the CS counterparts. At the higher temperature of 1300°C both the 2 and 3 mol % Y₂O₃ MS samples exhibit significantly higher hardness values of 11.6 GPa (±0.55) and 12.5 GPa (±0.64), respectively, compared to the CS samples with values of 7.2 GPa (±0.4) and 9.6 GPa (±0.6), respectively.
4.3.7 Microstructural Analysis of sintered zirconia

All samples sintered at 1300°C were examined using scanning electron microscopy (SEM). The fracture surfaces of 2 mol % Y$_2$O$_3$ doped ZrO$_2$ samples both conventionally and microwave sintered at 1300°C are shown in Figure 4.20. The grain size observed in the MS sample is significantly larger than that of the CS sample. There is considerable residual porosity evident in the CS sample compared with the MS sample.

![Figure 4.20](image)

Figure 4.20. Scanning electron micrographs of the fracture surfaces of 2 mol % Y$_2$O$_3$ doped ZrO$_2$ (a) conventionally sintered and (b) microwave sintered at a temperature of 1300°C. Scale bar = 1µm.

The fracture surfaces of both MS and CS 3 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions are shown in Figure 4.21. Similar grain sizes are observed in both compositions. There is also evidence of porosity present in both samples.

![Figure 4.21](image)

Figure 4.21. Scanning electron micrographs of the fracture surfaces of 3 mol % Y$_2$O$_3$ doped ZrO$_2$ (a) conventionally sintered and (b) microwave sintered at a temperature of 1300°C. Scale bar = 1µm.

The fracture surfaces of both MS and CS 4 and 5 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions are shown in Figure 4.22 & Figure 4.23, respectively. There are similar
grain sizes observed in both compositions. There is also again evidence of residual porosity present in all samples.

Figure 4.22. Scanning electron micrographs of the fracture surfaces of 4 mol % Y₂O₃ doped ZrO₂
(a) conventionally sintered and (b) microwave sintered at a temperature of 1300°C. Scale bar = 1µm.

Figure 4.23. Scanning electron micrographs of the fracture surfaces of 5 mol % Y₂O₃ doped ZrO₂
(a) conventionally sintered and (b) microwave sintered at a temperature of 1300°C. Scale bar = 1µm.

The grain size of Y₂O₃ doped ZrO₂ samples both conventionally (CS) and microwave (MS) sintered at 1300°C is presented in Table 4.6. The grain sizes in CS and MS samples are, for the most part, comparable with grain sizes in the range 180-220nm except for MS ZrO₂ samples containing 2 mol % Y₂O₃ which differ from other compositions having grain sizes on the order of 150nm larger (d = 353nm).
Table 4.6. Grain sizes obtained using the linear intercept method for $Y_2O_3$ doped $ZrO_2$ compositions both microwave (MS) and conventionally sintered (CS) at 1300°C.

<table>
<thead>
<tr>
<th>Sintering method</th>
<th>2 mol % $Y_2O_3$</th>
<th>3 mol % $Y_2O_3$</th>
<th>4 mol % $Y_2O_3$</th>
<th>5 mol % $Y_2O_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>353</td>
<td>200</td>
<td>183</td>
<td>180</td>
</tr>
<tr>
<td>CS</td>
<td>200</td>
<td>192</td>
<td>206</td>
<td>223</td>
</tr>
</tbody>
</table>

4.3.8 Summary of Mechanical Properties

A summary of properties determined for samples sintered using both MS and CS techniques is presented in Table 4.7 with a comparison to properties of Y-TZP bioceramics (Heimann 2002).

Table 4.7. Summary of MS and CS properties.

<table>
<thead>
<tr>
<th>Sample (mol %$Y_2O_3$)</th>
<th>Linear Shrinkage (%)</th>
<th>Relative Density (%)</th>
<th>E (GPa)</th>
<th>Poisson's ratio</th>
<th>Flexural Strength (MPa)</th>
<th>Hardness (GPa)</th>
<th>Phases Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-TZP*</td>
<td>-</td>
<td>&gt;99</td>
<td>210</td>
<td>-</td>
<td>900-1300</td>
<td>12-13</td>
<td>t</td>
</tr>
<tr>
<td>MS 1300</td>
<td>2</td>
<td>21.5</td>
<td>96.9</td>
<td>196</td>
<td>0.31</td>
<td>807</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>21.8</td>
<td>96.3</td>
<td>196</td>
<td>0.31</td>
<td>540</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.6</td>
<td>93.2</td>
<td>191</td>
<td>0.29</td>
<td>493</td>
<td>10.9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>21.2</td>
<td>95.3</td>
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<td>0.30</td>
<td>421</td>
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</tr>
<tr>
<td>CS 1300</td>
<td>2</td>
<td>18.6</td>
<td>90.6</td>
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<td>316</td>
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</tr>
<tr>
<td></td>
<td>3</td>
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<td>92.5</td>
<td>184</td>
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<td>507</td>
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<tr>
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<td>5</td>
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<td>206</td>
<td>0.31</td>
<td>471</td>
<td>12.4</td>
</tr>
<tr>
<td>MS 1200</td>
<td>2</td>
<td>17.1</td>
<td>90</td>
<td>183</td>
<td>0.28</td>
<td>440</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>18.2</td>
<td>90.2</td>
<td>187</td>
<td>0.30</td>
<td>462</td>
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<tr>
<td></td>
<td>4</td>
<td>16.2</td>
<td>87.7</td>
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</tr>
<tr>
<td></td>
<td>5</td>
<td>16.8</td>
<td>85.3</td>
<td>170</td>
<td>0.27</td>
<td>333</td>
<td>6.7</td>
</tr>
<tr>
<td>CS 1200</td>
<td>2</td>
<td>16.6</td>
<td>84.9</td>
<td>151</td>
<td>0.28</td>
<td>281</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>17.7</td>
<td>87.5</td>
<td>145</td>
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<td>358</td>
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<tr>
<td></td>
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<td>86.1</td>
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<tr>
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<td>84.7</td>
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<td>0.28</td>
<td>236</td>
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<tr>
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<td>86.6</td>
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<td>0.27</td>
<td>294</td>
<td>4.8</td>
</tr>
<tr>
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<td>3</td>
<td>16.9</td>
<td>87.3</td>
<td>165</td>
<td>0.27</td>
<td>303</td>
<td>6.3</td>
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<td></td>
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<td>14.5</td>
<td>82.9</td>
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</tr>
<tr>
<td></td>
<td>5</td>
<td>14.6</td>
<td>82.9</td>
<td>120</td>
<td>0.25</td>
<td>146</td>
<td>3.8</td>
</tr>
<tr>
<td>CS 1100</td>
<td>2</td>
<td>8.2</td>
<td>65.6</td>
<td>49</td>
<td>0.22</td>
<td>89</td>
<td>2</td>
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<tr>
<td></td>
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<td>42</td>
<td>0.22</td>
<td>85</td>
<td>2</td>
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<tr>
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<td>4</td>
<td>6.9</td>
<td>64.2</td>
<td>40</td>
<td>0.23</td>
<td>62</td>
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<td>61.3</td>
<td>42</td>
<td>0.20</td>
<td>39</td>
<td>0.9</td>
</tr>
</tbody>
</table>

*(Heimann 2002)
4.4 Discussion

4.4.1 Green powders

The particle size analysis using laser diffraction indicates that attrition milling for duration of 1hr decreases the mean particle size of the Y$_2$O$_3$-doped ZrO$_2$ powders. However it was not entirely possible to remove the bimodal distribution of the powders. There is a discrepancy between the particle size observed using laser diffraction and the particle size determined using the BET method. The $d_{50}$ calculated using laser diffraction was in the range 146-170nm while the ESD$_{BET}$ was in the range 42-65nm. Similar results have been observed previously for 3Y-TZP powders. Using laser diffraction, Hasanuzzaman et al. (2008) reported a particle size of 147nm and an ESD$_{BET}$ of 69nm for a similar powder. It was suggested that the ZrO$_2$ powders can be prone to agglomeration when dispersed in water which cannot be fully removed through sonication, therefore resulting in a larger $d_{50}$ observed using laser diffraction. The ESD$_{BET}$ values are consistent with particle sizes of 40-70nm observed using transmission electron microscopy which suggests that a similar effect is occurring here since it was also observed by TEM that particles are agglomerated into larger structures several hundred nanometres in size.

4.4.2 Dilatometry

Both 2 and 3 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions exhibit lower shrinkage onset temperatures and lower temperatures at which the maximum densification rate occurred (1230 and 1222°C, respectively) than the 4 and 5 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions (1298 and 1296°C, respectively) when subjected to non-isothermal heating of 5°C/min. This indicates that the lower mol % Y$_2$O$_3$ compositions exhibit higher sinterability. In the case of nano-crystalline 3 mol % Y$_2$O$_3$ doped ZrO$_2$ (Durán et al. 1996), a maximum densification rate was observed at a temperature of 1180°C. A similar value of 1200°C has also been observed (Theunissen et al. 1993) for Tosoh 3 mol % Y$_2$O$_3$ doped ZrO$_2$.

From the slope obtained in Figure 4.7 and assuming that grain boundary diffusion is the major densification mechanism, the apparent activation energies for densification ($E_A$) range from 524 and 512 kJmol$^{-1}$, for the 2 and 3 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions, to 648 and 655 kJmol$^{-1}$ for the 4 and 5 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions. Using a similar approach and assuming grain boundary diffusion, values ranging from 275-540 kJ mol$^{-1}$ have been reported for 3 mol % Y$_2$O$_3$ stabilised ZrO$_2$ powders (Theunissen et al. 1993, Durán et al. 1996), while Gibson and Dransfield
(1998) reported a value of between 605 and 645 kJ mol\(^{-1}\) for commercial 8 mol % Y\(_2\)O\(_3\) stabilised ZrO\(_2\) powders. This would suggest that an increase in the Y\(_2\)O\(_3\) content increases the apparent activation energy for densification. Whilst the E\(_A\) calculated using dilatometry are similar to those observed in literature, this approach does have some limitations. The main drawback is the fact that there is no single dominant densification mechanism present during sintering. Particularly during the early stages of sintering, there are multiple densification mechanisms at work and the activation energies calculated generally results from these multiple mechanisms (Fang and Wang 2008).

### 4.4.3 Densification effects

Higher densities were generally achieved in MS samples compared to CS samples at sintering temperatures of 1100-1300°C, as seen in Figure 4.8. The greatest microwave sintering effects were observed at a sintering temperature of 1100°C, where there was much greater densification by approximately 20% in MS samples compared with CS samples, irrespective of composition. The differences in densification between MS and CS samples tends to decrease as the sintering temperature/densification increases. This is consistent with microwave effects observed in literature for 3 and 8 mol % Y\(_2\)O\(_3\) doped ZrO\(_2\) (Nightingale et al. 1997, Janney et al. 1992, Goldstein et al. 1999), Al\(_2\)O\(_3\) ceramics (Brosnan K. H. et al. 2003) and also ZrO\(_2\)/Al\(_2\)O\(_3\) composites (Lee and Case 1999, Samuels and Brandon 1992).

The relative densities after both MS and CS sintering at various temperatures of Y\(_2\)O\(_3\) doped ZrO\(_2\) ceramics observed in the present study and compared with other studies in the literature are reported in Table 4.8. In terms of Y\(_2\)O\(_3\) doped ZrO\(_2\), Nightingale et al. (1997) determined that microwave sintering resulted in a downward shift in effective sintering temperature of approximately 50°C at temperatures of ~1300°C and this shift decreased as the temperature increased. Larger enhancements of greater than 100°C downward shift in effective sintering temperature were observed by both Goldstein et al. (1999) and by Janney et al. (1992) in 3 and 8 mol % Y\(_2\)O\(_3\) doped ZrO\(_2\). In the present study an intermediate shift in effective sintering temperature of between ~50 and ~100°C was observed.
Table 4.8. Relative densities after both MS and CS sintering at various temperatures of Y$_2$O$_3$ doped ZrO$_2$ ceramics – comparison of present study with literature.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Relative Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>3 mol % Y$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>MS</td>
</tr>
<tr>
<td>1100</td>
<td>86.6</td>
</tr>
<tr>
<td>1200</td>
<td>90</td>
</tr>
<tr>
<td>1250</td>
<td>-</td>
</tr>
<tr>
<td>1300</td>
<td>96.3</td>
</tr>
<tr>
<td>1350</td>
<td>-</td>
</tr>
<tr>
<td>1400</td>
<td>-</td>
</tr>
<tr>
<td>1450</td>
<td>-</td>
</tr>
<tr>
<td>1500</td>
<td>-</td>
</tr>
</tbody>
</table>

The enhancement in densification during microwave sintering has also been theorised to be related to an interaction between the electromagnetic field and oxygen vacancies and thus it would be expected that greater concentrations of Y$_2$O$_3$ would lead to a greater microwave enhancement. For example, (Janney et al. 1993) observed that zirconia doped with 12 mol % CeO$_2$ showed a much smaller enhancement of densification when using microwaves compared to 8 mol % Y$_2$O$_3$. The authors attributed the difference to the higher ionic conductivity of the Y$_2$O$_3$ doped ZrO$_2$ which is greater than that of CeO$_2$ doped ZrO$_2$ by a factor of approximately 100. An opposite effect was seen here, with MS of both 2 and 3 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions exhibiting slightly higher densification than the samples containing 4 and 5 mol % Y$_2$O$_3$. Rather than being directly attributable to the amount of Y$_2$O$_3$ dopant present, this is more likely an effect of the lower activation energies for densification in the 2 and 3 mol % Y$_2$O$_3$ compositions. In terms of increasing amounts of Y$_2$O$_3$, Nightingale et al. (1997) could not identify any microwave enhancements in ZrO$_2$ with between 3 and 8 mol % Y$_2$O$_3$. 


4.4.4 Microwave Sintering issues

In Figure 4.24 some of the difficulties observed during the microwave sintering of ZrO$_2$ are shown. At higher temperatures there was a tendency for isolated samples to be subjected to asymmetrical shrinkage and hence warping and cracking (Figure 4.24 (a)). Also there were variations in shrinkage of samples being microwave sintered as shown in Figure 4.24 (b). This became more prevalent as the sintering temperature decreased. These effects are symptomatic of localised hot spots within the microwave cavity. The first issue is a potential consequence of the rapid rise in ε” with increase in temperature, which can lead to localised hot spots and temperature gradients within a sample (Clark and Folz 2006). If this occurs it is referred to as thermal runaway (unstable accelerated heating) and can result in the destruction of a sample (Clark and Sutton 1996).

The hybrid heating method in this study utilized a nested crucible assembly consisting of a surrounding SiC layer into which the green Y$_2$O$_3$ doped ZrO$_2$ bodies were inserted. This method is designed to minimize thermal gradients within the individual samples and homogenize the temperature within the crucible itself through mutual heating, whilst providing the ability to conventionally heat them to a critical temperature beyond which they heat solely due to microwave radiation absorption (Ramesh et al. 1999). While the cracking of samples was limited, it was not entirely eliminated.

The limited size of the cavity combined with a fixed frequency, the absence of a mode stirrer or a rotating turntable can result in regions where EM fields are strong and regions where they are weak. While the crucible was placed in a position within the cavity to maximize the exposure to the microwaves, a non-homogenous EM field would explain the large variation observed in some MS samples.
4.4.5 Mechanical Properties & Porosity Effects

There is significant amount of porosity present in both CS and MS samples which generally decreases as the sintering temperature increases. Porosity has a significant effect on the physical properties of brittle materials. In the context of mechanical properties, the dependence of Young’s modulus, strength and hardness on porosity is generally well described by the following empirical exponential relationship (Rice 1998):

\[ A = A_0 \exp(-b_A P) \]  
(4.2)

where \( A_0 \) is the value of the property at zero porosity, \( b_A \) is a measure of the rate of decrease in \( A \) with increasing \( P \). This equation tends to hold for low to intermediate values, ranging from zero porosity (theoretically fully dense ceramics) to volume fraction porosities of between 0.3 and 0.4 (Rice 2000a). In Figure 4.25 the effect of volume fraction porosity on the elastic modulus of all conventionally sintered samples as well as the exponential empirical fit are shown. In the case of CS samples, the coefficient of determination (\( r^2 \)) to the exponential fit is 0.986 indicating a high correlation between experimental data and the empirical relationship. The value predicted for the fully dense elastic modulus (\( E_0 \)) is 229.5 GPa which agrees well with values reported in the literature.

\[ E = E_0 \exp(-b_E P) \]
\[ E_0 = 229.5 \]
\[ b_E = 4.42 \]
\[ r^2 = 0.986 \]

![Figure 4.25. Young’s modulus of \( \text{Y}_2\text{O}_3 \) doped \( \text{ZrO}_2 \) samples conventionally sintered (CS) vs. the volume fraction porosity.](image)

In the case of MS samples (Figure 4.26) there is a lower \( r^2 \) value of 0.909. A similar \( E_0 \) to that of the CS samples of 234.5 GPa is predicted. Luo and Stevens (1999) observed a similar agreement in 3Y-TZP ceramics between experimental data for elastic modulus, determined using an ultrasound pulse-echo technique, and porosity according to the empirical exponential relationship. A coefficient of determination of 0.985 for the exponential fit, an \( E_0 \) value of 216 GPa and \( b_E \) of 3.69 were determined over a volume fraction porosity range of 0.0 to 0.1.
fraction porosity range of 0-0.4. Winnubst, Keizer and Burggraaf (1983) also determined a similar relationship in ZrO$_2$ ceramics containing between 7.5 and 8.7 mol \% Y$_2$O$_3$. By using a pulse-echo technique for determining Young’s modulus, an exponential fit with coefficient of determination of 0.975, $E_0$ of 221 GPa and $b_E$ of 2.7 where determined. This relationship was also identified in ZrO$_2$ solid oxide fuel cells containing both 3 and 8 mol \% Y$_2$O$_3$ (Selçuk and Atkinson 1997).

![Figure 4.26. Young’s modulus of Y$_2$O$_3$ doped ZrO$_2$ samples microwave sintered (MS) vs. the volume fraction porosity.](image)

The relationship has also been experimentally observed in other ceramics. Ren et al. (2009) demonstrated that the Young’s modulus of both Al$_2$O$_3$ and HA followed this relationship over two ranges of porosity of $0.06 < P < 0.39$ and $0.5 < P < 0.51$. Similarly, this dependency has been observed in porous silicon nitride (Díaz and Hampshire 2004). The $E_0$ of both MS and CS samples are approximately 10-15 GPa higher than those observed in literature. However, the high correlation between Young’s modulus observed for both MS and CS samples suggests that, irrespective of sintering technique and mol \% Y$_2$O$_3$ dopant, it is primarily porosity which affects the Young’s modulus of sintered ZrO$_2$ samples.

The effect of porosity on the hardness of CS samples is shown in Figure 4.27. There is again a high correlation between the empirical exponential fit and the experimental data ($r^2$ of 0.954). A zero porosity hardness value ($H_0$) of 14.15 GPa and $b_H$ value of 5.59 were observed.
Figure 4.27. Hardness of Y$_2$O$_3$ doped ZrO$_2$ samples conventionally sintered (CS) vs. the volume fraction porosity.

In Figure 4.28 the hardness of MS samples versus the volume fraction porosity present is shown along with the empirical exponential fit. The $r^2$ value of 0.888 indicates a lower correlation than that observed in the CS samples. However, similar $H_0$ and $b_H$ values of 14.36 GPa and 5.59, respectively, were observed in both sintering techniques. These values correlate well to those observed in literature. This relationship was also observed by Luo and Stevens (1999), albeit with a lower $H_0$ value of 11.76 GPa. He et al. (1996) observed hardness values of 14.2-13.4 GPa in 5 mol % Y$_2$O$_3$ doped ZrO$_2$ sinter forged and pressureless sintered samples. The sintering of samples using MS energy has yielded hardness of 12.1 GPa in the case of 96% dense 3Y-TZP (Wilson and Kunz 1988), similar to samples observed in this study. In the same study CS samples with a relative density of greater that 99% exhibited a hardness value of 13.6 GPa. Values of greater than 14GPa have also been reported using microwave sintering (Goldstein et al. 1999).

Figure 4.28. Hardness of Y$_2$O$_3$ doped ZrO$_2$ samples microwave sintered (MS) vs. the volume fraction porosity.
The correlation of Hardness with Porosity for both MS and CS samples again indicates that the hardness of Y$_2$O$_3$ doped ZrO$_2$ compositions are primarily related to the amount of porosity present. The hardness of ceramics can also be dependent on the grain size. The hardness of polycrystalline materials is generally related to grain size by the Hall-Petch relationship; however this relationship has not been shown to apply in the case of many ceramics (Hoepfner and Case 2003). Rice et al. (1994) reviewed the relationship between hardness and grain size for a range of both dense oxide and non-oxide ceramics. It was indicated that there were generally conflicting trends with either hardness exhibiting no grain size dependence, decreasing hardness of single crystals with decreasing grain size or the more generally accepted decrease in hardness with increasing grain size. In the case of ZrO$_2$, little dependence of H$_v$ on grain size was observed for grain sizes in the range 0.5-50µm. On the other hand there have been differences observed between the hardness of fine grained Y-TZP and larger grained Mg-PSZ (Yang and Wei 2000). Y-TZP with grain size of 0.4 µm had a higher hardness of 12.4 GPa than coarse grained Mg-PSZ with a grain size of 12 µm and a hardness of 10.8GPa. In this study the MS 2 mol % Y$_2$O$_3$ doped ZrO$_2$ has a larger grain size of 0.35 µm and a hardness of 11.6GPa compared with the MS 3 mol % Y$_2$O$_3$ doped ZrO$_2$ composition that has a grain size of 0.2 µm and a hardness of 12.6 GPa. As the porosity levels in both samples are similar it indicates that the grain size may also contribute to hardness values.

In Figure 4.29 the strength of CS samples are plotted against the volume fraction porosity present. While the strength of samples does clearly follow a decreasing trend with increasing porosity, the fit with the empirical exponential relationship exhibits a poor correlation of 28%. This indicates that compositional factors such as the phases present play an important role in the strength of ZrO$_2$ ceramics. For example, 2 mol % Y$_2$O$_3$ compositions generally exhibited lower strengths than all other compositions despite similar porosities. This correlates with the higher amount of monoclinic ZrO$_2$ observed in the sintered pellets Figure 4.11. At this level of Y$_2$O$_3$ there is insufficient dopant present to form TZP and any remaining monoclinic will transform to tetragonal ZrO$_2$ on sintering above 1150°C with the consequent reversion to the monoclinic phase on cooling which is associated with a volume increase of approximately 5% and as such introduces microcracking in the sintered samples (Hannink et al. 2000). The increase in the size of flaws (microcracks) introduced significantly reduces the flexural strengths of the 2 mol % Y$_2$O$_3$ doped ZrO$_2$ compositions.
The stability of a tetragonal grain inside a tetragonal ZrO$_2$ matrix is controlled by three main factors; the grain size, the matrix constraint and the amount of stabiliser dopant (in this case Y$_2$O$_3$) (Heuer et al. 1982, Garvie and Swain 1985, Lange 1982). The high porosity of the conventionally sintered ZrO$_2$ with 2 mol% Y$_2$O$_3$ may have resulted in reduced matrix constraint and a spontaneous transformation to the monoclinic state.

In Figure 4.30 the effects of porosity on the biaxial flexural strengths of MS samples are shown. There is generally a decrease in strength with an increase in the porosity but it has an r$^2$ value of 0.675 to an exponential fit. While this correlation is greater than that observed in the CS samples it is still significantly lower than those determined for both hardness and stiffness. The 2 mol% Y$_2$O$_3$ doped ZrO$_2$ compositions, in particular, exhibit flexural strengths of approximately 300MPa higher than all other compositions at porosity values of 5% and lower. This again suggests that biaxial flexural strength is dependent on both porosity and other compositional factors such as the phases present.

Figure 4.29. Biaxial flexural strength of Y$_2$O$_3$ doped ZrO$_2$ samples conventionally sintered (CS) vs. the volume fraction porosity
In the case of Y-TZP it has been observed that the transformation toughening effect (stress induced tetragonal to monoclinic phase transformation) is grain size dependant (Bravo-Leon et al. 2002, Lange 1982). The larger the grain size the greater the propensity to undergo stress induced transformation to an equilibrium state and hence the greater the toughening contribution (Becher and Swain 1992). This correlates with the larger grain size and higher flexural strength of the MS ZrO$_2$ with 2 mol % Y$_2$O$_3$ compared with 3 mol % Y$_2$O$_3$ at porosity levels of less than 5%, despite similar densities and retention of the t-phase observed from the XRD of the sintered pellets (Figure 4.11).

Basu et al. (2005) observed similar results for Y$_2$O$_3$ doped ZrO$_2$ produced by hot-pressing similar mixed powders at 1450°C. Increases in flexural strength and fracture toughness were observed as Y$_2$O$_3$ content decreased. The addition of Y$_2$O$_3$-free monoclinic ZrO$_2$ particles to 3 mol% Y$_2$O$_3$ co-precipitated powders resulted in grain growth and increased transformability to t-ZrO$_2$. Yttria from the co-precipitated grains diffuses into the original monoclinic ZrO$_2$ grains resulting in a material with highly transformable tetragonal grains with higher flexural strength and fracture toughness reaching maximum flexural strength of 1269MPa for ZrO$_2$ with 2 mol % Y$_2$O$_3$. It was also noted that total Y$_2$O$_3$ content must remain above 1.75 mol% to avoid spontaneous transformation to m-ZrO$_2$.

While the maximum flexural strength of 800MPa achieved for ZrO$_2$ with 2 mol % Y$_2$O$_3$ in the present study was less than that for the hot-pressed material (Basu et al.
2005), it was significantly higher than that for ZrO$_2$ with 3 mol% Y$_2$O$_3$, suggesting that a similar effect occurred in the case of the MS samples sintered at a temperature of 1300°C. At lower sintering temperatures and thus higher porosities the strength of 2 mol % Y$_2$O$_3$ compositions are significantly reduced and similar to those of the 3 mol % compositions. Any toughening mechanism has been removed and porosity is the main controlling factor on the ZrO$_2$ compositions.
4.5 Conclusions

- The attrition milling of undoped m-ZrO₂ with co-precipitated Y₂O₃-containing ZrO₂ allowed control of the cubic/tetragonal phases present.

- The activation energies for sintering of the 2 and 3 mol % Y₂O₃-doped ZrO₂ compositions, determined using dilatometry, were lower than those found for the 4 and 5 mol % Y₂O₃ compositions.

- Microwave sintering achieved greater densification of samples than conventional sintering. These effects were most pronounced at a sintering temperature of 1100°C. As the sintering temperature/densification increased, the microwave enhancement decreased.

- There is a significant increase in the standard deviations of densities and mechanical properties for samples subjected to microwave sintering. This is thought to be associated with localised hotspots and a non-homogenised field within the microwave cavity. These deviations generally decreased as the microwave sintering temperature increased.

- Both elastic moduli and hardness of ZrO₂ ceramics are dependant mainly on the porosity present in the sample, irrespective of the sintering technique or the mol % Y₂O₃ present.

- Biaxial flexural strength also exhibits a dependency on porosity. However compositional effects such as the monoclinic or tetragonal ZrO₂ present and the microstructure also had an effect. This was generally observed at high levels of densification associated with a sintering temperature of 1300°C.

- The maximum biaxial flexural strength of 807 MPa was observed for the MS samples containing 2 mol % Y₂O₃. The maximum hardness of 12.5 GPa was observed in MS samples containing 3 mol % Y₂O₃.

- When considering a reinforcing phase for use in a HA composite, ZrO₂ compositions with both 2 and 3 mol % Y₂O₃ appear to be the best candidates. Maximising the tetragonal ZrO₂ phase within the composite is important in any attempt to enhance the toughening effect.
5. Hydroxyapatite-Zirconia Composites

5.1 Green powder Analysis

5.1.1 Phase Analysis by X-ray Diffraction (XRD)

The XRD pattern of Hydroxyapatite (HA) powder synthesized via the precipitation technique at 25°C is shown in Figure 5.1. The major peaks and corresponding planes were visually identified according to Elliott (1994). Using X’pert High score plus, a search match of the pattern compared to a JCPDS database was performed. The closest match identified is that of HA (Ca$_5$(PO$_4$)$_3$(OH)), JCPDS (9-0432). This JCPDS standard has previously been used for the identification of HA in literature (Evis et al. 2008, Gross and Berndt 1998, Pontier et al. 2003, Unyi et al. 2000).

![XRD pattern of HA powder synthesized at 25°C.](image)

While the powder is crystalline, the broadness of the diffraction peaks is indicative of a fine particle size. There is no significant evidence of either α-TCP (major peak 30.7°2θ) or β-TCP (major peaks at 31°2θ). However, due to the broad HA peaks in this region it is possible that minor amounts of these phases are present. XRD powder analysis was also performed on the commercial HA (C-HA) powder, shown in Appendix B. The pattern is also representative of HA. There is a higher level of crystallinity evident in the C-HA than in the synthesized HA. The peaks were identified according to Elliott (1994).
5.1.2 Transmission Electron Microscopy (TEM)

In Figure 5.2 the Transmission Electron Microscopy (TEM) images of HA synthesized at 25 and 45°C are shown. With an increase in the synthesis temperature from 25-45°C there is a substantial increase in the size of the particles. At a synthesis temperature of 25°C, the width of the particles range from approximately 10-20nm, while the length of the particles range from 20-60nm respectively. At the higher temperature of 45°C, both the width and length of the HA particles increase approximately to a range of 30-50nm and 100-300nm, respectively. Along with this increase in crystal size the morphology of the particles changes from that of an ellipse, in the case HA synthesized at 25°C, to a more needlelike structure in HA synthesized at 45°C.

Figure 5.2. TEM images of HA synthesized at (a) 25°C and (b) 45°C. Scale bar = 100nm.
5.1.3 Particle size analysis

The particle size analysis (PSA) using a laser diffraction technique indicates a unimodal particle size distribution Figure 5.3 with a $d_{50}$ of 0.192µm in the case of HA synthesized at 25°C.

![Particle Size Distribution](image)

**Figure 5.3.** Particle size analysis of HA synthesized at 25°C.

The particle size distribution of HA synthesized at 45°C and commercial HA also exhibit a unimodal distribution (See Appendix B); however, a wider particle size distribution and larger average particle size is also evident in both powders. A comparison of the particle size distributions is shown in Table 5.1. There is a substantial increase in the $d_{50}$ of HA synthesized at 45°C to 3.808µm. The commercial HA exhibited a smaller $d_{50}$ of 2.44 µm.

**Table 5.1.** Particle size of HA synthesized (S-HA) at 25 and 45°C and of commercial HA (C-HA) powder.

<table>
<thead>
<tr>
<th></th>
<th>$d_{10}$ (µm)</th>
<th>$d_{50}$ (µm)</th>
<th>$d_{90}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-HA 25°C</td>
<td>0.134</td>
<td>0.192</td>
<td>0.320</td>
</tr>
<tr>
<td>S-HA 45°C</td>
<td>1.67</td>
<td>3.808</td>
<td>7.778</td>
</tr>
<tr>
<td>C-HA</td>
<td>0.605</td>
<td>2.44</td>
<td>6.904</td>
</tr>
</tbody>
</table>
5.1.4 Accelerated Surface Area & Porosimetry using Brunauer Emet and Teller method (ASAP BET)

The surface area and estimated spherical diameter (ESD\textsubscript{BET}) calculated from the surface area are shown in Table 5.2 along with a comparison with the d\textsubscript{50} determined using laser diffraction. Similar to ZrO\textsubscript{2} powders, there is a large discrepancy between the ESD\textsubscript{BET} and the d\textsubscript{50} determined for each of the HA powders. The ESD\textsubscript{BET} values compare favourably with the particle size observed using TEM. This indicates that powder agglomeration is an issue with HA when using laser diffraction to analyse particle size. The higher surface area exhibited by the HA synthesized at 25°C is consistent with smaller particle size observed compared to the HA synthesized at 45°C.

Table 5.2. BET surface area and average particle size of synthesized (S-HA) and commercial HA (C-HA) determined using ASAP and PSA.

<table>
<thead>
<tr>
<th></th>
<th>S-HA 25°C</th>
<th>S-HA 45°C</th>
<th>C-HA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S\textsubscript{BET} (m\textsuperscript{2}/g)</td>
<td>151.5</td>
<td>15.7</td>
<td>19.3</td>
</tr>
<tr>
<td>ESD\textsubscript{BET} (nm)</td>
<td>12.5</td>
<td>121.2</td>
<td>98.5</td>
</tr>
<tr>
<td>d\textsubscript{50} (μm)</td>
<td>0.192</td>
<td>3.808</td>
<td>2.44</td>
</tr>
<tr>
<td>TEM (nm)</td>
<td>20-60</td>
<td>100-300</td>
<td>--</td>
</tr>
</tbody>
</table>

5.1.5 Energy Dispersive X-ray Spectroscopy & X-ray Fluorescence

The Energy Dispersive X-ray (EDX) spectrum of HA powder synthesized at 25°C is shown in Figure 5.4. The main constituents of HA, Calcium (Ca), Phosphorus (P) and oxygen (O) are all evident while the copper peak (Cu) is present because of the sample holder.
Using the intensities of the peaks for Ca and P it is possible to estimate the Ca:P ratio. In Table 5.3 the Ca:P ratio of HA determined using both EDX and also X-ray fluorescence (XRF) (performed at Ceram, Stoke on Trent, UK) are reported. There is a discrepancy between the ratio obtained using EDX and XRF, with the EDX ratios indicating a higher Ca:P ratio (>1.8) than for the normal stoichiometry of HA (1.667). The XRF results indicate a much closer ratio to that of stoichiometric HA, particularly in the cases of the commercial HA (1.67) and HA synthesized at 25°C (1.66). A full report of the XRF results can be found in Appendix B.

Table 5.3. Ca:P ratio of commercial and synthesized HA determined using EDX and XRF.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca:P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDX</td>
</tr>
<tr>
<td>C-HA</td>
<td>-</td>
</tr>
<tr>
<td>S-HA 25°C</td>
<td>1.81</td>
</tr>
<tr>
<td>S-HA 45°C</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Figure 5.4. EDX spectrum of HA synthesized at 25°C.
5.1.6 Back Scattered Scanning Electron Microscopy

Composites of the S-HA powders (synthesized at 25°C) with 5 wt % ZrO$_2$ (3 mol% Y$_2$O$_3$) were ball milled for 6 hours and compacted at 80MPa. Figure 5.5 shows back scattered electron images of the S-HA-ZrO$_2$ composite powder compact containing 5 wt % ZrO$_2$ pre- and post-ball milling for 6 hours. Prior to ball milling, there is considerable evidence of agglomeration of the ZrO$_2$ powders. After 6 hours of ball milling the agglomeration is no longer evident and an even distribution of the ZrO$_2$ particles is observed.

![Back Scattered Electron images from SEM (scale bar = 100 microns) of compacted composite powders (a) pre-ball milled and (b) post ball milled showing distribution of S-HA (dark) + 5 wt % ZrO$_2$ (light).](image)

Figure 5.5. Back Scattered Electron images from SEM (scale bar = 100 microns) of compacted composite powders (a) pre-ball milled and (b) post ball milled showing distribution of S-HA (dark) + 5 wt % ZrO$_2$ (light).
5.1.7 Dilatometry

The densification curves from dilatometry of both synthesized and commercial HA are shown in Figure 5.6. The onset temperature for densification and the temperature at which the greatest densification rate occurs are substantially lower for the synthesized HA compared to the commercial HA. This correlates with the lower particle size and greater surface area observed in the synthesized HA. In this case, the onset temperature for densification is 750°C and the temperature at which the maximum rate of densification occurs is 1041°C compared with an onset temperature of 975°C and temperature of maximum densification rate of 1148°C for the commercial HA.

![Densification curves](image)

Figure 5.6. Densification curves and maximum densification rates of synthesized HA (S-HA25) and commercial HA (C-HA) using a constant heating rate of 5°C/min.

On plotting ln[(Δl/l₀)/T] versus 1/T between a linear shrinkage of 1 and 10 percent (Figure 5.7), the slope of the line obtained is equal to -nEₐ/R when only one densification mechanism is present. The slopes determined for HA synthesized at 25 and 45°C and commercial HA are indicated in Figure 5.7. HA synthesized at 25°C exhibited a value for E of 155 kJ/mol⁻¹, HA synthesized at 45°C exhibited an activation energy of 275 kJ/mol⁻¹ and the commercial HA exhibited a value of 483 kJ/mol⁻¹. However, the slope associated with the C-HA and S-HA powder compacts are not entirely linear, suggesting that more than one single densification mechanism is operative. In this case calculating the activation energies of densification using the slope is not accurate as more than one mechanism is occurring.
Figure 5.7. Arrhenius plot used to determine the slope and apparent activation energy of densification for both the C-HA and S-HA powders.
5.2 C-HA-ZrO₂ composite

The initial composites investigated contained the commercial HA and ZrO₂ (containing 3 mol % Y₂O₃) in ratios of 100:0, 95:5, 90:10, 80:20 and 60:40 (in wt %), respectively. This was used to identify any potential effects of microwave sintering in composites containing a wide range of ZrO₂ contents.

5.2.1 Density

The effect of ZrO₂ loading on the relative density of commercial HA-ZrO₂ composites microwave (MS) and conventionally (CS) sintered at 1200°C is shown in Figure 5.8. The relative density of composites decreases as the ZrO₂ content increases in the case of both MS and CS composites. The relative densities of microwave sintered composites containing 5 and 10 wt % ZrO₂, are 83% (±2.5) and 73% (±3.3) respectively, compared to their conventionally sintered counterparts, with values of 89% (±0.5) and 83% (±1.1), respectively. The maximum densities achieved were in undoped HA, with similar values for both MS and CS samples of 92%. The standard deviations of relative densities in MS samples are larger than those in CS samples. Overall, zirconia clearly has a significant inhibiting effect on densification of HA-ZrO₂ composites, irrespective of the sintering technique, pinning the grain boundaries and preventing grain boundary mobility.

Figure 5.8. The effect of wt % ZrO₂ on the relative density of MS and CS C-HA-ZrO₂ composites sintered at 1200°C.
5.2.2 XRD Phase Analysis

In Figure 5.9 the phase assemblages of HA-ZrO₂ composites containing 0-40 wt % ZrO₂ microwave sintered at 1200°C are shown. There is no evidence of decomposition phases present in the undoped HA (C-HA). In compositions containing 5 wt % ZrO₂ there is evidence of the presence of cubic zirconia (c-ZrO₂) and a small amount of tricalcium phosphate (β-TCP). As the ZrO₂ content is increased to 10 wt % there is a clearly decomposition of HA to β-TCP, indicated by the peak at 31°2θ. The predominant ZrO₂-containing phase is calcium zirconate, CaZrO₃, however; there is also some evidence of c-ZrO₂. As the ZrO₂ content is increased to 20 & 40 wt %, there is an increase in c-ZrO₂, as might be expected, while the HA has almost entirely decomposed to β-TCP. A similar trend was observed in CS samples (Appendix B).

![Figure 5.9. XRD traces of C-HA-ZrO₂ composites microwave sintered at 1200°C.](image)

Quantitative phase analysis was carried out by analysing the XRD traces of composites using X’pert Highscore software suite (Panalytical, Netherlands) in order to indentify the amounts of HA, ZrO₂ and possible degradation phases present in the CS and MS sintered HA-ZrO₂ composites. Inorganic Crystal Structure Database (ICSD) files were matched to phases in the samples by X’Pert Highscore and converted to CIF files to perform Rietveld analysis. The phase analysis of C-HA-ZrO₂ composites is presented in Table 5.4. There is an approximate error of 4 wt% using this technique.
Table 5.4. Quantitative phase analysis of C-HA-ZrO$_2$ composites microwave (MS) and conventionally (CS) sintered at 1200°C.

<table>
<thead>
<tr>
<th>wt % ZrO$_2$</th>
<th>HA</th>
<th>α-TCP</th>
<th>β-TCP</th>
<th>TTCP</th>
<th>m-ZrO$_2$</th>
<th>t-ZrO$_2$</th>
<th>c-ZrO$_2$</th>
<th>CaZrO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MS 1200°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>98.7</td>
<td>-</td>
<td>-</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>93.7</td>
<td>0.6</td>
<td>-</td>
<td>2.3</td>
<td>-</td>
<td>0.2</td>
<td>2.8</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>61.6</td>
<td>-</td>
<td>27.0</td>
<td>3.2</td>
<td>-</td>
<td>0.1</td>
<td>1.7</td>
<td>6.9</td>
</tr>
<tr>
<td>20</td>
<td>15.8</td>
<td>8.4</td>
<td>44.6</td>
<td>11.4</td>
<td>-</td>
<td>-</td>
<td>7.6</td>
<td>12.2</td>
</tr>
<tr>
<td>40</td>
<td>2.0</td>
<td>3.0</td>
<td>55.3</td>
<td>7.5</td>
<td>-</td>
<td>3.1</td>
<td>28.2</td>
<td>1</td>
</tr>
<tr>
<td><strong>CS 1200°C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0</td>
<td>99.4</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>92.46</td>
<td>0.6</td>
<td>2.2</td>
<td>-</td>
<td>0.1</td>
<td>0.1</td>
<td>3.5</td>
<td>2.5</td>
</tr>
<tr>
<td>10</td>
<td>49.2</td>
<td>0.7</td>
<td>38.8</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>0.6</td>
<td>10.1</td>
</tr>
<tr>
<td>20</td>
<td>12.7</td>
<td>4.5</td>
<td>61.4</td>
<td>3.5</td>
<td>1.4</td>
<td>1.4</td>
<td>5.4</td>
<td>11.7</td>
</tr>
<tr>
<td>40</td>
<td>2.4</td>
<td>-</td>
<td>37.2</td>
<td>8.9</td>
<td>-</td>
<td>0.9</td>
<td>45.3</td>
<td>-</td>
</tr>
</tbody>
</table>

In the case of CS samples, an increase in ZrO$_2$ leads to an increase in the amount of decomposition phases, tetra-calcium phosphate, TTCP and, to a greater extent, β-TCP while the amount of HA decreases. The amount of CaZrO$_3$ increases with increasing ZrO$_2$ content and then decreases at 40 wt % ZrO$_2$, with a subsequent increase in the amount of c-ZrO$_2$. A similar trend is observed in the MS samples; however there is less degradation of HA occurring at 10 and 20 wt % ZrO$_2$. The low amount of t-ZrO$_2$ present, irrespective of the sintering technique, indicates that there is a reaction with CaO to form either c-ZrO$_2$ solid solution or CaZrO$_3$.

5.2.3 Microstructural Analysis of C-HA-ZrO$_2$ Composites

The polished and etched surfaces of C-HA-ZrO$_2$ composites were examined using scanning electron microscopy (SEM). Figure 5.10 shows SEM images of composites microwave sintered at 1200°C which confirm the density results that there is a general increase in porosity as the ZrO$_2$ loading of the microwave sintered composites is increased.
Figure 5.10. SEM images of the polished and etched surfaces of commercial C-HA-ZrO₂ composites microwave sintered at 1200°C containing (a) 0 wt % ZrO₂, (b) 5 wt % ZrO₂, (c) 10 wt % ZrO₂, (d) 20 wt % ZrO₂ and (e) 40 wt % ZrO₂.

The polished and etched surfaces of C-HA-ZrO₂ composites conventionally sintered at 1200°C can be seen in Figure 5.11. Again there is, generally, an increase in porosity evident as the ZrO₂ loading is increased.
5.2.4 Elastic Properties

The Young’s modulus and Poisson’s ratio of C-HA-ZrO₂ composites are shown in Figure 5.12. A similar trend to the relative density is observed, with an increase in the ZrO₂ content leading to a decrease in the Young’s modulus, irrespective of the sintering technique. The highest modulus values obtained were for undoped HA, with values of 108GPa (±8.0) and 106GPa (±5.1) for CS and MS samples respectively. The Poisson’s ratio generally decreases with increases in ZrO₂ content and range from 0.27 to 0.17.
Chapter 5 Hydroxyapatite-Zirconia Composites

Figure 5.12. Effect of wt % ZrO$_2$ on (a) the Young’s modulus and (b) Poisson’s ratio of MS and CS C-HA-ZrO$_2$ composites sintered at 1200°C.

The effects of the volume fraction porosity on the Young’s and bulk modulus of composites both microwave and conventionally sintered are shown in Figure 5.13. Irrespective of the sintering technique, both Young’s and bulk modulus exhibit a strong dependence on the volume fraction porosity present in the composites indicated by the high correlation of 0.967 or greater observed for the empirical exponential relationship $[E = E_0\exp(-bEP)]$.

Figure 5.13. The effects of volume fraction porosity on Young’s and bulk modulus of (a) microwave sintered (MS) and (b) conventionally sintered (CS) C-HA-ZrO$_2$ composites containing 0-40 wt % ZrO$_2$, sintered at 1200°C.
5.2.5 Biaxial Flexural Strength

The biaxial flexural strengths of C-HA-ZrO$_2$ composites MS and CS at 1200°C are shown in Figure 5.14. In MS samples there is a decrease in the strength as the ZrO$_2$ loading increases. In CS samples there is an increase in the strength for composites containing 5 wt % ZrO$_2$ and a subsequent decrease in strength as the amount of ZrO$_2$ increases further. The maximum strength observed is 118MPa (±18), in unfilled HA microwave sintered at 1200°C.

![Figure 5.14](image1)

**Figure 5.14.** Effect of ZrO$_2$ loading on the biaxial flexural strengths of MS and CS C-HA-ZrO$_2$ composites sintered at 1200°C.

The effect of porosity on the biaxial flexural strength of C-HA-ZrO$_2$ composites both microwave (MS) and conventionally sintered (CS) at 1200°C for 1 hour is shown in Figure 5.15. In the case of MS samples there is a high correlation of 0.869 to the empirical exponential relationship [$S = S_0\exp(-bSP)$] while CS samples exhibit a lower $r^2$ value of 0.613.

![Figure 5.15](image2)

**Figure 5.15.** The effects of volume fraction porosity on the biaxial flexural strength MS and CS C-HA-ZrO$_2$ composites containing 0-40 wt % ZrO$_2$, sintered at 1200°C.
5.2.6 Microhardness

The effect of ZrO\(_2\) loading on the hardness of both MS and CS C-HA-ZrO\(_2\) composites is illustrated in Figure 5.16. Similar to the biaxial flexural strengths, there is a decrease in the hardness as the ZrO\(_2\) content of the composites increases in the MS composites. A similar trend is observed in CS composites, with the exception of an initial increase in hardness associated with composites containing 5 wt % ZrO\(_2\). The highest hardness value of 5.5GPa (±0.6) is observed in microwave sintered unfilled HA.

![Figure 5.16](image)

**Figure 5.16.** Effect of ZrO\(_2\) loading on the Vickers hardness of MS and CS C-HA-ZrO\(_2\) composites sintered at 1200°C.

The effect of volume fraction porosity on the hardness of C-HA-ZrO\(_2\) composites is shown in Figure 5.17. In both the MS and CS composites there is a strong dependence of the hardness on the volume fraction porosity present. The MS samples exhibit a higher correlation between experimental data and the empirical exponential relationship \[ H = H_0 \exp(-b_HP) \] with an \( r^2 \) value of 0.933, while CS samples observe a \( r^2 \) value of 0.898.

![Figure 5.17](image)

**Figure 5.17.** The effects of porosity on the hardness MS and CS HA-ZrO\(_2\) composites containing 0-40wt % ZrO\(_2\), sintered at 1200°C.
5.3 Synthesized HA-ZrO$_2$ composites

Composites containing HA synthesized at 25°C containing 5 and 10 wt % ZrO$_2$ were comparatively sintered from 1000-1300°C. The use of lower amounts of ZrO$_2$ additions (<10 wt.%) were considered in view of the large amount of decomposition observed in the commercial HA with larger amounts of ZrO$_2$.

5.3.1 Density

The effects of the different sintering techniques on the relative densities of synthesized HA (S-HA) and composites containing S-HA and 5 or 10 wt % ZrO$_2$ (3 mol % Y$_2$O$_3$) are shown in Figure 5.18. In the case of (a) S-HA there is a significant increase in the relative densities of MS samples sintered at 1000, 1100 and 1200°C compared to their CS counterparts. The largest difference is observed at 1000°C with a relative density of 84.8 % (±1.1) in the case of MS samples compared to 68% (±2.3) for the CS samples. In MS samples a plateau is reached at 1200°C at which an increase in temperature leads to a slight decrease in the relative density. The densities of the CS samples, conversely, increase as the temperature increases to 1300°C and the maximum relative density is observed at this temperature in CS samples, with a value of 96.6% (±0.2).
A similar trend is observed in HA samples containing both 5 and 10 wt % ZrO₂ (3 mol % Y₂O₃). In the 5 wt % composites (Figure 5.18 (b)), MS samples again exhibit greater densities compared to their CS counterparts at sintering temperatures of 1000 and 1100°C. At 1200°C both CS and MS samples exhibit a similar density and at 1300°C CS samples achieve the highest relative density of 93.8% (±0.8). In the case of 10 wt % ZrO₂ additions (Figure 5.18 (c)), higher relative densities of MS samples at 1000 and 1100°C compared with CS samples are again evident, while both methods result in equivalent densities at higher temperatures. As with the commercial HA, increases in ZrO₂ loading result in a decrease in relative density at higher temperatures, irrespective of the sintering technique.
5.3.2 Phase Analysis

The XRD traces of synthesized HA (S-HA) microwave (MS) and conventionally sintered (CS) at temperatures from 1000 to 1300°C can be seen in Figure 5.19. In the case of MS samples (Figure 5.19 (a)), HA is the predominant phase present up to a sintering temperature of 1200°C, with minor amounts of β-TCP. At a temperature of 1300°C there is considerable decomposition indicated by the presence of both α and β-TCP. In CS HA there is initially an increase in β-TCP as the sintering temperature increases from 1000-1200°C followed by an increase in α-TCP at 1300°C.

![Figure 5.19. XRD traces of synthesized HA (a) microwave sintered (MS) and (b) conventionally sintered (CS) in the range 1000-1300°C.](image)

In Figure 5.20 the XRD traces of S-HA + 5 wt% ZrO₂ composites MS and CS sintered in the range 1000-1300°C are shown. In the MS samples sintered at 1000°C there is evidence of c-ZrO₂ and small amounts of β-TCP. Both these phases increase as the sintering temperature is increased to 1100°C. At 1200°C there is an increase in α-TCP and an increase in CaZrO₃. At 1300°C the HA has entirely decomposed to α-TCP and the main ZrO₂-containing phase is CaZrO₃. In CS samples there is evidence of both β-TCP and c-ZrO₂ at temperatures in the range 1000-1200°C. As the temperature is increased to 1300°C, there is evidence of large amounts of decomposition to α-TCP and again an increase in the amount of CaZrO₃ as the decomposition of HA occurs.
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Figure 5.20. XRD traces of synthesized HA + 5 wt% ZrO₂ (a) microwave sintered (MS) and (b) conventionally sintered (CS) in the range 1000-1300°C.

The XRD traces of S-HA + 10 wt% ZrO₂ composites MS and CS sintered in the range 1000-1300°C are shown in Figure 5.21. A similar trend to composites containing 5 wt % ZrO₂ is evident. MS of composites, in general, showed an onset of decomposition of HA at a lower temperature compared to CS. In both sintering techniques, as the amount of TCP decomposition phase increases the amount of CaZrO₃ present also increases.

Figure 5.21. XRD traces of synthesized HA + 10 wt% ZrO₂ (3mol% Y₂O₃) (a) microwave sintered (MS) and (b) conventionally sintered (CS) in the range 1000-1300°C.

The phase quantification using Rietveld analysis is shown in Table 5.5 which provides more detailed analysis of the effects of ZrO₂ and the different sintering techniques on phase stability of HA. A similar effect to the phase traces is observed, with increasing temperature and ZrO₂ content leading to an increase in the
decomposition of HA. At a temperature of 1300°C the MS samples exhibit higher decomposition compared with CS samples.

Table 5.5. Quantitative Phase analysis of synthesized HA, HA + 5wt% ZrO₂ and HA + 10wt% ZrO₂ composites microwave (MS) and conventionally sintered (CS) at temperatures in the range 1000-1300°C.

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>HA MS</th>
<th>HA CS</th>
<th>HA+5wt% ZrO₂ MS</th>
<th>HA+10wt% ZrO₂ MS</th>
<th>HA+5wt% ZrO₂ CS</th>
<th>HA+10wt% ZrO₂ CS</th>
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<tr>
<td></td>
<td>HA</td>
<td>α-TCP</td>
<td>β-TCP</td>
<td>TTCP</td>
<td>m-ZrO₂</td>
<td>t-ZrO₂</td>
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<td>-</td>
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5.3.3 Microstructural Analysis of synthesized HA-ZrO$_2$ Composites

The polished and etched surfaces of synthesized HA and HA-ZrO$_2$ composites were examined using scanning electron microscopy (SEM). In Figure 5.22, SEM images of the etched fracture surfaces of S-HA microwave sintered in the range 1000-1300°C can be seen. There is a large amount of grain growth evident at temperatures of 1200 and 1300°C.

![SEM images of polished and etched surfaces of S-HA microwave sintered at (a) 1000, (b) 1100, (c) 1200 and (d) 1300°C. Scale bar = 5μm.](image)

**Figure 5.22.** Scanning electron micrographs of polished and etched surfaces of S-HA microwave sintered at (a) 1000, (b) 1100, (c) 1200 and (d) 1300°C. Scale bar = 5μm.
In Figure 5.23, SEM images of the etched surfaces of S-HA conventionally sintered in the range 1000-1300°C can be seen. While there is also grain growth evident at temperatures of 1200 and 1300°C, it is considerably lower than that observed in the microwave sintered samples.

**Figure 5.23** Scanning electron micrographs of etched surfaces of S-HA conventionally sintered at (a) 1000, (b) 1100, (c) 1200 and (d) 1300°C. Scale bars of (a), (b) and (c) = 1μm and scale bar of (d) = 2μm.
SEM images of polished and etched surfaces of S-HA + 5 wt% ZrO\textsubscript{2} composites microwave sintered in the range 1000-1300°C are shown in Figure 5.24. Large grain growth is evident at a sintering temperature of 1300°C. The ZrO\textsubscript{2} particles are evident at the HA grain boundaries in Figure 5.24 (d).

Figure 5.24. Scanning electron micrographs of polished and etched surfaces of S-HA + 5 wt % ZrO\textsubscript{2} (3 mol % Y\textsubscript{2}O\textsubscript{3}) microwave sintered at (a) 1000, (b) 1100, (c) 1200 and (d) 1300°C. Scale bars of (a), (b) and (c) = 2µm and scale bar of (d) = 5µm.
SEM images of polished and etched surfaces of S-HA + 5 wt% ZrO$_2$ composites conventionally sintered in the range 1000-1300°C are shown in Figure 5.25. At a sintering temperature of 1300°C (Figure 5.25 (d)), there is evidence of ZrO$_2$ particles associated with porosity at the grain boundaries of the HA grains.

Figure 5.25. Scanning electron micrographs of polished and etched surfaces of S-HA + 5 wt% ZrO$_2$ (3 mol% Y$_2$O$_3$) conventionally sintered at (a) 1000, (b) 1100, (c) 1200 and (d) 1300°C. Scale bars of (a), (b) and (c) = 1µm and scale bar of (d) = 5µm.
Figure 5.26 shows SEM images of the polished and etched surfaces of S-HA + 10 wt% ZrO$_2$ composites microwave sintered in the range 1000-1300°C.

**Figure 5.26.** Scanning electron micrographs of polished and etched surfaces of S-HA + 10 wt % ZrO$_2$ (3 mol % Y$_2$O$_3$) microwave sintered at (a) 1000, (b) 1100, (c) 1200 and (d) 1300°C. Scale bar of (a) = 1µm (b) = 2µm and (c) and (d) = 5µm.
Figure 5.27 shows SEM images of the etched surfaces of S-HA + 10 wt% ZrO₂ composites conventionally sintered in the range 1000-1300°C.

The effect of temperature on the average grain size of S-HA and S-HA-ZrO₂ composites, determined using the linear intercept method, are shown in Figure 5.28. In both MS and CS samples there is an increase in grain size as the temperature increases. In MS S-HA (Figure 5.28 (a)) there is considerable grain growth in MS samples compared to CS at sintering temperatures of 1200 and 1300°C, with values of 9.8µm compared to 6.2µm.
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The effects of temperature on the grain size of (a) synthesised HA (S-HA), (b) S-HA containing 5 wt % ZrO$_2$ (3 mol % Y$_2$O$_3$) and (c) S-HA containing 10 wt % ZrO$_2$ (3 mol % Y$_2$O$_3$), sintered using microwave energy (MS) and conventional sintering (CS).

In composites containing 5 or 10 wt% ZrO$_2$ the grain growth observed in both sintering techniques is generally comparable. As with unfilled HA, there is an increase in grain size as the sintering temperature is increased. This grain growth is quite prevalent at temperatures of 1200-1300°C. Compared with pure HA, it appears that ZrO$_2$ inclusions reduce the amount of grain growth slightly at temperatures of 1300°C.
5.3.4 Energy Dispersive X-ray (EDX) Analysis

EDX analysis was performed on the fracture surfaces of composites to identify regions of high concentrations of ZrO\(_2\). Figure 5.29 shows a scanning electron micrograph of S-HA + 5 wt\% ZrO\(_2\) composite and semi-quantitative analysis by EDX (Spectrum 1) performed on a region associated with the presence of porosity and small particles. Semi-quantitative analysis indicated that there is approximately 30 wt \% ZrO\(_2\) associated with spectrum 1 and also a much higher Ca:P ratio than in HA.

![Figure 5.29](image1)

**Figure 5.29.** (a) SEM of the fracture surface of composite containing S-HA + 5 wt\% ZrO\(_2\) and (b) semi-quantitative results of EDX performed in the area indicated by spectrum 1.

In Figure 5.30, the semi-quantitative analysis of spectrum 2, a region consisting of large matrix grains and no porosity, indicated that the amount of ZrO\(_2\) in this region is significantly lower (~2\%) and Ca:P ratio is also lower than in Spectrum 1. This suggests that ZrO\(_2\) is prevalent at the grain boundaries of HA and associated with porosity.

![Figure 5.30](image2)

**Figure 5.30.** (a) SEM of the fracture surface of composite containing S-HA + 5 wt\% ZrO\(_2\) and (b) semi-quantitative results of EDX performed in the area indicated by spectrum 2.
5.3.5 Young’s Modulus

The effect of sintering temperature using two sintering techniques on the Young’s modulus of S-HA and S-HA-ZrO$_2$ composites is shown in Figure 5.31. In the case of S-HA (Figure 5.31 (a)), the MS samples have reached a modulus of 84 GPa (±4.4) at 1000°C while that of their CS counterparts is 48 GPa (±2) but as sintering temperature increases, modulus increases, reflecting the increases in density. At temperatures of 1000-1200°C the Young’s modulus of MS samples are greater than their CS counterparts. For the MS samples, modulus reaches a plateau at 1200-1300°C with values of 109 GPa (±6.3), whereas the maximum modulus achieved at 1300°C was 112 GPa (±7.3) for the CS S-HA.

![Figure 5.31](image)

Figure 5.31. The effects of sintering temperature on the Young’s modulus of (a) synthesised HA (S-HA), (b) S-HA containing 5 wt % ZrO$_2$ (3 mol % Y$_2$O$_3$) and (c) S-HA containing 10 wt % ZrO$_2$ (3 mol % Y$_2$O$_3$), sintered using microwave energy (MS) and conventional techniques (CS).

In the case of composites containing 5 wt % ZrO$_2$ (Figure 5.31 (b)), the MS samples have reached a modulus of 84 GPa (±10.4) at 1000°C while that of their CS counterparts is 48 GPa (±7) but, as sintering temperature increases, CS samples again exhibit an increase in the modulus to a maximum of 105 GPa (±4.8) at 1300°C whereas
MS samples on the other hand exhibit an increase in the Young’s modulus to 98 GPa (±5.1) at a temperature of 1100°C beyond which there is a slight reduction. The composites containing 10 wt % ZrO₂ (Figure 5.31 (c)) again exhibit similar trends but as the amount of ZrO₂ increases there is a decrease in the maximum Young’s modulus attained, reflecting the effect of density. At 1000°C MS samples have achieved higher Young’s moduli (68±13 GPa) than their CS counterparts (47±6.2 GPa) increasing to 85 GPa (±2.5) for MS and 76 GPa (±4.8) for CS at 1100°C and then reaching a plateau at higher temperatures.

Table 5.6 shows the Poisson’s ratio, shear and bulk moduli of S-HA and composites containing 5 and 10 wt% ZrO₂. A similar trend to that observed for the Young’s modulus is generally evident for the bulk and shear moduli. The Poisson’s ratio tends to increase as the temperature increases, irrespective of the sintering technique.

Table 5.6. Elastic properties of synthesized HA and HA-ZrO₂ composites sintered from 1000 to 1300°C using microwave (MS) and conventional (CS) techniques.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>S-HA</th>
<th>S-HA + 5 wt % ZrO₂</th>
<th>S-HA + 10 wt % ZrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk Modulus (GPa)</td>
<td></td>
<td>Shear modulus (GPa)</td>
</tr>
<tr>
<td></td>
<td>CS</td>
<td>MS</td>
<td>CS</td>
</tr>
<tr>
<td>1000</td>
<td>22 (±4.2)</td>
<td>52 (±8.0)</td>
<td>16 (±1.4)</td>
</tr>
<tr>
<td>1100</td>
<td>50 (±3.1)</td>
<td>69 (±8.4)</td>
<td>32 (±2.1)</td>
</tr>
<tr>
<td>1200</td>
<td>64 (±1.9)</td>
<td>78 (±8.1)</td>
<td>38 (±1.6)</td>
</tr>
<tr>
<td>1300</td>
<td>79 (±5.9)</td>
<td>80 (±6.0)</td>
<td>44 (±2.9)</td>
</tr>
</tbody>
</table>

The effect of porosity on the Young’s modulus of microwave and conventionally sintered S-HA and S-HA-ZrO₂ composites is shown in Figure 5.32. There is a high correlation in both MS and CS samples between experimental results and the empirical exponential relationship \[ E = E_o \exp(-bP) \] with \( r^2 \) values of 0.887 and 0.937.
respectively. This indicates that irrespective of the sintering technique the volume fraction porosity is a major determinant of Young’s modulus for both the unfilled S-HA and the S-HA-ZrO₂ composites. The zero porosity modulus evident in both techniques is similar, with a value of 131GPa in MS samples and a value of 128GPa in CS samples.

**Figure 5.32.** Young’s modulus of synthesized HA and HA-ZrO₂ composites vs. the volume fraction porosity of (a) MS samples and (b) CS samples.
5.3.6 Biaxial Flexural Strength

The biaxial flexural strengths of synthesized HA and HA-ZrO$_2$ composites microwave (MS) and conventionally sintered (CS) from 1000-1300°C are shown in Figure 5.33. In terms of MS S-HA (Figure 5.33 (a)) there is an initial increase in the strength with an increase in sintering temperature from 1000 to 1100°C, above which there is a slight decrease in strength with an increase in temperature beyond 1100°C. MS samples sintered at 1000 and 1100°C exhibit greater strengths than their conventional counterparts, with values of 112 MPa (±15) and 138 MPa (±10.8) compared to 54 MPa (±10) and 89 MPa (±12.8), respectively. The strengths of CS samples increase further with increase in sintering temperature above 1100°C attaining values similar to those for MS samples sintered at 1200°C and reaching a maximum at a sintering temperature of 1300°C with a value of 164 MPa (±19) compared to 130 MPa (±12) for the MS S-HA samples.

![Figure 5.33](image-url)

**Figure 5.33.** The effects of sintering temperature on the biaxial flexural strength of (a) synthesised HA (S-HA), (b) S-HA containing 5 wt % ZrO$_2$ (3 mol % Y$_2$O$_3$) and (c) S-HA containing 10 wt % ZrO$_2$ (3 mol % Y$_2$O$_3$), sintered using microwave energy (MS) and conventional techniques (CS).

In the case of composites containing 5 wt % ZrO$_2$ (Figure 5.33 (b)), microwave sintering gives higher strengths at 1000°C of 85 MPa compared to 52 MPa for CS
samples and as the temperature increases to 1100°C, both sintering regimes promote an increase in strength to 108 MPa (±7.6) for MS samples and 100 MPa (±25.7) for CS samples followed by decreases in strength with any further increase in temperature which are more pronounced for MS samples. This trend is also evident in composites containing 10 wt % ZrO$_2$ with maximum strengths being achieved at 1100°C of 111 MPa (±16.8) for MS samples and 92 MPa (±6.1) for CS samples. As the ZrO$_2$ content increases there is generally a reduction in biaxial flexural strengths, which is more prevalent as the temperature increases.

The effects of porosity on the strength of HA-ZrO$_2$ composites can be seen in Figure 5.34. In MS samples (Figure 5.34 (a)), while there is a general decrease in strength as the porosity increases, there is a low correlation ($r^2$=0.21) between the empirical exponential relationship \[ S = S_0 \exp(-bE_P) \] and the experimental results. This indicates that perhaps other compositional factors, such as decomposition phases present as well as the porosity, have an effect on the strength of the composites. The CS samples exhibit a higher correlation ($r^2$=0.628) but this relatively low correlation again suggests that the strength is dependent on other compositional factors as well as the amount of porosity present.

![Graph](image_url)

**Figure 5.34.** Biaxial flexural strength of synthesized HA and HA-ZrO$_2$ composites vs. the volume fraction porosity of (a) MS samples and (b) CS samples.
5.3.7 Microhardness

The effects of temperature on the microhardness of S-HA and S-HA composites both MS and CS sintered in the range 1000-1300°C are shown Figure 5.35. In terms of MS S-HA (Figure 5.35 (a)) there is an initial increase in the hardness with an increase in sintering temperature from 3 GPa (±0.4) at 1000°C to 5 GPa (±0.4) at 1200°C, followed by a slight decrease in hardness with an increase in temperature beyond 1200°C. The hardness values for the CS samples increase as the sintering temperature is increased from 1.1 GPa (±0.3) at 1000°C to 5.6 GPa (±0.45) at 1300°C.

![Figure 5.35](image.png)

**Figure 5.35.** The effects of sintering temperature on the hardness of (a) synthesised HA (S-HA), (b) S-HA containing 5 wt % ZrO₂ (3 mol % Y₂O₃) and (c) S-HA containing 10 wt % ZrO₂ (3 mol % Y₂O₃), sintered using microwave energy (MS) and conventional sintering (CS).

In the case of S-HA composites containing 5 wt % ZrO₂ (Figure 5.35 (b)), the hardness values of both CS and MS samples are similar to those for S-HA and marginally increase as the sintering temperature increases to 1300°C. In composites containing 10 wt % ZrO₂ there is slight increase in hardness values up to a temperature of 1200 °C above which there is a plateau, irrespective of the sintering technique. As with the results observed using the commercial powder, the hardness values of composites decrease significantly as the ZrO₂ content increases.
The effects of volume fraction porosity on the hardness of HA-ZrO$_2$ composites are shown in Figure 5.36. Irrespective of composition or sintering technique, there is generally a close correlation between the level of porosity in a sample and the hardness with an $r^2$ correlation value of 0.94 in the case of MS and 0.92 in the case of CS samples. There is a similar Hardness at zero porosity ($H_0$) value observed in both MS and CS samples of 6.9 and 6.4GPa respectively.

Figure 5.36. Hardness of synthesized HA and HA-ZrO$_2$ composites vs. the volume fraction porosity of (a) MS samples and (b) CS samples.
5.4 **HA-ZrO$_2$ Composites + 2.5 wt% CaF$_2$**

5.4.1 **Density**

The effects of temperature on the relative density of microwave sintered HA-ZrO$_2$ composites containing 2.5 wt% CaF$_2$ compared to composites without CaF$_2$ are shown in Figure 5.37. The CaF$_2$ additions considerably increase the relative density of HA composites containing 5 and 10 wt % ZrO$_2$. As seen previously, without CaF$_2$ the maximum relative densities attainable in HA-ZrO$_2$ composites containing 5 or 10 wt % ZrO$_2$ are 92% ($\pm$0.6) and 82.5% ($\pm$2.3), respectively. Through the addition of 2.5 wt% CaF$_2$ the relative densities of composites with similar ZrO$_2$ contents are increased to 96.3% ($\pm$1.5) and 95.2% ($\pm$2.3), respectively. While the relative density of the composite containing 5 wt % ZrO$_2$ and 2.5 wt% CaF$_2$ increases as the temperature increases to 96% ($\pm$1?) at 1300°C, the composite containing 10 wt% ZrO$_2$ and a similar level of CaF$_2$ reaches a maximum relative density of 95% ($\pm$0.1) at 1200°C but decreases with a further increase in temperature.

![Figure 5.37](image_url)

**Figure 5.37.** Effect of temperature on the relative density of composites consisting of HA + 2.5wt% CaF$_2$ and 5 or 10 wt% ZrO$_2$ compared with composites without CaF$_2$ additions microwave sintered in the range 1000-1300°C.
5.4.2 Phase Analysis by XRD

The phase assemblages of composites containing 5 and 10 wt % ZrO₂ and 2.5 wt% CaF₂, microwave sintered between 1000 and 1300°C are shown in Figure 5.38. In composites containing 5 wt % ZrO₂ (Figure 5.38. (a)) the addition of CaF₂ enabled a major HA phase to be maintained, even at a sintering temperature of 1300°C. With composites containing 10 wt % ZrO₂ (Figure 5.38. (b)), the HA phase is maintained up to a temperature of 1200°C above which there is then significant decomposition to α-TCP.

Figure 5.38. XRD phase patterns of synthesized HA composites containing (a) 5 wt % ZrO₂ +2.5 wt % CaF₂ and (b) 10 wt % ZrO₂ +2.5 wt % CaF₂ microwave sintered from 1000-1300°C

In Table 5.4 the results of Rietveld analysis of composites containing 5 or 10 wt % ZrO₂ and 2.5 wt% CaF₂ are shown. In the case of composites containing 5 wt % ZrO₂ and 2.5 wt% CaF₂, there is initially a slight increase in the amount of β-TCP as the temperature increases, followed by an increase in α-TCP at a temperature of 1300°C. However the major phase is primarily HA. CaZrO₃ is the predominant ZrO₂–containing phase present. The composite containing 10 wt % ZrO₂ initially exhibits an increase in the amount of TTCP, followed by a substantial decomposition to α-TCP at a sintering temperature of 1300°C. CaZrO₃ is the major ZrO₂–containing phase; however there is also evidence of c-ZrO₂.
Table 5.7. Quantitative phase analysis of composites consisting of 2.5 wt% CaF$_2$ and 5 or 10 wt% ZrO$_2$ microwave sintered in the range 1000-1300°C.

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>wt % Phases Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 %ZrO$_2$</td>
<td>HA</td>
</tr>
<tr>
<td>1000</td>
<td>94.5</td>
</tr>
<tr>
<td>1100</td>
<td>87.1</td>
</tr>
<tr>
<td>1200</td>
<td>86.7</td>
</tr>
<tr>
<td>1300</td>
<td>86.2</td>
</tr>
<tr>
<td>10 wt %</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>84.4</td>
</tr>
<tr>
<td>1100</td>
<td>83.6</td>
</tr>
<tr>
<td>1200</td>
<td>77.2</td>
</tr>
<tr>
<td>1300</td>
<td>32.4</td>
</tr>
</tbody>
</table>

5.4.3 Microstructural Analysis of HA-ZrO$_2$ + 2.5 wt% CaF$_2$

Figure 5.39 illustrates the polished and etched of HA composites containing 5 wt% ZrO$_2$ and 2.5 wt% CaF$_2$, microwave sintered in the range 1000-1300°C. At sintering temperatures of 1200 and 1300°C there is evidence of decreased amounts of porosity when compared to composites that do not contain CaF$_2$ (Figure 5.24).
Figure 5.39. Scanning electron micrographs of the polished and etched surfaces of S-HA + 5wt% ZrO$_2$ + 2.5wt% CaF$_2$ composites microwave sintered at (a) 1000, (b) 1100, (c) 1200 and (d) 1300°C. Scale bar of (a) and (b) = 1µm, (c) = 2µm and (d) = 5µm.

The effect of temperature on the grain size of microwave sintered HA-ZrO$_2$-CaF$_2$ composites is shown in Figure 5.40. The grain size is approximately 1 µm at a sintering temperature of 1000°C for composites with both 5 and 10 wt % ZrO$_2$, increasing to approximately 2 µm at a sintering temperature of 1100°C and as sintering temperature increases to 1200°C, more significant grain growth occurs and is slightly more pronounced in composites containing 10 wt % ZrO$_2$ and 2.5 wt % CaF$_2$ compared to samples containing 5 wt % ZrO$_2$ and a similar amount of CaF$_2$. Significant levels of grain growth occur at the maximum sintering temperature of 1300°C to 12.9 µm for composites with 5 wt % ZrO$_2$ and 14.1µm for composites with 10 wt % ZrO$_2$. 

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Figure 5.40. Effect of sintering temperature on the grain size of HA-ZrO₂-CaF₂ composites MS sintered in the range 1000-1300°C.

5.4.4 Young’s Modulus

Figure 5.41 illustrates the effect of sintering temperature on the Young’s modulus of composites containing 5 or 10 wt% ZrO₂ and 2.5 wt% CaF₂. The inclusion of CaF₂ increases the modulus significantly. In composites containing 5 and 10 wt% ZrO₂ and CaF₂, the maximum Young’s modulus values observed are, respectively, 112 GPa (±2.2) and 108 GPa (±3.4). By comparison, similar composites without the CaF₂ additions exhibited stiffness values of 95.4 GPa (±9.6) and 81.9 GPa (±6.4), respectively. The Young’s modulus of composites containing CaF₂ exhibit a plateau at a sintering temperature of 1200°C, beyond which an increase in temperature does not increase the modulus.

Figure 5.41. Effect of sintering temperature on the Young’s modulus of composites consisting of 92.5 wt% HA, 2.5 wt% CaF₂ and 5 or 10 wt% ZrO₂ compared with composites without CaF₂ additions microwave sintered in the range 1000-1300°C.
The bulk modulus, shear modulus and the Poisson’s ratio of HA-ZrO$_2$ composites containing 2.5 wt% CaF$_2$ microwave sintered in the range 1000-1300°C are shown in Table 5.1. The bulk and shear moduli follow similar trends to that observed with the Young’s modulus. The Poisson’s ratio of composites adopt values of between 0.246 and 0.259 and tend to increase slightly with increasing temperatures.

**Table 5.8.** Effect of temperature on the bulk modulus, shear modulus and Poisson’s ratio of composites containing 2.5 wt% CaF$_2$ and 5 or 10 wt% ZrO$_2$ microwave sintered from 1000-1300°C.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>S-HA+5 wt%ZrO$_2$+2.5 wt% CaF$_2$</th>
<th>Bulk Modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>61.7 (±5.3)</td>
<td>37.5 (±5.3)</td>
<td>0.246 (±0.01)</td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>66.9 (±12.4)</td>
<td>39.6 (±5.3)</td>
<td>0.251 (±0.02)</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>78.2 (±2.4)</td>
<td>44.4 (±5.3)</td>
<td>0.267 (±0.01)</td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td>79.2 (±5.4)</td>
<td>43.6 (±5.3)</td>
<td>0.261 (±0.01)</td>
<td></td>
</tr>
<tr>
<td>S-HA + 10 wt % ZrO$_2$+2.5 wt% CaF$_2$</td>
<td>57.6 (±4.4)</td>
<td>33.0 (±2.5)</td>
<td>0.251 (±0.02)</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>71.1 (±3.3)</td>
<td>40.9 (±1.6)</td>
<td>0.255 (±0.01)</td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>71.5 (±3.0)</td>
<td>43.0 (±1.3)</td>
<td>0.260 (±0.01)</td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td>72.0 (±8.2)</td>
<td>42.0 (±2.4)</td>
<td>0.259 (±0.01)</td>
<td></td>
</tr>
</tbody>
</table>

**5.4.5 Biaxial Flexural Strength**

Figure 5.42 illustrates the effect of temperature on the biaxial flexural strength of microwave sintered composites containing 5 or 10 wt% ZrO$_2$ and 2.5 wt% CaF$_2$ compared to similar composites without CaF$_2$. Unlike the Young’s modulus there was no perceived strength enhancement through the addition of CaF$_2$. In all cases a maximum strength was reached at a sintering temperature of 1100°C beyond which any further increase in temperature led to decreases in the strengths.
Chapter 5 Hydroxyapatite-Zirconia Composites

Figure 5.42. Effect of sintering temperature on the biaxial flexural strength of HA composites consisting of 2.5wt% CaF$_2$ and 5 or 10 wt% ZrO$_2$ compared with composites without CaF$_2$ additions microwave sintered in the range 1000-1300°C.

5.4.6 Microhardness

The effects of temperature on the microhardness of microwave sintered composites containing 2.5wt% CaF$_2$ compared to composites without CaF$_2$ are shown in Figure 5.43. There is a substantial increase in the hardness of microwave sintered HA-ZrO$_2$ composites containing CaF$_2$. For example, the maximum hardness of composites containing 5 and 10 wt% ZrO$_2$ is increased from 3.7 (±0.5) and 2.4 GPa (±0.6), respectively, to 5.6 (±0.9) and 5.1 GPa (±0.6) through the addition of CaF$_2$.

Figure 5.43. Effect of sintering temperature on the microhardness of composites consisting of 92.5 wt% HA 2.5wt% CaF$_2$ and 5 or 10 wt% ZrO$_2$ compared with composites without CaF$_2$ additions microwave sintered in the range 1000-1300°C.
5.5 Discussion

5.5.1 Green Powders

Phase analysis using XRD indicates that the powder synthesized using a co-precipitation method exhibited a nano-crystalline nature and was identified as Hydroxyapatite (HA). The broad nature of the diffraction peaks has previously been observed in HA prepared via a precipitation technique (Gibson et al. 2001, Osaka et al. 1991). TEM analysis of the HA synthesized at 25 and 45°C indicates that the morphology and crystallite size of the HA particles is dependent on the synthesis temperature. Increasing the temperature from 25 to 45°C resulted in large crystal growth and a change in morphology from that of an ellipse to a needle like structure. Both Towler (1997) and Bernache-Assollant, Ababou, Champion and Heughebaert (2003) observed similar effects using precipitation techniques, with higher synthesis temperatures leading to a larger and more elongated, rod shaped morphology.

The specific surface area of HA synthesized at 25°C, determined using BET, was considerably larger than that of HA synthesized at 45°C with values of 151.5 and 15.7 m²/g, respectively. The large increase in particle size, observed using TEM, with increased temperature coincides with this decrease in the specific surface area. El Hammari, Laghzizil, Saoiabi, Barboux and Meyer (2006) reported a similar specific surface area of 140 m²/g for HA powders produced using a modified wet precipitation technique. Using the specific surface area, the equivalent spherical diameter (ESD_{BET}) of each powder was determined. In the case of HA synthesized at 25°C, an ESD_{BET} size of 12.5 nm was determined. HA synthesized at 45°C and commercial HA powder exhibited values of 121.2 nm and 98.5 nm, respectively. The average particle sizes (d_{50}) for the HA powders determined using laser diffraction differ considerably to ESD_{BET} values. The observed d_{50} values for S-HA 25°C, S-HA 45°C and commercial HA were 0.192 µm, 3.808 µm and 2.44 µm respectively. This discrepancy is similar to that found for ZrO₂ powders in the previous chapter and suggests that the HA powders are prone to agglomeration when exposed to water, despite the addition of a dispersant and sonication.

To determine the Ca:P ratio of the HA powders both EDX and XRF techniques were utilized. Using the intensities of the calcium and phosphorus peaks determined from EDX analysis, Ca:P ratios of 1.81 and 1.88 were estimated for HA synthesized at 25 and 45°C, respectively. By comparison, XRF analysis (performed by Ceram, Stoke-on-Trent,
UK) indicated Ca:P ratios closer to that of stoichiometric HA of 1.66 and 1.70, for similar powders. While EDX has been used previously in literature for the determination of stoichiometric Ca:P ratios (Ciobanu et al. 2009, Sadat-Shojai et al. 2010), the high ratios observed using EDX are indicative of a calcium efficient powder, with would suggest that a CaO phase is present. However CaO was not observed in the phase analysis (no observed peaks at 29 or 30° 20) it suggests that the use of EDX to determine the Ca:P ratio in this case was inaccurate.

Dilatometric analysis of synthesized and commercial HA powders indicate that the synthesized powder exhibits a lower temperature for the onset of sintering and greater linear shrinkage compared to the commercial HA powder. In the case of HA synthesized at 25°C, an onset temperature of 750°C and a maximum sintering rate temperature of 1041°C was found. Using a similar precipitation synthesis technique for HA, Bianco, Cacciotti, Lombardi and Montanaro (2009) observed similar dilatometric results with an onset temperature of densification of 800°C and a maximum sintering rate temperature of 1050°C. The higher onset temperature of densification and maximum sintering rate temperature of the commercial HA powder are indicative of the larger particle size of the powder and lower specific surface area. Gibson, Ke, Best and Bonfield (2001) observed similar results when examining the effect of HA powder characteristics on the sintering of HA. It was found that HA powder with a higher specific surface area exhibited a large initial increase in densification. The apparent activation energies for densification (E_A) determined from the initial stages of sintering using Equation 5.1 were 155 kJ/mol for S-HA 25°C, 275kJ/mol for S-HA 45°C and 483 kJ/mol in the case of commercial HA.

Based on the particle size/morphology, the greater specific surface area, the near stoichiometric Ca:P ratio of 1.66 and the dilatometric results, it was concluded that HA synthesized at 25°C was the more applicable powder for sintering and hence was used in the sintering of composites.
5.5.2 Phase Analysis & Thermal stability of HA and HA-ZrO\textsubscript{2} composites

5.5.2.1 HA

As seen previously, (Chapter 2 HA-ZrO\textsubscript{2} Composites) it has been shown that the decomposition of HA at elevated temperatures occurs by two individual steps (Cihlář et al. 1999). Initially, the dehydroxylation of the HA structure occurs (Equation 5.1) followed by the formation of TCP (Equation 5.2).

\begin{align*}
Ca_{10}(PO_4)_6(OH)_2 & \rightarrow Ca_{10}(PO_4)_6(OH)_{2-x}2xO_x + xH_2O \\
Ca_{10}(PO_4)_6(OH)_2 & \rightarrow 2Ca_3(PO_4)_{2} + Ca_4P_2O_9 + H_2O
\end{align*}

(5.2)  
(5.3)

From the phase analysis (section 5.3.2), it can be seen that with pure synthesized HA either microwave (MS) or conventionally sintered (CS) there are minor amounts of β-TCP present at a sintering temperature of 1000°C. An increase in temperature up to 1200°C in both cases leads to a small increase in the amount of β-TCP and TTCP; however, at 1300°C there is considerable decomposition to α-TCP in the case of MS samples. CS samples retain a majority HA phase but also show significant increases in the amount of α-TCP present. The decomposition of HA first to β-TCP and then, as temperature increases, to α-TCP has been well documented (Raynaud et al. 2002a, Evis 2007, Suchanek and Yoshimura 1998). Both Muralithran et al. (2000) and Ruys et al. (1995a) observed the decomposition of HA at a critical temperature of 1350°C. In the present study it appears that the microwave sintering has decreased the critical temperature at which decomposition occurs by approximately 50°C. This observation is, however, contradictory to results observed by both Nath et al. (2006) and Veljovic, Zalite, Palcevskis, Smiciklas, Petrovic and Janackovic (2009) who reported no decomposition phases at a sintering temperature of 1200°C. It is worth noting, however that the lower sintering temperature and shorter hold times of 30 and 15 mins, respectively, in these studies compared to 1300°C and 1hr in the present study make a direct comparison difficult.

The stability of sintered HA is also highly dependent on the initial calcium to phosphorus ratio of the powders (Raynaud et al. 2002b, Hench 1991). If the Ca:P ratio is less than 1.667, HA can decompose to TCP. Using XRF, the Ca:P ratios of HA synthesized at 25°C and commercial HA were determined to be 1.66 and 1.67 respectively. The slight calcium deficiency of the synthesized HA correlates with the
greater amounts of decomposition phases (determined using Rietfeld analysis) present in both MS and CS samples sintered at 1200°C compared to the commercial HA which exhibited less than 1.3% decomposition in both MS and CS sintered samples.

5.5.2.2 HA-ZrO₂ composites

While HA tends to remain stable up to temperatures greater than 1300°C, the formation of secondary decomposition phases can occur at significantly lower temperatures in the presence of ZrO₂ (Kim et al. 2001, Ramachandra Rao and Kannan 2002, Evis 2007). Two of the decomposition reactions associated with HA-ZrO₂ composites can be seen below (Kim et al. 2001, Chang et al. 1997).

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow 2\text{Ca}_3(\text{PO}_4)_2 + \text{CaO} + \text{H}_2\text{O} \quad (5.4)
\]

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + \text{ZrO}_2 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + \text{CaZrO}_3/c-\text{ZrO}_2 + \text{H}_2\text{O} \quad (5.5)
\]

At temperatures in excess of 1100°C, in the presence of ZrO₂ the CaO formed through the decomposition reaction shown in Equation 5.4 can form a solid solution with the ZrO₂ as indicated by the CaO-ZrO₂ phase diagram shown in Figure 5.44. Initially limited amounts of CaO can dissolve into the ZrO₂ to form calcium stabilized cubic ZrO₂. As the temperature and decomposition of HA both increase the release of CaO increases to a point where CaZrO₃ is formed instead of c-ZrO₂ (Evis 2007).

![Figure 5.44. Partial phase diagram of the binary CaO–ZrO₂ system (Stubican et al. 1981).](image)

This is consistent with the phase analysis results observed in both commercial HA-ZrO₂ composites and synthesized HA-ZrO₂ composites. In synthesized HA-ZrO₂ composites containing 5 wt% ZrO₂ (Section 5.3.2:Figure 5.20) MS and CS at temperatures of 1000 and 1100°C, there is evidence of c/t-ZrO₂ and minor amounts of
β-TCP. As the sintering temperature for MS samples increases to 1200°C there is evidence of decomposition to α-TCP and associated with this, there is an increase in the amount of CaZrO$_3$ present and a reduction in c/t-ZrO$_2$. In CS samples a similar effect occurs at a higher temperature of 1300°C. A similar effect, but with greater amounts of decomposition are observed in composites containing 10wt% ZrO$_2$ either microwave or conventionally sintered. The effects of temperature, ZrO$_2$ loading and sintering technique on the relative amount of HA present compared to the total amount of apatitic phases is shown in Figure 5.45. It can be seen that, as the temperature and ZrO$_2$ content is increased, significant decomposition of HA occurs. It is also evident that microwave sintering accelerated the decomposition of HA in the presence of ZrO$_2$ at 1300°C.

![Figure 5.45. Percentage HA phase with respect to total decomposition phases of composites with and without CaF$_2$ additions.](image)

In the commercial HA-ZrO$_2$ composites, irrespective of the sintering technique (Section 5.2.2), again a similar trend of decomposition occurs. As the wt% ZrO$_2$ loading increases to 5 and 10 wt % ZrO$_2$ there is considerable decomposition of HA to α-TCP and again an increase in CaZrO$_3$ present. This suggests that the level of Y$_2$O$_3$ content in the ZrO$_2$ reinforcing phase is irrelevant as once decomposition occurs the release of CaO will dissolve into the ZrO$_2$, forming a cubic phase thus removing any possible toughening mechanism. With higher concentrations of ZrO$_2$ (40 wt %) c-ZrO$_2$ becomes the dominant phase present. This indicates that while the CaO still forms a solid solution with ZrO$_2$, the amount of ZrO$_2$ is so large (40 wt %) that there is only enough CaO to form a c-ZrO$_2$ phase. To summarize, the decomposition of both commercial and

5.5.2.3 CaF₂ Additions

Previous studies have shown that the addition of CaF₂ or MgF₂ to HA-ZrO₂ composites enables the formation of fluorapatite (FHA) through the partial substitution of fluorine (F⁻) for the hydroxyl (OH⁻) ion in HA (Evis and Doremus 2007a, Hae-Won et al. 2002). FHA exhibits greater thermal stability with less decomposition and dehydroxylation at elevated temperatures compared to HA (Krajewski et al. 1990), thus limiting some of the decomposition issues when adding ZrO₂.

In this study the XRD traces of microwave sintered composites containing 2.5 wt% CaF₂ shown in Figure 5.38 and the quantitative analysis shown in Table 5.7, indicate that a HA phase was predominantly maintained, with the exception of the composite containing 10 wt % ZrO₂ and 2.5 wt % CaF₂ microwave sintered at 1300°C. The increased phase stability of HA indicates that partial substitution of F⁻ for OH⁻ has occurred. Figure 5.46 illustrates the increased phase stability of HA achieved in microwave sintered composites with 2.5 wt% CaF₂. Similar results were observed with CaF₂ using conventional sintering (Hae-Won et al. 2002) and also MgF₂ using both conventional sintering and hot pressing (Evis and Doremus 2007a, Evis et al. 2008).

![Figure 5.46. Percentage HA phase with respect to total decomposition phases of composites with and without CaF₂ additions.](image)

It was also observed that CaZrO₃ is the major ZrO₂-containing phase present in both composites containing 5 and 10 wt% ZrO₂ (with minor amounts of c-ZrO₂ present with
10 wt % $\text{ZrO}_2$ composition). The substitution of $F^-$ for the $\text{OH}^-$ ion results in the release of $\text{CaO}$, which is free to react with the tetragonal $\text{ZrO}_2$ additions to form either a solid solution of $\text{c-ZrO}_2$ or the compound $\text{CaZrO}_3$ as shown in the following equations proposed by (Hae-Won et al. 2002):

$$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + x\text{CaF}_2 = \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{F}_{2x} + x\text{CaO} + x\text{H}_2\text{O}$$  \quad (5.6)

$$\text{CaO} + t\text{-ZrO}_2 = c\text{-ZrO}_2/\text{CaZrO}_3$$  \quad (5.7)

The formation of the $\text{CaZrO}_3$ phase in composites containing $\text{CaF}_2$ is different to that of $\text{CaF}_2$ free composites as it is formed from the $\text{CaF}_2$ as opposed to the decomposition of $\text{HA}$. While a predominant $\text{HA}$ phase can be maintained, the presence of $\text{CaZrO}_3$ indicates that no transformation toughening mechanism can be obtained in the composites.

5.5.3 Density

5.5.3.1 HA

As with the results of microwave sintered $\text{ZrO}_2$ (Chapter 4) there is an increase in the relative density of microwave sintered $\text{HA}$ compared to conventionally sintered samples at a similar temperature. Increases in relative densities of $\text{HA}$ using microwave sintering techniques have previously been observed in literature (Nath et al. 2006, Veljovic et al. 2009, Vijayan and Varma 2002, Ramesh et al. 2007).

In the present study a plateau was reached with MS samples in the relative density at $1200^\circ\text{C}$ beyond which an increase in sintering temperature resulted in a slight decrease in the relative density. Nath et al., (2006) observed a similar reduction albeit with a temperature shift of $100^\circ\text{C}$ lower. This plateau effect has also been observed in conventionally sintered $\text{HA}$ (Muralithran and Ramesh 2000, Ruys et al. 1995a), spark plasma sintered (SPS) $\text{HA}$ (Gu et al. 2002) and high frequency induction heat sintering of $\text{HA}$ (Khalil et al. 2007). The decrease in density is generally attributed to the decomposition of $\text{HA}$ to TCP which is consistent with the decomposition of $\text{HA}$ observed in MS samples at $1300^\circ\text{C}$ as indicated by the phase analysis.

5.5.3.2 HA-$\text{ZrO}_2$ Composites

The addition of $\text{ZrO}_2$ to either commercial or synthesized $\text{HA}$ resulted in significant retardation of the densification process which increased as the $\text{ZrO}_2$ additions increased,
irrespective of the sintering technique as seen in section 5.2.1 and section 5.3.1. In the case of synthesized HA-ZrO₂, while MS increased the relative densities at temperatures of 1000 and 1100°C (as seen in Figure 5.18) compared to CS samples, any further increase in temperature could not increase the relative density significantly. The retardation of the densification of HA with ZrO₂ inclusions is well documented in literature in the case of conventional sintering (Zhang et al. 2006, Evis et al. 2005, Evis 2007), and hot pressing (Evis and Doremus 2007b, Nayak et al. 2008, Ramachandra Rao and Kannan 2002). The retardation effect is associated with the decomposition of HA at elevated temperatures, which results in the release of bonded water increasing the porosity of the composites (Evis 2007). This is consistent with the densities of composites observed in this study using both microwave and conventional sintering techniques and the decomposition of HA observed using phase analysis.

5.5.3.3 Calcium Fluoride additions

The inclusion of 2.5 wt% CaF₂ to HA-ZrO₂ composites containing 5 or 10 wt% ZrO₂ lead to a considerable increase in the relative densities compared to similar samples without CaF₂, observed in Figure 5.37. Relative densities of 96.3% (±1.5) and 95.2% (±2.3) were observed in MS composites compared to 92% (±0.6) and 82.5% (±2.3) in compositions with similar ZrO₂ additions but no CaF₂. This increase in density was observed in previous studies when using either CaF₂ or MgF₂ additions (Evis and Doremus 2007a, Evis et al. 2008, Hae-Won et al. 2002). The substitution of F⁻ for OH⁻ increases the stability of the HA phase and halts the release of H₂O caused by the decomposition of HA, thus leading to increased relative densities of the microwave sintered composites containing CaF₂. This is consistent with increased phase stability of HA and relative densities observed in composites containing CaF₂.

5.5.4 Mechanical Properties

5.5.4.1 Young’s Modulus

As seen in Chapter 4 the porosity has a significant effect on the physical properties of brittle materials. In the context of mechanical properties, the dependence of Young’s modulus, strength and hardness on porosity is generally well described by the following empirical exponential relationship (Rice 1998):

\[ A = A_0 \exp(-b_A P) \]  \hspace{1cm} (5.8)

where \( A_0 \) is the value of the property at zero porosity, \( b_A \) is a measure of the rate of decrease in A with increasing P. A comprehensive study on the effects of porosity on the Young’s modulus was performed by Ren et al. (2009). Using a similar ultrasound
technique to this study for determining the Young’s modulus of HA with differing volume fraction porosity, it was found that there was a high correlation between experimental data and the exponential relationship ($r^2 = 0.98$). Furthermore, Ren et al. (2009) combined the effects of porosity on the stiffness observed in similar studies (Liu 1997, He et al. 2008, Arita et al. 1995) and again found that the Young’s modulus versus the volume fraction porosity was well described by the empirical exponential relationship. In terms of HA-ZrO$_2$ composites, Kumar et al. (2005) observed a similar correlation in spark plasma sintered composites containing 20 wt% ZrO$_2$. A comparison of the exponential relationship of composites observed in this study and in literature is presented in Table 5.9.
Table 5.9. Comparison of the exponential relationship between Young’s modulus and porosity ($E = E_0 \exp(-b_EP)$) of HA and HA-ZrO$_2$ found in this study compared to literature.

<table>
<thead>
<tr>
<th>Study</th>
<th>Composition</th>
<th>$E_0$ (GPa)</th>
<th>$b_E$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present Study</td>
<td>C-HA + (0-40 wt% ZrO$_2$)</td>
<td>MS</td>
<td>145</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>CS</td>
<td>MS</td>
<td>152</td>
<td>4.09</td>
</tr>
<tr>
<td>(Hoepfner and Case 2003)</td>
<td>S-HA + (0-10 wt% ZrO$_2$)</td>
<td>MS</td>
<td>131</td>
<td>2.98</td>
</tr>
<tr>
<td></td>
<td>CS</td>
<td>CS</td>
<td>128</td>
<td>2.96</td>
</tr>
<tr>
<td>(Kumar et al. 2005)</td>
<td>HA</td>
<td>CS</td>
<td>125</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>HA Combined*</td>
<td>CS</td>
<td>128</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>HA + 20 wt% ZrO$_2$</td>
<td>SPS</td>
<td>151</td>
<td>2.4</td>
</tr>
</tbody>
</table>


The empirical exponential trend was observed in CS and MS HA-ZrO$_2$ composites using both commercial (Figure 5.13) and synthesized HA (Figure 5.32). The high correlation observed in this study ($r^2>0.89$) and the similar results to other studies, despite the difference in sintering technique, difference in HA powders and difference in ZrO$_2$ loadings, suggests that porosity induced by the introduction of ZrO$_2$ and decomposition of HA is the major determinant on the Young’s modulus of HA-ZrO$_2$ composites.

Through the addition of CaF$_2$ to MS HA-ZrO$_2$ composites it was shown that a substantial increase in the Young’s modulus is possible when compared to similar composites without CaF$_2$ additions (Figure 5.41). While a maximum Young’s modulus value of 112 GPa ($\pm2.2$) can be obtained using CaF$_2$, this value is equivalent to that observed in ZrO$_2$ free CS sintered HA (112 GPa ($\pm7.3$) at 1300°C. Thus, it appears that the higher Young’s modulus is directly related to the increased density of composites containing CaF$_2$ and the CaZrO$_3$ phase present does not provide an additional enhancement in stiffness.

5.5.4.2 Biaxial Flexural Strength

As with Young’s modulus, the strength of HA ceramics shows a dependency on the porosity present. In the case of CS and MS commercial HA-ZrO$_2$ composites there is a relatively high correlation between the empirical exponential trend and experimental data ($r^2$ of 0.62 and 0.869). Similarly, CS synthesized HA-ZrO$_2$ composites exhibit an $r^2$ correlation of 0.618 to this trend. However, in the case of MS synthesized HA-ZrO$_2$ composites...
there is a poor correlation of 0.21. This suggests that other factors are affecting the strength of the ZrO₂ composites. In Figure 5.47 the effect of grain size of HA-ZrO₂ composites on the biaxial flexural strengths is shown. In CS and MS there is no correlation between the grain size and the strengths. This suggests that grain size plays a minimal role on the strength of the HA and HA-ZrO₂ composites.

![Figure 5.47. Strength versus the inverse root of average grain size (D⁻¹/₂) of synthesized HA and HA-ZrO₂ composites MS and CS in the range 1000-1300°C.](image)

It has been observed that the presence of decomposition phases can reduce the strength of HA material (Suchanek and Yoshimura 1998, Royer et al. 1993, Jarcho et al. 1976). It has been proposed that TCP present at the grain boundaries weakens the cohesion between grains, thus reducing the strength. Contrary to this, it has also been suggested that higher strengths are observed when both HA and TCP are present (Royer et al. 1993). It was suggested that the strengthening mechanism was surface compression due to the β-α-TCP phase transformation. In the case of MS synthesized HA-ZrO₂ composites containing 5 and 10 wt% ZrO₂, the biaxial flexural strengths (Figure 5.33(b &c)) tend to reach a maximum and decrease with increasing temperature, despite similar densities. When comparing this to phase analysis, significant decomposition to TCP tends to occur at 1100°C and increases with increasing temperature (Figure 5.45). Thus, it is proposed that increasing TCP content has a deleterious effect on the strength of HA-ZrO₂ composites along with porosity.
5.5.4.3 Hardness

The effect of porosity on the hardness of HA ceramics has previously been observed (Hoepfner and Case 2003, Best and Bonfield 1994, Wang and Chaki 1993). Hoepfner and Case (2003) applied the empirical exponential relationship to the experimental data and found good agreement with a coefficient of determination ($r^2$) of 0.91. In the case of HA-ZrO$_2$ composites spark plasma sintered (SPS), experimental data again exhibited a strong correlation ($>0.9$) with the empirical exponential relationship (Kumar et al. 2005). In the present study a strong correlation between hardness and porosity was observed in commercial HA-ZrO$_2$ composites containing 0-40 wt % ZrO$_2$ (Figure 5.17) and also in synthesized HA composites containing 0-10 wt% ZrO$_2$ (Figure 5.36). In Table 5.10 a comparison of the empirical relationship observed in this study to literature results is shown. The high correlation observed in this study ($r^2>0.89$) despite the difference in sintering technique, difference in HA powders and difference in ZrO$_2$ loadings, suggests that porosity induced by the introduction of ZrO$_2$ and decomposition of HA is the major determinant on the hardness of composites.

Table 5.10. Comparison of the exponential relationship between hardness and porosity ($H = H_0 \exp(-b_H P)$) found in this study compared to literature.

<table>
<thead>
<tr>
<th>Study</th>
<th>Composition</th>
<th>$H_0$ (GPa)</th>
<th>$b_H$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present Study</td>
<td>C-HA + (0-40 wt% ZrO$_2$)</td>
<td>MS</td>
<td>7.2</td>
<td>5.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CS</td>
<td>5.65</td>
<td>4.498</td>
</tr>
<tr>
<td></td>
<td>S-HA + (0-10 wt% ZrO$_2$)</td>
<td>MS</td>
<td>6.9</td>
<td>6.52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CS</td>
<td>6.4</td>
<td>5.97</td>
</tr>
<tr>
<td>(Hoepfner and Case 2003)</td>
<td>HA</td>
<td>CS</td>
<td>6.00</td>
<td>6.03</td>
</tr>
<tr>
<td>(Kumar et al. 2005)</td>
<td>HA + 20 wt% ZrO$_2$</td>
<td>SPS</td>
<td>5.94</td>
<td>3.32</td>
</tr>
</tbody>
</table>

It was also found that the introduction of CaF$_2$ to HA-ZrO$_2$ composites could significantly increase the hardness compared to CaF$_2$ free composites as observed in Figure 5.43. Microhardness values of 5.6 GPa ($\pm 0.9$) and 5.1 GPa ($\pm 0.6$) in composites containing CaF$_2$ and 5 or 10 wt% ZrO$_2$ were observed. While this is a significant increase in hardness over CaF$_2$ free composites (with values 3.7 GPa($\pm 0.5$) and 2.4 GPa ($\pm 0.6$)); the hardness values are comparable to unfilled HA. For example, synthesized HA CS at 1300°C exhibited a hardness of 5.6 GPa ($\pm 0.6$) and commercial HA MS at
1200°C exhibited a value of 5.47GPa (±0.45). The comparative results indicate that CaF$_2$ increases the hardness through the suppression of the decomposition of HA and thus a decrease in porosity of composites; however there is no additional increase in hardness observed with the presence of the ZrO$_2$ phase. This correlates with phase analysis, indicating that CaZrO$_3$ is the dominant ZrO$_2$ phase and does not exhibit any toughening effect. A similar conclusion was observed in the case of MgF$_2$ additions (Evis and Doremus 2007a).
5.6 Conclusions

- Using a co-precipitation method, HA synthesized at 25°C produced a nano-scale powder with a Ca:P ratio similar to that of stoichiometric HA. Increasing the synthesis temperature to 45°C resulted in an increase in the particle size and morphology from a rod-like structure to a needle-like one. The increase in temperature also led to a reduction in the specific surface area of the powder and an increase in the Ca:P ratio. The powder properties associated with HA synthesized at 25°C reduced the onset sintering temperatures and temperature of maximum rate of densification compared to a coarser particle commercial powder.

- In commercial HA-ZrO$_2$ composites consisting of 0-40wt% ZrO$_2$, the relative density of composites decreased as the ZrO$_2$ loading increased irrespective of the sintering technique use. Coinciding with the reduction in relative density, the decomposition of HA increased as the amount of ZrO$_2$ increased, irrespective of the sintering technique.

- Microwave sintering of synthesized HA resulted in an increase in relative density compared with conventionally sintered samples at temperatures of 1000-1200°C. However, a plateau was reached at 1200°C beyond which increasing temperature led to a slight decrease in relative density. The density of conventionally sintered samples increased as the temperature increased to 1300°C and the maximum relative density of 96.6% was observed at this temperature.

- In both microwave and conventionally sintered HA, decomposition of HA takes place and similar levels of β-TCP decomposition phases were present at temperatures of up to 1200°C. However microwave sintering hastened the degradation of HA to α-TCP at a sintering temperature of 1300°C.

- Microwave sintering of synthesized HA-ZrO$_2$ composites containing 5 and 10 wt% ZrO$_2$ exhibited enhanced densification compared to conventionally sintered samples at temperatures of 1000 and 1100°C. This enhancement was removed with any further increase in sintering temperature. As with the commercial HA-ZrO$_2$ composites sintered at temperatures of 1200°C and greater, the relative densities of synthesized HA composites decreased as the ZrO$_2$ loading increased, irrespective of the sintering technique.

- As with commercial HA-ZrO$_2$ composites, increasing the ZrO$_2$ loading of synthesized HA composites increased the level of decomposition of HA to TCP.
The decomposition became more prevalent with increasing sintering temperature and was higher in microwave sintered samples than for conventionally sintered samples. It is suggested that this decomposition results in the release of H$_2$O, hence increasing the porosity of the HA-ZrO$_2$ composites.

- Phase analysis indicated that CaO released through the decomposition of HA reacted with the ZrO$_2$ reinforcing phase to form either a c-ZrO$_2$ solid solution and/or CaZrO$_3$ above temperatures of 1100°C. This occurs in both sintering techniques and suggests that the Y$_2$O$_3$ content of the ZrO$_2$ phase is irrelevant as a tetragonal phase will be altered by the release of CaO.

- The Young’s modulus of commercial HA composites and synthesized HA-ZrO$_2$ composites exhibited a strong correlation with the empirical exponential relationship with porosity in both the case of microwave and conventionally sintered samples. This suggests that porosity, resulting from the addition of ZrO$_2$ to HA, is the major determinant on the Young’s modulus of the composites.

- Similarly, the hardness of commercial HA composites and synthesized HA-ZrO$_2$ composites also exhibited a strong correlation with the empirical exponential relationship with porosity in both the case of microwave and conventionally sintered samples. This again suggests that porosity resulting from the addition of ZrO$_2$ to HA is the major determinant on the hardness of the composites.

- The flexural strengths of composites, while exhibiting some relationship with porosity also appear to be dependent on the amount of decomposition phase present. In particular, in the case of synthesized HA-ZrO$_2$ composites, an increase in the amount of TCP present resulted in a decrease in the strengths of composites.

- The addition of 2.5 wt % CaF$_2$ to microwave sintered synthesized HA-ZrO$_2$ composites resulted in a significant increase in the relative density. It is suggested that a substitution of F$^-$ for OH$^-$ occurred, resulting in the partial formation of Fluoro-HA, increasing the thermal stability, limiting the formation of H$_2$O, and thus increasing density.

- While the addition of CaF$_2$ increased the density of composites, CaO formed in this case from the substitution of F$^-$ for OH$^-$ reacts with t-ZrO$_2$ again forming CaZrO$_3$ and/or c-ZrO$_2$.

- The increased density of CaF$_2$ containing composites led to an increase in the Young’s modulus and the hardness. However the biaxial flexural strengths of composites were not increased by the inclusion of CaF$_2$. While there was an
increase in mechanical properties compared to HA-ZrO$_2$ composites, the Young’s modulus and the hardness only exhibited values comparable to unfilled HA. The strengths were inferior to unfilled HA. This indicates that no toughening enhancement was achieved which might be expected due to the CaZrO$_3$ phase present.
6. **In vitro & In vivo Biological Evaluation of Composites**

In vitro and in vivo studies were performed on the best performing composite materials to evaluate their biological response in the context of a potential skeletal graft material. The studies were performed at the University of Sheffield.

6.1 Materials & Methods

6.1.1 Materials

In vitro evaluation was carried out on two different compositions of microwave sintered HA composite disks, 2mm thick and 8mm in diameter, hereafter referred to as HA-B containing 5 wt.% and HA-C containing 10 wt.% of ZrO$_2$ doped with 3 mol% yttria (3Y-TZP). The control disks were heat cured acrylic (2 mm x 8 mm). In vivo evaluation was undertaken by implanting granules of the HA-B, containing 5 wt.% of ZrO$_2$ doped with 3 mol% yttria, into rat femurs for 4 weeks. The implanted material consisted of granules ground to a size of approximately 90-350μm.

6.1.2 Cell Viability

Immortalized rat osteosarcoma cells (ROS 17/2.8, Merck Inc.) were cultured in DMEM supplemented with 10% (v/v) fetal calf serum (BioSera Ltd., Ringmer, UK), 2mM L-glutamine, 100 units/ml penicillin, 100 g/ml streptomycin and 250 μg/ml amphotericin B (Sigma, Poole, UK). Cells were incubated at 37°C in 5% CO$_2$ in tissue culture flasks and passaged by incubating with trypsin-EDTA (Sigma, Poole, UK).

6.1.3 Alamar Blue Assay

Discs (acrylic, HA-B and HA-C) were sterilised in 70% (v/v) ethanol, before being washed in PBS three times and placed into 24 well plates. ROS cells (1 x 10$^4$) were added onto the discs and incubated at 37°C in 5% CO$_2$. After 48 or 72 hours the media was replaced with media containing 10% alamar blue, covered with foil and incubated. After 4 hours the fluorescence ($\lambda_{ex} = 540$ nm, $\lambda_{em} = 585$ nm) was measured using an Infinite M200 plate reader with Magellan Software (Tecan, Switzerland).

6.1.4 DNA Quantification

Cells were lysed by repeated freeze thawing using molecular biology grade water and the amount of DNA was quantified using a fluorescent DNA Quantification Kit (Sigma). Briefly, unknown DNA samples were mixed with 2 μg/ml bisBenzimide H33258 solution and the fluorescence ($\lambda_{ex} = 360$ nm, $\lambda_{em} = 460$ nm) was measured using
an Infinite M200 plate reader with Magellan Software (Tecan, Switzerland). These readings were then compared to standard curves to determine the amount of DNA in the samples.

6.1.5 Scanning Electron Microscopy (SEM)

Discs were fixed in 2.5% glutaraldehyde in 0.1 M phosphate buffer overnight at 4C, washed three times in 0.1 M phosphate buffer and fixed in 2% aqueous osmium tetroxide for 2 hours at room temperature. Specimens were then dehydrated through a graded series of ethanol at room temperature and air dried overnight. Once dry, samples were mounted on stubs, attached with Sticky Tabs, and coated with approximately 25 nm of gold in an Edwards S150B sputter coater. Specimens were examined in a Phillips/FEI XL-20 SEM at an accelerating voltage of 20kV.

6.1.6 Surgery

Juvenile male Wistar rats aged 4-6 weeks at the time of surgery were used for this study. Animals were housed in groups in conventional laboratory conditions and provided with standard laboratory food and water *ad libitum*. The HA-ZrO$_2$ composite material for implantation (HA-B) was in the form of granules with a size range (90-350µm), which were quite sharp and angular in shape. The original protocol stated that the composites would be cast into 1mm diameter rods cut to 2mm lengths; however it was not possible to create composites with these dimensions and so particulate material was used instead.

Animals were anaesthetised using Isoflurane in oxygen; under aseptic conditions the mid-shaft of the right femur was exposed using sharp and blunt dissection and a defect created using a 1mm diameter round stainless steel dental bur running at slow speed in a dental handpiece under saline irrigation. Approximately 4 - 8 granules (90-350µm) of the HA/ZrO$_2$ composite were placed into the bone defect using fine tweezers, (n=6 per material).

Wounds were closed using resorbable sutures at 28 days. Animals were sacrificed using a schedule one method. The right femurs were dissected free and placed in formalin. The femurs were demineralised in formic acid and processed to paraffin
embedded sections stained with haematoxylin and eosin. Evaluation of the bone response was carried out using conventional light microscopy.

### 6.1.7 Statistical Analysis

The differences between groups were analysed by the Mann-Whitney U test (GraphPad Prism version 5.01 for Windows, GraphPad Software, San Diego, CA, [www.graphpad.com](http://www.graphpad.com)) which is a non-parametric test for assessing whether two independent samples of observations have equally large values. The results are considered statistically significant at a $P$ value of $\leq 0.05$.

### 6.2 Results

#### 6.2.1 Cell Viability (Incubation with Alamar Blue)

Cell viability after 48 hours and 72 hours growth on both test materials and the acrylic control is shown in Figure 6.1.

![Figure 6.1.](image)

*Figure 6.1.* % Cell viability after 48 hours (left) and 72 (right) hours compared to cells grown on tissue culture plastic (100%). Mean ± SEM, $n = 6$ discs, + $P < 0.05$, ++ $P < 0.01$, ** $P < 0.01$ compared to tissue culture plastic control, Mann-Whitney).

Initially at 48 hours, differences were seen in cell viability when comparing cells grown on the test materials and tissue culture plastic (100%). Cells grown on HA-C (74%; $P < 0.01$) were less viable compared with HA-B (85%; $P < 0.01$). However, after 72 hours of culture these differences were less marked and there was no significant difference in cell viability between both test materials.
6.2.2 DNA Quantification

DNA Quantification showed that there was no significant difference in the amount of DNA between cells grown on acrylic and cells grown on both test materials (HA-B and HA-C) after 48 and 72 hours (Figure 6.2).

![Figure 6.2. Amount of DNA after a) 48 hours and b) 72 hours. Mean ± SEM, n = 6 discs.](image)

* P < 0.05, ** P < 0.01, Mann-Whitney.

6.2.3 Qualitative Examination: Light Microscopy & SEM

Light microscopy indicated that cells were growing on and adjacent to all the materials after 72 hours, as indicated in Figure 6.3.
Figure 6.3. Light Microscopy of tissue culture wells after 72 hours. Cells (small arrows) are seen adjacent to the materials (large arrows) which are not transparent and appear dark. The dark spots represent debris, presumably from the disks themselves.

The initial appearance of the surface of the test samples prior to exposure to culture media, the effect of incubation in the media and the exposure to media and ROS cells are shown in Figure 6.4. Cells were found to have migrated onto and colonized all of the materials. Incubation with culture media alone for 72 hours had no effect on the surface appearance of acrylic, HA-B and HA-C. After culture with ROS cells for 72 hours, cells had migrated onto and attached closely to the surface of all materials and were forming a confluent layer.
Figure 6.4. SEM images of initial appearance of discs (Acrylic, HA-B and HA-C), after culturing for 72 hours with tissue culture media or media and ROS cells (Scale bars 20 μm)
6.3  *In vivo* Evaluation

The histological features of composite HA-B after 4 weeks implantation are shown in Figure 6.5. All surgical sites were well healed and the cortical defect was closed and filled with lamellar bone. In some instances, particulate material was seen in this region and was in direct contact with bone. There was no evidence of an inflammatory response in any of the sections examined and the materials were well tolerated by bone and marrow tissue. The granules of material were in direct contact with either bone or normal marrow tissue. Where material was in direct contact with the endosteal bone, the bone was in continuity with the material (Figure 6.5 (b)). In other areas there was a thin rim of bone around the particles (Figure 6.5 (b)) and sometimes bone bridges between granules. There was no evidence of resorption of the material. Where material was seen at the bone / connective tissue interface, a thin layer of fibrous connective tissue was seen over the material (Figure 6.5 (c)).

![Figure 6.5](image)

**Figure 6.5.** HA-B is seen within cortical bone (B) and marrow (M) with evidence of bone in contact with material with no intervening fibrosis. Material can be seen in the soft tissues surrounding the bone in image (c) (marked X) and is surrounded by periosteum and a thin layer of fibrous connective tissue with no inflammation. Scale bar in images (a) and (c) are 1mm while scale bar in images (c) and (d) are 100µm.
6.4 Discussion

The *in vitro* evaluation indicated that both test materials induced a favourable response in the ROS cells with some evidence that the order of “biocompatibility” was:

\[ \text{HA-B (5 wt.% ZrO}_2\text{)} \geq \text{HA-C (10 wt.% ZrO}_2\text{)} \]

These results suggest that the increase in ZrO$_2$ content leads to a slight decrease in the in the osteoconductive response with results found by Lee, Tsai, Chang, Yang and Yang (2002) which suggested that reduced ZrO$_2$ content is associated with an improvement in bone response in HA-ZrO$_2$ composites.

The animal model used to assess the bone response to the test materials was the rat femur healing model which is well established; this and the similar rat tibia model have been used by the Sheffield group and others for several years (Zreiqat et al. 2002, Heimann and Vu 1997). A defect in the immature rat femur will heal rapidly and implanted materials will often encourage increased bone formation in the medullary space; this region is normally occupied by marrow and has little trabecular bone except for the proximal and distal end of the bone. This model is useful for establishing whether a material will elicit a favourable or unfavourable response in bone. Those that excite an unfavourable response in this model are unlikely to be worthy of more long term studies. This model is useful as an early screen for new materials intended for medical implantation. *HA-B*: (HA with 5wt% ZrO$_2$ (3Y-TZP)) elicited a favourable osteoconductive response in bone and would appear suitable for further evaluation in more rigorous non healing models. The material did not cause an inflammatory response in bone, but if excess material were to escape into soft tissue a different response may be elicited and care should be taken to interpret these results in the context of bone only.

6.5 Conclusions

- *In vitro* and *in vivo* evaluation has been carried out on two microwave sintered HA composites: **HA-B**: HA with 5 wt.% ZrO$_2$ (3Y-TZP), and **HA-C**: HA with 10 wt.% ZrO$_2$ (3Y-TZP).
- *In vitro* evaluation indicated that both test materials induced a favourable response in rat osteosarcoma cells; the order of ‘biocompatibility’ was:
HA-B ≥ HA-C

- *In vivo* evaluation showed the HA-B material to be osteoconductive and biocompatible in the rat tibia model used and are worthy of further consideration as bone substitutes.
7. **Summary Conclusions & Future Work**

7.1 **Zirconia**

There were two main objectives of the present study. The first objective was to investigate the effect of microwave sintering on physical, mechanical and chemical properties of Y$_2$O$_3$ (2-5 mol%) doped ZrO$_2$ compositions compared with conventional sintering.

The second objective was to investigate the effect of microwave sintering on HA-ZrO$_2$ composites using HA prepared in the laboratory and zirconia with the optimum Y$_2$O$_3$ content for Y-TZP found in stage 1. The mechanical, chemical and physical properties of the microwave and conventionally sintered composites were compared.

In vivo and in vitro examination of microwave sintered samples of an optimum HA-ZrO$_2$ composite composition was determined.

7.1.1 **Powder Processing**

Through attrition milling of undoped m-ZrO$_2$ with co-precipitated Y$_2$O$_3$-containing ZrO$_2$ it was possible to prepare powder compositions containing 2 to 5 mol% Y$_2$O$_3$ which contained some monoclinic ZrO$_2$ phase and also varying quantities of cubic/tetragonal ZrO$_2$ phases. Subsequently it was observed that the activation energies for sintering of the 2 and 3 mol % Y$_2$O$_3$-doped ZrO$_2$ compositions (containing t- ZrO$_2$), determined using dilatometry, were lower than those found for the 4 and 5 mol % Y$_2$O$_3$ compositions (containing c-ZrO$_2$).

7.1.2 **Comparative Sintering**

Microwave sintering (MS) achieved greater densification of Y$_2$O$_3$-doped ZrO$_2$ samples than conventional sintering (CS). These effects were most pronounced at a sintering temperature of 1100°C. As the sintering temperature/densification increased, the microwave enhancement decreased. There is a significant increase in the standard deviations of densities and mechanical properties for samples subjected to microwave sintering. This is thought to be associated with localised hotspots and a non-homogenised field within the microwave cavity. These deviations generally decreased as the microwave sintering temperature increased.

7.1.3 **Mechanical Properties**

Both elastic moduli and hardness of Y$_2$O$_3$-doped ZrO$_2$ ceramics are dependant mainly on the volume fraction porosity present in the sample, irrespective of the sintering technique or the mol % Y$_2$O$_3$ present. Biaxial flexural strength also exhibits a
dependency on porosity. However compositional effects such as the monoclinic or tetragonal ZrO$_2$ present and the microstructure also have an effect. This was generally observed at high levels of densification associated with a sintering temperature of 1300°C. The maximum biaxial flexural strength achieved of 807 MPa was observed for the MS samples containing 2 mol % Y$_2$O$_3$. The maximum hardness of 12.5 GPa was observed in MS samples containing 3 mol % Y$_2$O$_3$. When considering a reinforcing phase for use in a HA composite, ZrO$_2$ compositions with both 2 and 3 mol % Y$_2$O$_3$ appear to be the best candidates. Maximising the tetragonal ZrO$_2$ phase within the composite is important in any attempt to enhance the toughening effect.

7.2 Hydroxyapatite-Zirconia Composites

7.2.1 HA synthesis

Using a co-precipitation synthesis method HA was synthesized at temperatures of 25°C and 45°C. A synthesis temperature of 25°C produced a nano-scale powder with a Ca:P ratio similar to that of stoichiometric HA. Increasing the synthesis temperature to 45°C resulted in an increase in the particle size and a reduction in the specific surface area of the powder and an increase in the Ca:P ratio. The powder properties associated with HA synthesized at 25°C resulted in a reduction of the onset sintering temperatures and temperature of maximum rate of densification compared to a coarser particle size commercial powder.

7.2.2 Comparative Sintering of unfilled HA

Microwave sintering of synthesized HA resulted in an increase in relative density compared with conventionally sintered samples at temperatures of 1000-1200°C. However, a plateau was reached at 1200°C beyond which an increase in the temperature led to a slight decrease in relative density. The density of conventionally sintered samples increased as the temperature increased to 1300°C and the maximum relative density of 96.6% was observed at this temperature. HA begins to decompose above 1100°C. Similar levels of decomposition phase were present at temperatures of up to 1200°C in both microwave and conventionally sintered HA. However microwave sintering hastened the degradation of HA to α-TCP at a sintering temperature of 1300°C.

7.2.3 Comparative Sintering of HA-ZrO$_2$ composites

In commercial HA-ZrO$_2$ composites consisting of 0-40wt% ZrO$_2$, the relative density of composites decreased as the ZrO$_2$ loading increased irrespective of the
sintering technique use. Coinciding with the reduction in relative density, the decomposition of HA increased as the amount of ZrO$_2$ increased, irrespective of the sintering technique. Microwave sintering of synthesized HA-ZrO$_2$ composites containing 5 and 10 wt% ZrO$_2$ resulted in enhanced densification (reaching 82% and 91%) compared to conventionally sintered samples (70% and 87%) at temperatures of 1000 and 1100°C respectively. This enhancement was removed with any further increase in sintering temperature. Similar to the commercial HA-ZrO$_2$ composites, both microwave and conventional sintering at temperatures of 1200°C and 1300°C the relative density of composites decreased as the ZrO$_2$ loading increased, irrespective of the sintering technique.

As with commercial HA-ZrO$_2$ composites, increasing the ZrO$_2$ loading of synthesized composites increased the decomposition of HA to TCP. The decomposition became more prevalent with increasing sintering temperature and was increased in microwave sintered samples compared to conventionally sintered samples. It is suggested that this decomposition results in the release of H$_2$O, hence increasing the porosity of composites. Phase analysis indicated that CaO released through the decomposition of HA reacted with the ZrO$_2$ reinforcing phase to form either c-ZrO$_2$ solid solution and/or CaZrO$_3$ above temperatures of 1100°C. This occurs in both sintering techniques and suggests that the Y$_2$O$_3$ content of the ZrO$_2$ phase is irrelevant as release of CaO, resulting from the decomposition of HA, reacts with the tetragonal ZrO$_2$ forming c-ZrO$_2$ and/or CaZrO$_3$.

Through the addition of 2.5 wt % CaF$_2$ to microwave sintered synthesized HA-ZrO$_2$ composites the relative density was significantly increased compared with similar composition without CaF$_2$. For example, relative densities of 96.3% (±1.5) and 95.2% (±2.3) were observed in CaF$_2$ containing MS composites compared to 92% (±0.6) and 82.5% (±2.3) in compositions with similar ZrO$_2$ additions but no CaF$_2$. The substitution of F$^-$ for OH$^-$ resulted in the partial formation of Fluoro-HA, increasing the thermal stability and limiting the formation of H$_2$O, thus increasing the relative density. While the addition of CaF$_2$ increased the density of composites, CaO, formed in this case from the substitution of F$^-$ for OH$^-$, reacts with t-ZrO$_2$ again forming CaZrO$_3$ and/or c-ZrO$_2$. 
7.2.4 Mechanical Properties of HA and HA-ZrO$_2$ Composites

The maximum stiffness values were observed in unfilled HA of 109 GPa for MS samples and 112 GPa for CS samples. The Young’s modulus of commercial HA composites and synthesized HA-ZrO$_2$ composites exhibited a strong correlation ($r^2$ greater than 0.89) with the empirical exponential relationship $[E = E_0 \exp(-bE_P)]$ with porosity in both the case of microwave and conventionally sintered samples. This suggests that porosity resulting from the addition of ZrO$_2$ to HA is the major determinant of the Young’s modulus of the composites. Similarly, the hardness of commercial HA composites and synthesized HA-ZrO$_2$ composites also exhibited a strong correlation with the empirical exponential relationship with porosity in both the case of microwave and conventionally sintered samples. This again suggests that porosity resulting from the addition of ZrO$_2$ to HA is the major determinant of the hardness of the composites.

The maximum flexural strengths were again observed in the unfilled HA. In microwave sintered samples the maximum strength observed was 130 MPa, while the highest strength observed in conventionally sintered sample was 164 MPa. This maximal strength coincided with the highest relative density achieved of 96.6%. Increasing Zirconia content generally reduced the flexural strengths. The flexural strengths of composites, while exhibiting some relationship with porosity also appear to be dependent on the amount of decompositional phases present. In particular, in the case of synthesized HA-ZrO$_2$ composites, an increase in the amount of TCP resulted in a decrease in the strengths of composites.

The increased density of CaF$_2$ containing composites led to an increase in the Young’s modulus and the hardness of ZrO$_2$ containing composites. For example, the maximum hardness of composites containing 5 and 10 wt% ZrO$_2$ was increased from 3.7 and 2.4 GPa, respectively, to 5.6 and 5.1 GPa through the addition of CaF$_2$. However the biaxial flexural strengths of composites were not increased by the inclusion of CaF$_2$. While there was an increase in mechanical properties compared to HA-ZrO$_2$ composites without CaF$_2$, values for the Young’s modulus and the hardness were only comparable to unfilled HA. The strengths were inferior to unfilled HA. The addition of ZrO$_2$ provided no additional enhancement to the mechanical properties of HA.
7.2.5 Biological Evaluation of HA-ZrO$_2$ Composites

In vitro evaluation was carried out on microwave sintered HA composites containing 5 and 10 wt% ZrO$_2$ (3 mol% Y$_2$O$_3$) and indicated that both test materials induced a favourable response in rat osteosarcoma cells; the order of ‘biocompatibility’ was:

HA-5 wt% ZrO$_2$ ≥ HA-10 wt% ZrO$_2$

This suggested that the increase in ZrO$_2$ content led to a slight decrease in the biological response. In vivo evaluation of the composite containing HA and 5 wt% ZrO$_2$ revealed the material was osteoconductive and biocompatible in the rat tibia model. While the ZrO$_2$ content did not decrease the osteoconductive properties of the HA, it is hard to envisage the use of the material in the context of a low-load bearing bone graft material. The addition of ZrO$_2$ resulted in significant reduction in the densities of the composites in the case of both microwave or conventionally sintered composites, which significantly reduced the mechanical properties below that of undoped HA.
The microwave sintering of the tailored Y$_2$O$_3$ doped ZrO$_2$ ceramics led to increased densities and mechanical properties over conventional sintering techniques. However, full densification of the sintered samples was not achieved. It is envisioned that using the microwave sintering device an optimised sintering schedule could be employed to further enhance the density and mechanical properties of Y$_2$O$_3$-doped ZrO$_2$. The use of a two stage sintering technique, proposed by Chen and Wang (2000) and shown to enable the sintering of fine grained dense appears to be an area worthy of investigation. Similarly, examining the effects of duration of sintering at lower temperatures on the HA and HA-ZrO$_2$ composites is worthy of further investigation.

The mechanical properties of the ZrO$_2$, HA and HA-ZrO$_2$ composites were characterised in terms of elastic moduli, biaxial flexural strengths and the microhardness. One significant limitation to the study is the lack of fracture toughness measurements (K$_{IC}$), an important characteristic in brittle material. There are several techniques for determining the K$_{IC}$ of the sintered ceramics such as notch beam testing and indentation toughness that can be investigated.

Further examination of nature of HA decomposition in the presence in ZrO$_2$ using FTIR or DTA analysis.

While it was shown that CaF$_2$ increased the densities of HA-ZrO$_2$ composites, any possible toughening effect was removed through the release of CaO and subsequent formation of CaZrO$_3$ and the mechanical properties were comparable to unfilled HA. Perhaps an alternative approach to consider is to use a precipitation technique to first prepare a flourapatite (FHA) powder and then add the ZrO$_2$ phase. In this case the greater thermal stability of FHA and the lack of CaO may allow the sintering of a dense composite containing FHA and t-ZrO$_2$. 
References


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