FHA bioceramic and zirconia toughened FHA bioceramic composite

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FHA Bioceraic and Zirconia Toughnened FHA Bioceramic Composite

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Chapter 1 Introduction

1.1 Background

Synthetic hydroxyapatite (HA; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) has been widely investigated and used as a substitute for damaged bone and teeth due to its biocompatibility and excellent bioactivity with human bone tissues. However, the intrinsic poor mechanical properties of the HA ceramics have somehow restricted the applications of them in load-bearing areas. Therefore, many attempts have been made to reinforce HA by incorporating second phases such as ceramic particles, whiskers, and polymeric fibers. Among them, yttria stabilized tetragonal zirconia (YTZP) has been favored due to its biocompatibility and excellent mechanical properties. Nevertheless, extensive reaction between the HA phase and the ZrO_2 phase to form tricalcium phosphate (TCP; $\text{Ca}_3(\text{PO}_4)_2$) is a big disadvantage of this approach. During the past few decades, partially fluorine-substituted hydroxyapatite (FHA; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{F}_{2x}$, $0 < x < 1$) has attracted much interest based on the extensive findings of partially fluoridated hydroxyapatite in bone and teeth and the stimulation of fluoride on bone growth. Therefore, in his work the author managed to produce nanoparticle FHA powders by precipitation method and prepare FHA-YTZP composites by both conventional sintering and spark plasma sintering.

1.2 HA and FHA solid solution bioceramics

Synthetic hydroxyapatite (HA) has been used extensively as bone implant materials due to its identical chemical composition to and high biocompatibility with natural bone. However, as synthetic HA possesses very low mechanical strength, applications of it are restricted exclusively to areas free of dynamic load bearing. Another drawback of HA is the decomposition of synthetic HA into β or α -TCP at temperatures higher than 1000°C. Thus, fluoroapatite (FA) has been investigated during recent years since it exhibits higher thermostability and better corrosion resistance in biological environment than HA.

Despite of its many advantages over HA, pure FA has not been utilized as an implant material because it is difficult to prepare and has insufficient bioactivity. Moreover, so far no standard FA synthesis has been adopted by the research communities. Therefore, FHA solid solution has been studied in order to combine the excellent stability of FA with the superior bioactivity of HA. To study the sintering behavior of the FHA ceramics, in this project the author managed to synthesize nanosized FHA powders by a modified precipitation method and prepared FHA ceramics by conventional sintering at selected temperatures.

1.3 FHA-YTZP biocomposites from nanosized FHA powders

Due to its low mechanical strength, FHA cannot be solely used as an implant material for load bearing applications. At the meanwhile, yttria stabilized tetragonal zirconia polycrystal (YTZP) has been widely studied because of its biocompatibility with bone and superior mechanical properties.

However, zirconia is of bioinert nature, which will not form any direct biological bonding with bone, unlike what bioactive ceramics will do, e.g., HA and FA. A relatively thick fibrous tissue will exist at the interface between bone and it, and thus, failure might generate from the interface layer.

To combine the bioactivity of FHA and the mechanical strength of YTZP, FHA-YTZP composites have been investigated. In this report, the author managed to produce FHA-YTZP composites with different YTZP contents by both conventional sintering and spark plasma sintering, considering that FHA would provide the bioactivity and YTZP would provide the mechanical strength.

1.4 Objective and Scope

The objective of the project is to prepare and characterize bioceramic composites using nanosized FHA powders and nanosized YTZP powders for applications in bone replacement because of their potential mechanical strength and good bioactivity.

The scope of this project includes:

1. Preparation and investigation of conventionally sintered FHA ceramics with different fluorine contents at selected temperatures for better phase stability and sinterability.
2. Preparation and investigation of conventionally sintered and spark plasma sintered FHA-YTZP composites with different YTZP contents at selected temperatures for better phase stability and desirable mechanical properties, which were suitable for biomedical applications.

1.5 Organization of the Report

This report begins with the general introduction of background, objective and scope of the project, all of which are presented in Chapter 1. The previous studies and other background information relevant to the project are summarized in Chapter 2. The detailed procedures of the work, i.e. sample preparation and characterization methods are covered in Chapter 3. Finally, the experimental results are presented and discussed in Chapter 4 and 5, and the conclusions and future work are presented in Chapter 6 and 7, respectively.

Chapter 2 Literature review

2.1 Introduction to ceramics

The term “ceramics” originates from the ancient Greek word “keramos”, and is currently defined as the art and science of making and using solid articles which are essentially composed in large part of inorganic nonmetallic materials [1]. This definition includes not only materials such as pottery, porcelain, refractories, structural clay products, abrasives, porcelain enamels, cements, and glass but also nonmetallic magnetic materials, ferroelectrics, manufactured single crystals, glass-ceramics, and a variety of other products which were not in existence until a few years ago and many which do not exist today.

The first ceramic objects in the archaeological record are fired clay figures appearing about 22,000 years ago in China [2]. This art form gradually became used for more practical objects such as bowls and storage vessels on a much larger scale about 6,000 years ago. Being subjected to thousands years of revolutions and developments, the ceramic industry has become one of the largest and most important industries in the world. One important characteristic of the ceramic industry is that it is basic to the successful operation of many other industries. For example, glass products are essential to the automobile industry as well as to the architectural, electronic, and electrical industries. Uranium oxide fuels are essential to the nuclear-power industry. Various special electrical and magnetic ceramics are essential to the development of computers and many other

electronic devices. As a matter of fact, ceramics materials play an important role in almost every industrial production line, office, home, and are critical for the civilization of human race.

2.2 Introduction to bioceramics

During the past four decades, a revolution has occurred in the use of ceramics to improve the quality of life. This revolution is the innovative use of specially designed ceramics for the repair, reconstruction, and replacement of diseased or damaged parts of the body. For example, insoluble porous glasses have been used as carriers for enzymes, antibodies, and antigens, offering the advantages of resistance to microbial attack, pH changes, solvent conditions, and temperature [3]. Ceramics have been used in dentistry as restorative materials such as porcelain crowns, inlays, veneers, cements, glass- or silica-filled resin composites, dentures, and so forth [4]. Ceramics used for these purposes are termed “bioceramics.”

In general, bioceramics consist of three major categories, i.e., bioinert, bioactive and bioresorbable [5].

1. **Bioinert** ceramics, such as alumina and zirconia, are the materials that are nontoxic, biologically inactive and will form a bond to the tissue through fibrous encapsulation.
2. **Bioactive** ceramics are capable of eliciting specific biological response at the

interface of them, resulting in the formation of a bond between the tissue and the ceramics. Bioactive glass, hydroxyapatite (HA) and fluoroapatite (FA) fall into this category.

3. **Bioresorbable** ceramics are able to be absorbed and replaced by bone, thus no foreign materials are retained in the biological system. The most widely observed materials in this category are α and β tricalcium phosphate (TCP).

As a matter of fact, no material implanted in a living tissue is definitely inert because all materials elicit a response from a living tissue. The mechanism of tissue attachment is directly related to the type of tissue response at the implant-tissue interface. There are four types of tissue response (Table 2-1) and four different means of attaching prostheses to the skeletal system (Table 2-2) [6].

The bioceramics that are supposed to discuss in this chapter could be divided into three categories; bioinert crystalline ceramics, bioactive apatites, and bioresorbable calcium phosphates, corresponding to the different tissue responses and types of attachment after implantation, and the different applications of these bioceramics in the biomedical areas.

Table 2-1 Types of implant-tissue response

Implant Type	Tissue response
Toxic	The surrounding tissue dies
Nontoxic and bioinert	A fibrous tissue of variable thickness forms
Nontoxic and bioactive	An interfacial bond forms
Nontoxic and biodegradable	The surrounding tissue replace it

Table 2-2 Types of bioceramics-tissue attachment and their classification

Type of attachment	Example
Dense, nonporous, bioinert ceramics attach by bone growth into surface irregularities by cementing the device into the tissues or by press-fitting into a defect	Alumina (single crystal and polycrystal)
For porous bioinert implants, bone ingrowth occurs that mechanically attaches the bone to the material	Alumina (polycrystalline) and hydroxyapatite-coated porous metals
Dense, nonporous surface-reactive ceramics, glasses, and glass-ceramics attach directly by chemical bonding with the bone	Hydroxy/fluoroapatite, bioactive glasses and glass-ceramics
Dense, nonporous resorbable ceramics are designed to be slowly replaced by bone	Tricalcium phosphate (TCP) and calcium phosphate salts

2.3 Bioinert crystalline ceramics

2.3.1 Introduction to bioinert crystalline ceramics

Single oxide ceramics, i.e., alumina and zirconia, are bioceramics of inert nature, which do not form a direct bonding to bone. Alumina is in the pure aluminium oxide form, whereas zirconia is partially stabilized by additional oxides, e.g., yttria, calcia or magnesia. These bioinert ceramics exhibit super mechanical properties, corrosion and wear resistance. Since the oxides are the highest oxidation state of the metal, they are stable even in the most invasive industrial and biomedical environments. Alumina and zirconia are widely utilized as load-bearing hard tissue replacements and fixation implants in dentistry and surgery.

Although the use of alumina as implants can be traced back to the 1930s as described by Hulbert et al. [7], alumina has only been extensively used since 1980s due to the grain size reduction of the sintered ceramics from 10 micrometers down to 2 micrometers induced by new powder processing technology, which significantly improves the performance of the alumina ceramic hip balls. Alumina and partially stabilized zirconia are currently in extensive use as implants in consequence of their high strength, excellent corrosion and wear resistance and stability, nontoxicity and biocompatibility *in vivo*. A summary of alumina and zirconia based implants is presented in Table 2-3.

Table 2-3 Biomedical applications of oxide ceramics

Materials	Applications
Alumina	Hip ball & cup, Knee joint, bone screws, dental implants and dental crowns & brackets
Zirconia	Hip ball, dental implants and dental post, brackets and inlay

2.3.2 Alumina

Alumina is the compound to which the greatest attention has been paid. This is due to the fact that it is a ceramic material widely used for porcelains and therefore more characterized, from an engineering point of view, than any other known ceramics. High-density, high-purity (>99.5%) Al_2O_3 is used in load-bearing hip prostheses and dental implants because of its combination of excellent corrosion resistance, good biocompatibility, high wear resistance, and high strength. Although at least seven forms of Al_2O_3 have been reported, when heated above 1200°C , all other structures are irreversibly transformed to the hexagonal α - Al_2O_3 [8,9]. Most Al_2O_3 devices in clinical applications are very fine-grained polycrystalline α - Al_2O_3 produced by pressing and sintering at temperatures of about 1600°C . A very small amount (<0.5%) of MgO is generally used as an aid to sintering and to limit grain growth during sintering. Up to now alumina has been used in orthopedic surgery for nearly 40 years, motivated mainly by two factors:

- Excellent biocompatibility and very thin capsule formation, which permits cementless fixation of prostheses
- Exceptionally low coefficients of friction and wear rates

2.3.2.1 Physical and mechanical properties

Resulting from a strong chemical bond between the Al and O ions, as expected from the value of heat of formation (-400k cal/mol), alumina has a high melting point. The strength, fatigue resistance, and fatigue toughness of polycrystalline α -Al₂O₃ are noticeable functions of grain size and purity. Alumina with an average grain size of <4 μ m and >99.7% purity exhibits good flexural strength and excellent compressive strength [10]. The specific physical and mechanical properties of alumina as compared to zirconia are shown in Table 2-4.

2.3.2.2 Chemical properties

Alumina is chemically stable and corrosion resistant. It is insoluble in water and only very slightly soluble in strong acids and alkalies. Therefore, practically no release of ions from alumina occurs in a biological environment in which the physiological pH level is about 7.4.

2.3.2.3 Tribologic properties

The superb tribologic properties (friction and wear) of alumina occur only when the grains are very small (<4 μ m) and have a very narrow size distribution, which conditions

lead to very low surface roughness values. If large grains are present, they can be pull out and lead to very rapid wear of bearing surfaces due to local dry friction. It was reported that the wear resistance of the alumina head/UHMWPE cup combination over metal/UHMWPE had improved from three to four times clinically [10].

Table 2-4 Physical and mechanical properties of alumina and zirconia (at 25°C)

* Zirconia presented is the yttria-partially stabilized material

Property	Alumina	Zirconia
Crystallography	Hexagonal	Tetragonal
a-axis (Å)	4.76	3.64
c-axis (Å)	13.0	5.27
Melting point (°C)	2040	2680
Density (g/cm ³)	3.98	6.08
Hardness (GPa)	22	12.2
Modulus of elasticity (GPa)	366	201
Poisson's ratio	0.26	0.30
Thermal coefficient of expansion 25-200 °C	6.5	10.1
Flexural Strength (MPa)	551	1074
Compressive strength (MPa)	3790	7500
Tensile strength (MPa)	310	420
Fracture toughness (MPa m ^{1/2})	4.0	6-15

2.3.3 Zirconia

Similar to alumina, zirconia is also widely utilized clinically due to its superior mechanical properties and good wear resistance. Zirconia ceramics are termed polymorphic because they undergo several transformations on cooling from a molten state to room temperature. Zirconia exhibits three well-defined polymorphs, namely, the monoclinic, tetragonal and cubic phases. The monoclinic phase is stable up to about 1170°C at which it transforms to the tetragonal phase, stable up to 2370°C, while the cubic phase exists up to the melting point 2680°C [11-13]. Therefore, in order to consider the behavior of zirconia it is necessary to evaluate the transformations that it undergoes in relation to the cooling process once the preshaped object has been sintered. The characteristics of the different phases of zirconia are shown in Table 2-5.

Table 2-5. Outline of the salient properties of zirconia

Phase	Transformation temperature (°C)	Unit cell constants (Å)	Space group	Density (kg/m ³)
Monoclinic	1170	a = 5.156 b = 5.191 c = 5.304 β = 98.90	P2 ₁ /c	5560
Tetragonal	2370	a = b = 5.094 c = 5.177	P4 ₂ /nmc	6100
Cubic	/	a = b = c = 5.124	Fm3m	6090

2.3.3.1 Yttria stabilized tetragonal zirconia polycrystall (YTZP)

Zirconia is not suitable for use as the only material from which a body is manufactured because in the transition from tetragonal to monoclinic during cooling, tensions are generated inside the ceramic body by the different contraction relationships between the granules, which can cause fractures. The transformation from the tetragonal to the monoclinic phase is accompanied with an increase of volume of about 5% and with a change in shape, both of which factors generate a relevant tangential effort along particular crystallographic axis of each grain. This phenomenon, which has a destructive action, prevents the use of zirconia as a massive material.

Generally, additives such as calcia, magnesia and yttria must be mixed with zirconia to stabilize the material in either the tetragonal or the cubic phase. Yttria stabilized tetragonal zirconia polycrystall (YTZP) is 100% tetragonal, and is preferable for medical implant applications.

2.3.3.2 Physical and mechanical properties of YTZP

Zirconia ceramics have a high density because of heavy zirconium ions, and a low microhardness and elastic modulus, together with high strength and fracture toughness compared to other ceramics including alumina. Yttria partially stabilized TZP ceramics (YTZP) even have a strength and fracture toughness approximately twice that of alumina ceramics used in the biomedical field, as shown in Table 2-4, which makes zirconia implants less sensitive to stress concentrations.

2.3.3.3 Wear resistance

Several reports demonstrated a high wear resistance of zirconia against UHMWPE and the superiority of zirconia ceramics over alumina ceramics in terms of low wear and low friction.

2.3.3.4 Transformation toughening of zirconia

It was first proposed by Garvie et. al. [14] that the metastable tetragonal zirconia showed substantially stronger fracture strength than the partially stabilized monoclinic zirconia due to the absorption of energy during the martensitic transformation of tetragonal particles to monoclinic. Ever since then the transformation toughening of zirconia ceramics had received great interest and been intensively studied. Theoretically, the toughness of a traditional brittle ceramic could be increased by a factor of 4 or more through the transformation toughening mechanism. Generally, there are a number of essential requirements for successful transformation toughening [14,15]:

- There must be a metastable phase present in the material and the transformation of this phase to a more stable state must be capable of being stress-induced in the crack-tip stress field.
- The transformation must be virtually instantaneous and not require time-dependent process such as long-range diffusion.
- It must be associated with a change of shape and/or volume.
- The transformed product must not be substantially more brittle than the parent phase from which it forms, to ensure a net increase of toughness of the material.

2.3.3.5 Drawbacks

Although zirconia ceramics seem to possess superior wear resistance and mechanical properties, there are two possible potential limitations for the use of zirconia as bioceramics: degradation and radiation. It is well known that the phase transformation is accelerated in aqueous environment, but little is known about how this phase transformation will occur in biological environment, particularly under dynamic loadings [16]. Another severe problem is the radioactive U-235 impurity detected in some “pure zirconia”, both alpha and gamma-irradiation were measured from zirconia femoral balls. Although the radioactivity was fairly low, more work is required to verify this matter [17].

2.3.3.6 Competition between zirconia and alumina as biomedical materials

As mentioned above, both zirconia and alumina are bioceramics of inert nature, and with superior mechanical properties as compared to human natural bone. Because neither of these two bioceramics can form firmly direct bonding with bone hard tissues, which possibly make them vulnerable to fixation problem after a long period of implantation, the most important reason of all that they are used as implants is their excellent mechanical properties that no other bioactive bioceramics can match. Between these two bioceramics, alumina possesses significantly lower strength and fracture toughness than zirconia does, which makes alumina more sensitive to stress concentration and dynamic flow. Thus, since the major applications of these bioceramics are implants in the load-bearing areas, the superior strength and fracture toughness of zirconia has been an outstanding advantage for it as an implantation material. Recently zirconia and zirconia

biocomposites have attracted more and more interest.

2.4 Bioresorbable calcium phosphate

2.4.1 Introduction to bioresorbable calcium phosphates

Fast absorption and replacement of bioresorbable ceramics by bone upon implantation are the advantage of them over other bioceramics. Among them, tricalcium phosphate (TCP) is most often mentioned and has been long investigated for clinical applications as periodontal pocket obliteration, alveolar ridge augmentation, and bone space fillers due to their good bioactivity and higher Young's modulus and compressive strength than those of human bones [18-29].

Tricalcium phosphate is known to have two phases, that is, the α - and β -whitlockite. The latter develops at high temperatures ($>1000^{\circ}\text{C}$) in dry air, but reacts rather easily with water to give rise to a substance identical, from a crystallographic point of view, to hydroxyapatite [30,31]. The α -TCP is also known to hydrate to a calcium-deficient hydroxyapatite in dilute aqueous solutions and at elevated temperatures ($60\text{-}100^{\circ}\text{C}$) [31]. This calcium phosphate is unique in that it can hydrolyze by itself to form cement. The rate of the α -TCP hydration tends to increase with temperature and decrease with increasing pH of the ambient solution.

2.4.2 Resorbability of tricalcium phosphates

There are three factors that contribute to the resorbability of calcium phosphate ceramics:

1. Physiochemical dissolution, which depends on the solubility product of the material and local pH of its environment. New surface phases may be formed, such as amorphous calcium phosphate, and anionic-substituted hydroxyapatite.
2. Physical disintegration into small particles as a result of preferential chemical attack of grain boundaries.
3. Biological factors, such as phagocytosis, which causes a decrease in local pH concentration.

The most widely investigated bioresorbable ceramic is TCP. It is found that the dissolution rate of TCP was 12.3 times higher than that of hydroxyapatite in buffered lactic acid solution (pH 5.2). The dissolution rate of several calcium phosphates in calcium and phosphate free solution with pH 7.3 increased in the following order [4,32]:

Fluoroapatite < Hydroxyapatite « β -Tricalcium phosphate < α -Tricalcium phosphate

2.4.3 Factors influencing the resorbability of tricalcium phosphate

The rate of bioresorbability increases as:

1. Surface area increases (powders > porous solid > dense solid)

2. Crystallinity decreases
3. Crystal perfection decreases
4. Crystal and grain size decreases
5. There are ionic substitutions of CO_3^{2-} , Mg^{2+} , and Sr^{2+} in HA

The rate of bioresorbability decreases as:

1. F^- substitution in HA
2. Mg^{2+} substitution in β -TCP
3. Lower β -TCP/HA ratios in biphasic calcium phosphate

Because of these variables it is necessary to control the microstructure and phase state of a resorbable calcium phosphate bioceramic in addition to achieving precise compositional control to produce a given rate of resorption in the body. So far, there are few data on the kinetics of these reactions and the variables influencing the kinetics.

2.5 Hydroxyapatite

2.5.1 Introduction to hydroxyapatite

Hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) seems to be the most promising ceramic material for artificial teeth or bones due to its chemical similarity with bone hard tissues and excellent bioactivity with skin and muscle tissues [33]. It was first identified as being the mineral component of bone in 1926. However, it is not until about 25 years ago that

synthetic hydroxyapatite is accepted as a potential biomaterial for use in orthopedics, bone grafts and dentistry. It is one of a limited number of materials that will form strong chemical bonds with bone *in vivo*, while remaining stable under the harsh conditions encountered in the human body.

Unfortunately, due to the low reliability in wet environments and its brittleness, low mechanical strength and poor fatigue resistance, hydroxyapatite is not suitable for heavy load bearing applications, which was verified by various researchers when they studied the tensile strength of pure hydroxyapatite implants [34-37]. Therefore, hydroxyapatite is presently restricted to applications that involve non-or low load-bearing conditions in service, such as bone fillers and bone graft substitutes in orthopedics as well as ossicular bone replacements and materials for maxillofacial reconstruction.

2.5.2 Introduction to the synthesis of hydroxyapatite

Ever since hydroxyapatite was identified as the mineral component of human bone, numerous synthesis methodologies of preparing hydroxyapatite have been developed, such as solid-state synthesis [38-40], precipitation [41-43], and sol-gel methods [44-49]. It seems that the precipitation and sol-gel methods are the most promising in producing homogeneous powders with fine grain size. During recent years, precipitation and sol-gel methods have been extensively investigated and utilized in preparing homogeneous or heterogeneous calcium phosphates and their composites with particle sizes in the nano region [48,49].

2.5.3 Synthesis of hydroxyapatite by precipitation method

Precipitation method is well known for its commercial-efficiency in producing nanosized hydroxyapatite powders due to the simple experimental procedures, low operating temperatures, and high yields of fine and pure products [50-57]. In this method, chemical reactions take place between Ca and P precursors, which are normally in the form of salts, acids, or alkali, under a controlled pH and temperature of the aqueous solution. The precipitated powders are typically calcined at 400-700°C to develop a stoichiometric apatite structure. However, fast precipitation during phosphate solution titration to calcium solution leads to chemical inhomogeneity in the final product. Slow titration and diluted solutions must be used to improve chemical homogeneity and stoichiometry of the resultant powders. Moreover, careful control of the solution condition is critical in the wet precipitation. Otherwise, a decrease of solution pH below about 9 could lead to the formation of Ca-deficient HA structure.

Precipitation method was first developed by using calcium nitrate-4hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$) as the precursors for Ca and P, and ammonia (NH_4OH) to adjust the pH of the solution. The reaction is based on the following equation:

2.5.4 Synthesis of hydroxyapatite by sol-gel method

The term sol-gel is currently used to describe any chemical procedure or process capable of producing ceramic oxides, non-oxides and mixed oxides from solutions. The sol-gel process has been used to produce ceramic powders, coatings and bulk materials including glasses. There are several advantages of the sol-gel technique upon other apatite preparation techniques, including:

1. Increased homogeneity due to mixing on the molecular scale.
2. Reduced firing temperatures due to small particle sizes with high surface areas, ability to produce uniform fine-grained structures.
3. Use of different chemical routes (alkoxide or aqueous based) and their ease of application to complex shapes with a range of coating techniques, e.g. dip, spin and spray coating.

Various sol-gel techniques have been used to synthesize hydroxyapatite powder [58-69]. The sol-gel processing route using metal alkoxides as the starting materials is noteworthy on preparing powders from calcium phosphate precursors. Several other ultrafine chemical processing methods (not specifically the alkoxide route) have been reported and have proved to be attractive in refining precursor characteristics for hydroxyapatite and calcium phosphate ceramics [54,60]. Unfortunately, the powder precursors prepared by some of these methods exhibit a low sinterability, due to the formation of agglomerates, although the individual crystallite sizes were nanocrystalline. It is known that various investigators also encountered difficulty in achieving exact stoichiometry due to the

volatility of the alkoxy phosphorous compounds used.

2.5.5 Experimental parameters in precipitation and sol-gel method

To produce pure, uniform and stoichiometric hydroxyapatite powders through precipitation or sol-gel method, several important process parameters e.g., aging time, pH, reaction temperature, precursor concentration, and addition rate, should be fully understood, each of which has a strong influence on the purity and morphology of the product. Among them, the aging time and pH control have been most widely investigated due to their importance.

2.5.5.1 Aging time

In a number of recent reports on the synthesis of sol-gel hydroxyapatite, aging of the precursor solution has been found to be critical in developing an apatitic phase [48,64,70,71]. Critical aging time is required to complete reaction between Ca and P molecular precursors to form a desired intermediate complex that permits a further transformation to apatite phase under appropriate thermal treatment. By increasing the aging time, the hydroxyapatite precipitate undergoes recrystallization. As a result, occluded impurities are removed and crystal strain is reduced as the free energy of the crystal decreases, while the crystal structure becomes perfect and the exposed area is decreased. Needle-like and rod-like structures redissolve and are recrystallized in more orderly morphologies such as spheres with the shapes of the primary particles approaching a homogeneous distribution, which phenomenon can be also accompanied with a decrease in surface area.

It was reported by M. Liu et al. [64,70] that an approximate aging time of 10 hours was required for a well developed, single phase apatite formation, as illustrated in Figure 2-1 (The shadowed area indicates optimal aging parameters for single-phase apatite forming). The apatite obtained in the shadowed area has a Ca/P ratio of 1.67 ± 0.02 .

Figure 2-1 Phase evolution map for apatite formation in terms of aging time and temperature

2.5.5.2 pH control

pH can affect chemical precipitation by altering the solubility of the precipitates; the solubility of hydroxyapatite decreases as pH increases. As a result, nucleation would be favored at higher pH, decreasing crystallite size. Furthermore, different pHs affect agglomeration by inducing a surface charge on the particles in solution. Similar surface charges in the solution of the particles repel each other reducing agglomeration in the

solution. Moreover, the different pHs during the chemical precipitation are expected to affect crystal morphology with the morphology becomes increasingly rod-like with increasing pH. Finally, the most important of all, it is also known that when preparing calcium phosphates by precipitation or sol-gel from aqueous solutions, several phases are formed at different pH values, namely calcium hydrogen phosphate (CaHPO_4), calcium hydrogen phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), hydrated calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$) and hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$).

It was reported by F. Moztarzadeh et al. [72] that according to pH variation, four regions could be distinguished:

- 0- pH = 0-4, no precipitate.
- 1- pH = 4-8, CaHPO_4 , $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$.
- 2- pH = 8-10, structural transition observed.
- 3- pH = 10-13, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

2.5.5.3 Other parameters

There are still many other parameters which have their own influence on the yields of the processes, such as precursor concentration and addition rate. By varying the precursor concentration, the synthesis of nanocrystalline hydroxyapatite can be further controlled by affecting the kinetics of hydroxyapatite synthesis; the kinetics of the reaction is slowed down with reducing precursor concentration [73,74]. It was reported by L. J. Jha et al. [75]

that increasing fluoride ion concentration tended to reduce the aspect ratio of the crystallites produced.

Addition rate has a double-edge effect on the morphology of the precipitate. Nucleation and crystal growth rates can be controlled by the addition rate. It is believed that rapid addition of precursors results in localized high concentrations of precursors, exceeding the solubility of hydroxyapatite in those regions, which favors nucleation and formation of small particles, while rapid addition is also expected to result in a nonuniform particle morphology and distribution. Conversely, slow addition of precursors results in a more homogenous mixture of reactants favoring crystal growth and formation of large particles. Furthermore, slow addition of precursors is anticipated to result in a uniform particle morphology and distribution [76,77].

2.5.6 Solid-state synthesis of hydroxyapatite

Although presently sol-gel method and precipitation method have been widely employed in research areas to prepare high quality hydroxyapatite particles, as discussed above, the disadvantages that the composition of the product being greatly affected by even a slight difference in the reaction conditions and the long time required to develop the hydroxyapatite of a stoichiometric composition, have rendered these two methods inconceivable for industrial scale production. Therefore, when producing highly crystallized hydroxyapatite in mass, it seems that the dry process is more suitable than the wet process because it shows high reproducibility and low processing cost in spite of the risk of contamination and impurity due to the high temperature generally employed.

There are various calcium and phosphorous compounds reported to be used as the starting materials in the solid-state synthesis of hydroxyapatite, for example, dicalcium phosphate anhydrate (CaHPO_4), dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), monocalcium phosphate monohydrate ($\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$), calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$), and calcium oxide (CaO) [78-81]. In this synthesis method, the calcium and phosphorous containing starting materials are generally first sufficiently mixed together either in solutions or by ballmilling, then the mixed powder is dried and subjected to heat treatment at $900^\circ - 1000^\circ\text{C}$ to trigger the reactions between the precursors and give rise to hydroxyapatite. An example of the reaction is shown below:

2.5.7 Mechanical properties of hydroxyapatite

Fracture toughness (K_{Ic}) of pure, dense HA ceramics is in the range of $0.8\text{-}1.2 \text{ MPa} \cdot \text{m}^{1/2}$ with an average of $1.0 \text{ MPa} \cdot \text{m}^{1/2}$ [82]. It was also found that fracture toughness decreased almost linearly with increasing porosity. Fracture energy is in the range of $2.3\text{-}20 \text{ J/m}^2$.

Bending strength, compressive strength, and tensile strength of dense HA ceramics are in the ranges of $38\text{-}250 \text{ MPa}$, $120\text{-}900 \text{ MPa}$, and $38\text{-}350 \text{ MPa}$, respectively. The scattering of data is caused by statistical nature of strength distribution, influence of remaining microporosity, grain size, impurity etc. Strength increases with increasing Ca/P ratio, reaching the peak value around $\text{Ca/P} = 1.67$, followed by a sudden decrease when $\text{Ca/P} > 1.67$. Grain size and porosity were reported to influence the fracture path, while they had little effect on fracture toughness [83]. The average bending strength of the HA single

crystals (diameter in the range of 15-55 μm) was 468 MPa, 361 MPa, and 501MPa, for measurements in air, water, and simulated body fluid (SBF), respectively. The presence of small amounts of carbonate ions (up to 0.7 wt%) did not affect the strength of the HA single crystals in air, but slightly decreased it in water [84].

Weibull modulus of the dense HA ceramics is reported to be 5-18, which indicates that HA behaves as a typical brittle ceramic [85]. Slow crack growth coefficient (n) is in the range of 26-80 under dry condition, while it drops to the value of 12-49 under wet conditions indicating high susceptibility for slow crack growth under wet conditions [86]. It has been suggested that grain boundaries, with Ca/P ratio lower than that of HA, are especially susceptible to slow crack growth [87].

Young's modulus (E) of dense HA ceramics is in the range of 35-120 GPa. It depends mostly on measurement technique, also on remaining porosity, presence of impurity, etc. Vickers' hardness of dense HA ceramics is between 3.0 GPa and 7.0 GPa, while wear resistance and friction coefficient of them are comparable to those of human enamel [83]. Dense HA ceramics exhibit superplasticity at 1000°C-1100°C with a deformation mechanism based on grain boundary sliding.

2.5.8 Sintering and decomposition of hydroxyapatite

It has been widely reported that HA is thermally unstable at temperatures higher than about 1200°C differing with particle sizes of green bodies and sintering techniques employed [88-101]. According to E. Adolfsson et al. [91], the decomposition reaction is

divided into two steps, according to the formulae below:

It can be inferred from these equations that the decomposition temperature is a function of the partial pressure of water vapor, as reported by K. Yamashita et al. [83]. Hence, if the water loss is maintained at a low level, the equilibrium in the first reaction is shifted to the left and the second reaction does not occur (or occurs only to a limited degree). The employment of pressure assisted sintering could possibly prevent the decomposition reaction. E. Adolfsson et al. [91] managed to sinter high-density HA ceramics without notable decomposition using a hot isostatically pressed (HIP) technique.

2.6 Fluoroapatite and fluorohydroxyapatite

2.6.1 Introduction to fluoroapatite and fluorohydroxyapatite

In the past several decades, fluorine-substituted hydroxyapatite (fluoroapatite, FA, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) has been investigated as an implant material due to its stability both at high temperatures and in biological environments [92-96]. Unlike hydroxyapatite, which normally decomposes to tricalcium phosphate at above 1200°C , fluoroapatite has shown

phase stability even at higher temperatures [96]. Another merit of FA is its high corrosion resistance in biological environment and slightly higher mechanical strength [97].

However, considering its reported lack of good biological properties as compared to those of hydroxyapatite [98,99] and its possible biotoxicity due to the high fluorine content of it [100], fluoroapatite alone may not be a good biomaterial. For practical applications, the mechanical properties, bioactivity, biostability, and biodegradability should be tailored for particular situations. Therefore, recently partially fluorine-substituted hydroxyapatite (fluorohydroxyapatite, FHA; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{F}_{2x}$, $0 < x < 1$) has attracted much interest based on the extensive findings of partially fluoridated hydroxyapatite in bone and in teeth and based on the stimulation of fluoride on bone growth [101,102].

2.6.2 Lattice parameter of fluoroapatite

The substitution of F^- for OH^- in hydroxyapatite is known to causes a contraction in the a-axis dimension without changing the c-axis, as shown in Table 2-6.

Table 2-6 Comparison of lattice dimensions of hydroxyapatite and fluoroapatite

Calcium Phosphate	a-axis (nm)	c-axis (nm)
Hydroxyapatite	0.9441	0.6882
Fluoroapatite	0.9375	0.6880

2.6.3 Synthesis of fluorohydroxyapatite

Precipitation method and sol-gel method have been the most preferred methods to synthesize fluorohydroxyapatite due to the well-developed processing routine similar to that of hydroxyapatite [103-114]. Slightly differing from the synthesis of hydroxyapatite, in the synthesis of fluorohydroxyapatite the F^- precursor is added before the adjustment of pH, that is, before giving rise to the hydroxyapatite precipitates, to ensure the simultaneous substitution of F^- for OH^- during the nucleation process. M. Okazaki et al. [106-108] have studied different types of heterogeneous fluorohydroxyapatite synthesized by varying the fluoride supply step during the experimental period and reported that the fluoride supply step greatly affected the solubility behavior of hydroxyapatite.

Another approach to synthesize fluorohydroxyapatite is the “reaction sintering” method [115-118]. In this method, designed amount of metal fluoride such as CaF_2 is mixed with hydroxyapatite before subjected to sintering. After that, during the heat treatment process the F^- ions are gradually taken into the hydroxyapatite matrix to form fluorohydroxyapatite. The formation of fluorohydroxyapatite was confirmed by H. W. Kim et. al. [117,118] after they sintered of a mixed powder of calcium fluoride, hydroxyapatite, and yttria stabilized zirconia or alumina, at the temperature range of $900^{\circ}C - 1500^{\circ}C$.

2.7 Fluorohydroxyapatite based biocomposites

2.7.1 Introduction to fluorohydroxyapatite based biocomposites

Because of a sufficient understanding of fluorohydroxyapatite processing, both during powder preparation and ceramics fabrication, it seems that it is possible to prepare easily dense and/or porous fluorohydroxyapatite ceramics with controlled microstructure and chemical composition, which makes the ceramics suitable for different non load-bearing applications. However, fluorohydroxyapatite ceramics are still not preferable for load-bearing applications due to their low mechanical reliability. Preparation of fluorohydroxyapatite based ceramic composites can partially solve this problem. Moreover, the fluorohydroxyapatite composites can be fabricated to control the biological properties, such as bioactivity and biodegradation.

In recent years, due to their superior mechanical properties and high corrosion resistance, alumina and yttria stabilized zirconia have been widely investigated as reinforcement materials in hydroxyapatite and fluorohydroxyapatite ceramics to improve the mechanical properties and reliability [118-142]. In this chapter, zirconia strengthened hydroxyapatite/fluorohydroxyapatite composites will be reviewed.

2.7.2 Alumina toughened hydroxyapatite composites

Alumina, which is classified as a bioinert material, has been widely investigated as a reinforcing agent for hydroxyapatite [118-125]. It was reported by E. Adolfsson et al. [124] that the decomposition of hydroxyapatite in the presence of alumina took place at

surprisingly low temperatures, i.e., below 1000°C, whereas E. Champion et al. [125] reported that when large alumina platelets were added, the fracture toughness of the hydroxyapatite increased without excessive reaction between the hydroxyapatite and the Al_2O_3 . However, the improvement in strength was minimal because of the formation of microcracks around the platelets due to the large difference in thermal coefficient between Al_2O_3 and hydroxyapatite. On the other hand, when fine Al_2O_3 powder was used, the formation of the microcrack was circumvented; however, the improvement in mechanical properties was limited due to relatively low mechanical properties of the Al_2O_3 itself. The difficulty in producing dense alumina-hydroxyapatite composites without cracking or deformation, and the intrinsically lower mechanical properties of alumina than those of zirconia, have made the alumina enhanced hydroxyapatite composites somehow not as favorable as the zirconia toughened hydroxyapatite composites.

2.7.3 Zirconia toughened hydroxyapatite composites

Zirconia has been commonly used as reinforcement for many ceramics because of its high strength and fracture toughness. Bioinertness is another merit of ZrO_2 . As discussed in Chapter 2.3.3, zirconia is generally utilized in the form of yttria stabilized tetragonal zirconia (YTZP), especially in the manufacturing of biocomposites. Recently, zirconia toughened hydroxyapatite and zirconia toughened fluorohydroxyapatite have received great attention and been intensively studied [125-141].

2.7.3.1 Phase stability of zirconia toughened hydroxyapatite composites

It is generally accepted that when a ZrO_2 phase, such as YTZP, is added to hydroxyapatite, high temperatures of 1200–1400°C are commonly required to sinter these composites to high density, whereas hydroxyapatite has been reported to be thermally unstable above 1220°C. It has been reported by many researchers that the introduction of zirconia into the hydroxyapatite matrix would elicit massive reactions between the zirconia phase and the hydroxyapatite phase during sintering of the zirconia-hydroxyapatite composites to form cubic calcia-stabilized ZrO_2 , and subsequently calcium zirconate (CaZrO_3) and tricalcium phosphate (TCP), as described below [129,133-135,140]:

Increasing the sinter temperature further increased the amounts of β -TCP and CaZrO_3 . At a sinter temperature of 1400°C, virtually no hydroxyapatite remained and some α -TCP formed from β -TCP. This phase decomposition and reaction meant that the advantage of combining a low-strength bioactive ceramic (hydroxyapatite) with a high-strength, bioinert ceramic (YTZP) was minimized. The problem of decomposition and reaction between the hydroxyapatite and the ZrO_2 phases during sintering has limited the applications of this composite, as the mechanical and biological properties are compromised by the formation of undesirable secondary phases.

2.7.3.2 Sintering of zirconia toughened hydroxyapatite composites

The composite approach applied to hydroxyapatite has brought another problem. Since the densification temperature of zirconia (1400°C-1500°C) is much higher than that of

hydroxyapatite (1100°C-1200°C), it is very difficult to densify the zirconia toughened hydroxyapatite composites by pressureless sintering; and therefore, some more complicated and expensive techniques, such as wet sintering [142], hot isostatic pressing (HIP) [143-145], and spark plasma sintering (SPS) [146-149] have been investigated for this purpose. J. A. Delgado et. al. [142] employed a sintering atmosphere of oxygen moisture during the sintering of zirconia-hydroxyapatite composites and reported the prevention of decomposition of hydroxyapatite, which was believed to be because that the high concentration of moisture affected the equilibrium of the decomposition process of the hydroxyapatite phase and hence retarded the decomposition. E. Adolfsson et. al. [145] managed to produce high density zirconia-hydroxyapatite composites without decomposition of hydroxyapatite at a temperature of 1200°C and a pressure of 160MPa by HIP. The reduced sintering temperature due to the assistance of pressure, associated with a close sintering system, is considered to have negative effects on the decomposition of hydroxyapatite. Similar results were also achieved by H. Guo et. al. [146], who used SPS to produce gradient zirconia-hydroxyapatite composites and reported only slight decomposition of hydroxyapatite after sintering at 1200°C for 5 minutes. The fast sintering time together with close sintering system are redeemed to contribute to the inhibition of decomposition of hydroxyapatite.

In most cases, however, even in the case of employing these complicated sintering techniques, slight decomposition of hydroxyapatite with subsequent formation of TCP or CaO still occurs. While TCP increases biodegradability of the hydroxyapatite ceramics, the existence of CaO may cause decohesion of the material due to stresses arising from

formation of CaZrO_3 and related volume changes. Generally speaking, in spite of significantly improved strength and toughness, the zirconia-hydroxyapatite composites have not found wide applications due to the decrease of bioactivity and the difficulty in densification.

2.7.3.3 Zirconia toughened fluorohydroxyapatite

Due to the superior and tailorable thermostability of fluorohydroxyapatite, as shown in chapter 2-6, fluorohydroxyapatite has started to be of interest as a new matrix material substituting hydroxyapatite in the zirconia-hydroxyapatite composites [93,115,117,119, 141]. H. W. Kim et. al. [119] successfully produced fully dense zirconia-fluorohydroxyapatite composites without decomposition of hydroxyapatite by pressureless sintering at 1400°C for 3 hours. Differing from the hydroxyapatite phase stabilized either by a close sintering system or low sintering temperature, as discussed in the former chapter, the hydroxyapatite phase in the zirconia-fluorohydroxyapatite composites is structurally stabilized by the existence of fluorine. However, the competition between fluorine and zirconia on the decomposition of hydroxyapatite is still to be investigated, the literature so far has not provided much information on the interreaction of these two phases in zirconia toughened fluorohydroxyapatite composites.

2.7.3.4 Biological properties of zirconia toughened hydroxyapatite composites

Practically, there has been few literatures discussing the biological properties, either *in vitro* or *in vivo*, of zirconia toughened hydroxyapatite or zirconia toughened fluorohydroxyapatite composites due to the difficulty in producing dense composites. The

physical variations such as porosity and roughness which occur as a result of insufficient densification of the composites have given certain difficulty for cellular assessments. At the first estimation, the bioactivity of the zirconia toughened hydroxyapatite/fluorohydroxyapatite composites should decrease to a certain degree with the increment of the zirconia content, because that the zirconia phase is bioinert whereas the apatite is well known for its bioactivity. In another word, the biological properties of the zirconia-apatite composite might be a result of a trade-off between the mechanical properties of the zirconia phase and the bioactivity of the apatite. In addition, the effect of fluorine on the biological properties should not be neglected, although little difference has been observed in the bioactivity between hydroxyapatite and fluorohydroxyapatite.

M. Inuzuka et. al. [154] doped zirconia with small amount of hydroxyapatite and carried out SBF testings on the densified hydroxyapatite-zirconia composites. A complete covering of the composite surface with bone-like apatite after a 5-day immersion in SBF was evidenced in their report, which suggested that the HA-Zirconia composites had bioactivities. Recently, H. W. Kim et. al. [119, 142, 153] performed in-depth investigation on the biological properties of dense fluorohydroxyapatite-zirconia composites by means of evaluating osteoblast-like MG63 cell responses of the composites. The cell proliferation rate and viability were observed by counting live cells directly and assessing the incorporation of ^3H -thymidine into the DNA of replicating cells in their reports. Whereas counting the cells provided information on the total cell population, measuring the incorporation of ^3H -thymidine provided a parameter that reflected the ability of the cells to synthesize DNA at a specific culture period, that is, the metabolic activity and cell

viability. It was reported by H. W. Kim et. al. that the ZrO_2 ceramic did not adversely affect the cellular responses by itself, and the osteoblast-like MG63 cells on the FHA- ZrO_2 composite had good viability and maintained their cellular functional activity. However, considering the bioactivity of HA, ZrO_2 would be expected to have a somewhat negative effect, because HA ceramics were known to enhance all aspects of the bone cell responses, from the proliferation to the expression of many phenotypes and mineralization, that is, the whole bone-forming process.

Chapter 3 Experimental Procedures

3.1 Introduction

For the completion of the postgraduate program, experimental work on two main areas had been deliberately done during the past five years:

- Preparation and characterization of FHA ceramics.
- Preparation and characterization of FHA-YTZP composites.

Specifically, the sample preparation work included:

- Preparation of FHA powders with different fluorine contents by precipitation.
- Preparation of FHA ceramics with different fluorine contents by conventional sintering at selected sintering temperatures.
- Preparation of FHA-YTZP composite powders with different YTZP contents by co-precipitation.
- Preparation of FHA-YTZP composites with different YTZP contents by conventional sintering and spark plasma sintering at selected temperatures.

The sample characterization work comprised of density, microstructure, phase stability, corrosion resistance in citric acid, thermal properties, and mechanical properties such as microhardness, Young's modulus, and fracture toughness.

The outline of the experimental procedures is illustrated in Figure 3-1.

Figure 3-1 Outline of experimental procedures

3.2 Preparation of dense FHA ceramics

3.2.1 Starting materials

The starting materials used in this study were calcium nitrate 4-hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, BDH Limited Company, Inc.), ammonia fluoride (NH_4F , Fluka Chemie Company, Inc.), diammonia hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, Merck KgaA Company, Inc.), and 28wt% ammonia solution (NH_4OH , Ajax Laboratory Chemicals Company, Inc.).

3.2.2 Preparation of FHA powders

FHA solid solution powders with different proportions of FA were prepared by a precipitation method. Calcium nitrate 4-hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was first dissolved in distilled water in a glass beaker and kept vigorously stirred on a hotplate to form a 0.5 M solution, into which diammonia hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) solution was added dropwise to reach Ca/P ratio of 1.67. Then different amounts of ammonia fluoride (NH_4F) solutions, i.e., 0, 0.02 M, 0.04 M, 0.06 M, 0.08 M and 0.1 M were added to the stirred solutions respectively. After 10 minutes of stirring, ammonia (NH_4OH) solution was added into the mixed solutions to adjust pH to 10-11, followed by constant stirring for 12 hours. The suspensions were left to settle for 24 hours before they were washed several times with distilled water to remove any residual ions. The washed slurries were dried in a WTC Binder Drying Oven at 60°C for 48 hours until solid ceramic bulks were obtained. The bulks were then ballmilled using Fritsch Planetary Ball Mill with zirconia balls in ethanol for 1 hour to break soft agglomerates and dried again in oven. The bulks formed after drying were ground into fine powders using a mortar and a pestle. The as-prepared

FHA solid solution powders ($\text{Ca}_{10}\text{PO}_4(\text{OH})_{2(1-x)}\text{F}_{2x}$, $x=0, 0.2, 0.4, 0.6, 0.8, 1.0$) were named HA, HA02F, HA04F, HA06F, HA08F and FA, corresponding with the different values of x . For example, the FHA powder synthesized by mixing 0.02 M NH_4F with 0.5 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was named HA02F because of $x=0.2$. The phase purity and morphology of the as-prepared powders were observed thereafter.

The preparation steps were demonstrated in Figure 3-2.

3.2.3 Preparation of dense FHA ceramics

The obtained powders were pressed into green bodies, and sintered in a furnace (Carbolite high-temperature furnace) at different temperatures in air.

3.2.3.1 Pressing

The as-prepared powders were uniaxially pressed at 300 MPa in a 13-mm die using an Enerpac 15 Tons Press. The high pressure of 300 MPa was used to form dense green compacts, which were for further sintering to obtain nearly full-dense samples.

3.2.3.2 Sintering

The green bodies were heated from the room temperature to 700°C at a heating rate of 5°C/min, followed by dwelling for 1 hour. In this stage, the lubricant in green bodies was burnt out. To avoid the decomposition of the FHA green compacts and retaining desirable high densities of the final products, different sintering temperatures, i.e., 950°C, 1100°C, and 1300°C, were attempted. The samples were cooled to the room temperature at the rate

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Figure 3-2 Flowchart showing the preparation of FHA by precipitation

of 10°C/min. The ultimate samples were named HA950, HA1100, HA1300, HA02F950, HA02F1100, HA02F1300, HA04F950, HA04F1100, HA04F1300, HA06F950, HA06F1100, and HA06F1300 correspondingly. Here the numbers 950, 1100 and 1300 stand for the sintering temperatures for the ceramics and the HA, HA02F, HA04F and

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HA06F represent the compositions of the FHA ceramics. The sintering schedules are shown in Figure 3-3.

(950°C)

(1100°C)

(1250°C)

Figure 3-3 Sintering schedules for FHA ceramics

3.3 Preparation of FHA-YTZP composite powders and ceramics

3.3.1 Starting materials

The starting materials used in this study were calcium nitrate 4-hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, BDH Limited Company, Inc.), ammonia fluoride (NH_4F , Fluka Chemie Company, Inc.), diammonia hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$, Merck KGaA Company, Inc.), yttrium nitrate ($\text{Y}(\text{NO}_3)_3$, Aldrich Chemical Company, Inc.), 30 wt% zirconyl chloride solution (ZrOCl_2 , Aldrich Chemical Company, Inc.), and 28 wt% ammonia solution (NH_4OH , Ajax Laboratory Chemicals Company, Inc.).

3.3.2 Preparation of FHA-YTZP composite powders

FHA-YTZP composite powders with different proportions of YTZP were prepared by a co-precipitation method. Calcium nitrate 4-hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) was first dissolved in distilled water and kept vigorously stirred on the IEC hotplate to form a 0.5 M solution, into which diammonia hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) solution and 0.06 M ammonia fluoride (NH_4F) solution were added dropwise with a Ca/P ratio of 1.67 being kept. After 10 minutes of stirring, the ammonia (NH_4OH) solution was added into the solutions to adjust pH to 10-11, followed by constant stirring for 2 hours. Simultaneously zirconyl chloride hydrochloride solution was mixed together with stoichiometric yttrium nitrate solution with a molecular ration of 1:0.06. The amount of zirconyl chloride hydrochloride solution and yttrium nitrate differed to form FHA-YTZP composite with expected composition, i.e., 0, 2.5 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 40 wt% and 60 wt% of

the YTZP mass. Then the pH of the mixed solution was adjusted to 10 using ammonia solution, followed by constant stirring for 2 hours, and was added to the FHA solutions being stirred. The as-prepared FHA-YTZP solution was kept stirring for another 4 hours and left to settle for 24 hours before they were washed several times with distilled water to remove any residues. The washed slurries were dried in a WTC Binder Drying Oven at 60°C for 48 hours until solid ceramic bulks were obtained. The bulks were then ballmilled in a Fritsch Planetary Ball Mill with ethanol for 1 hour to break soft agglomerates and dried again in oven. The bulks formed after drying were ground into powders using a mortar and a pestle. These powders were named HA06F, HA06F2.5YTZP, HA06F5YTZP, HA06F10YTZP, HA06F20YTZP, HA06F40YTZP, and HA06F60YTZP, corresponding to the amounts of YTZP added.

The preparation procedure is outlined in Figure 3-4.

3.3.3 Preparation of FHA-YTZP composite ceramics by conventional sintering

The obtained powders were pressed into green bodies, and sintered in a furnace (Carbolite high-temperature furnace) at different temperatures in air.

3.3.3.1 Pressing

The as-prepared powders were uniaxially pressed at 300 MPa in a 13-mm die using an Enerpac 15 Tons Press. The high pressure of 300 MPa was used to form dense green compacts, which were for further sintering to obtain nearly full-dense samples.

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Figure 3-4 Flowchart showing the preparation of FHA-YTZP composites

3.3.3.2 Sintering

The green bodies were heated from the room temperature to 700°C at a heating rate of 5°C/min, followed by dwelling for 1 hour. In this stage, the lubricant in green bodies was burnt out. To minimize the decomposition of FHA or reaction between FHA and YTZP, and to retain desirable high densities of the final products, different sintering temperatures,

i.e., 1200°C, 1300°C, and 1400°C, were attempted. The samples were cooled to the room temperature at the rate of 10°C/min. The ultimate samples were named HA06F5YTZP1200, HA06F10YTZP1200, HA06F15YTZP1200, HA06F20YTZP1200, HA06F40YTZP1200, HA06F60YTZP1200, HA06F5YTZP1300, HA06F10YTZP1300, HA06F15YTZP1300, HA06F20YTZP1300, HA06F40YTZP1300, HA06F60YTZP1300, HA06F5YTZP1400, HA06F10YTZP1400, HA06F15YTZP1400, HA06F20YTZP1400, HA06F40YTZP1400, and HA06F60YTZP1400 correspondingly. Here the numbers 1200, 1300 and 1400 stand for the sintering temperatures for the ceramics and the HA06F5YTZP, HA06F10YTZP, HA06F15YTZP, HA06F20YTZP, HA06F40YTZP and HA06F60YTZP represent the compositions of the FHA-YTZP ceramics. The sintering schedules are shown in Figure 3-5.

3.3.4 Preparation of FHA-YTZP composite ceramics by SPS

The FHA-YTZP composite powders with different amounts of YTZP were sintered by a novel SPS technique. The Spark Plasma Sintering (SPS) system **Dr. Sinter[®] Model SPS-1050** employed in the study was produced by Sumitomo Coal Mining Group (SCM), Izumi Technology Company, Ltd., as shown in Figure 3-6.

The spark plasma sintering (SPS) process involves first compressing the starting powder materials then applying ON/OFF pulse-controlled power from a direct current pulse generator to concentrate a high-density energy in the areas of necks between particles in order to achieve densification.

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Figure 3-5 Sintering schedules for FHA-YTZP ceramics

Figure 3-6 Photograph of the SPS machine

The SPS system is used to fabricate high-quality, uniformly sintered compacts at a low temperature and in a short time. With this process one can control the microstructure of materials including crystal growth, and can sinter materials that can not be sintered with conventional techniques.

Specifically, powders were carefully added to a 13-mm graphite die that had two graphite punches on both sides, which were specially designed for the SPS system. Two pieces of graphite foils were placed between the punches to the powders to improve the electro-conductivity of the whole system.

Sintering

In this study, the as-prepared composite powders loaded in the die were first heated to 600°C with a ramping time of 5 minutes from the room temperature, followed by sintering at 1200°C for 10 minutes with a ramping time of 5 minutes from 600°C. The samples were then cooled from 1200°C to 600°C with a ramping time of 5 minutes and slowly to the room temperature. The ultimately sintered samples were named HA06F1200, HA06F5YTZP1200, HA06F10YTZP1200, HA06F20YTZP1200, HA06F40YTZP1200, and HA06F60YTZP1200. Here the number 1200 stands for the sintering temperature for the composite ceramics and the HA06F, HA06F5YTZP, HA06F10YTZP, HA06F20YTZP, HA06F40YTZP, and HA06F60YTZP present the compositions of the composite ceramics.

An example of the sintering schedule is demonstrated in Figure 3-7.

Figure 3-7 Sintering schedule for FHA-YTZP composites by SPS

3.4 Characterization

The prepared powders and the final sintered samples were subjected to various methods of analysis and testing. The types of characterization and the facilities used are listed in Table 3-1.

3.4.1 Phase analysis using X-Ray Diffractometer (XRD)

All samples including powders and sintered bulks were subjected to phase analysis. Determination of the phases present in the samples was carried out by using XRD. The powdered sample was placed on the cavity of a glass plate and the surface of the powder was smoothed, while the sintered sample was ground using the Phoenix Beta Grinder before being polished using the Imptech 20 VV Polisher, and then placed on a flat glass plate. The thickness of the sample together with the glass plate was measured and the

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height of the machine holder was adjusted accordingly. Monochromatic CuK α radiation was used under 50 kV and 20 mA. The XRD data were collected over the 2 θ range of 10-90 $^{\circ}$ at a sampling speed of 2 $^{\circ}$ /min. The determination of the 2 θ values and peak heights, as well as the phase analysis of the collected XRD data was achieved by using the built-in computer software.

Table 3-1 Characterization methods and corresponding facilities used

Characterization	Facility
X-Ray diffraction (XRD)	Lab XRD-6000 Shimadzu
Scanning electron microscopy (SEM)	JOEL, JSM-5410 LV
Field Emission SEM	JSM-6340F
Transmission electron microscopy (TEM)	JEM-2010
TGA	NETZSCH STA 449C
Dilatometer	Anter Unitherm 1161
Density	Balance and Caliper
Hardness	Matsuzawa. MXT70 Digital Micro Hardness Tester
Young’s Modulus	Shimadzu HMV-2000 Microhardness Tester

3.4.2 Microstructural analysis using Scanning Electron Microscopy (SEM) and Field Emission SEM

A powdered sample was vigorously dispersed in ethanol using the Ultrasonic LC20H machine for 30 minutes. The formed powder slurry was then dropped onto a copper tape attached to a sample holder, and then dried slowly in air, while the sintered sample was carefully ground in the Phoenix Beta Grinder, polished in the Imptech 20 VV Polisher, and/or thermally etched for half an hour at 1200°C to reveal the grains. After that, by using the SPI-Module Sputter Coater machine, the well-dispersed powders or sintered samples were coated with gold films. Carbon films were applied in the SPI-Module Carbon Coater machine. The coated sintered sample was attached to the sample holder by using a carbon tape. The samples were then examined under SEM; coated fracture surfaces were also examined.

3.4.3 Microstructural analysis using Transmission Electron Microscopy (TEM)

The powdered samples were dispersed in ethanol, followed by deposition on copper grids and dried in air. The samples were examined under TEM thereafter for detailed morphological observation of nanoparticles due to its high resolution. The sintered samples were first ground into fine powders using a jade pestle, and then the powders were subjected to similar process and observed under TEM.

3.4.4 Thermogravity analysis (TGA)

HA is structurally unstable and tend to decompose in temperatures higher than 1200°C. When some content of zirconia is added, the decomposition of HA is further triggered. Therefore, thermogravity analysis was employed in this project to determine how exactly the temperature influenced the decomposition of HA by detecting the mass variation during the increase of temperature due to the decomposition of HA and evaporation of the resultant water.

Firstly, FHA and FHA-YTZP flakes were prepared by dry pressing the powders under a pressure of 300Mpa. The as-prepared flakes were crashed into pieces using a pestle and the shatters with desirable dimension were weighed and put into one crucible, the mass of the empty crucible was measured. Same amount of alumina powder (AP50) was put into another crucible, the mass of which was also measured, and used as a reference. The two crucibles were placed in the TGA machine and the weights of the sample mass, the sample crucible mass, the reference mass, and the reference crucible mass were input in the software the machine provided. After setting the heating temperature, heating rate and air flow rate, the machine would start the heating process and gave the TGA data automatically.

3.4.5 Sintering analysis using dilatometer

HA starts densification at nearly 900°C and reaches its maximum densification at about 1300°C, while zirconia starts densification at 1100°C and reaches its full densification at about 1500°C. For FHA-YTZP composites, the sintering process differs in the shrinkage

rate, densification rate, and densification onset/finish temperature with compositions. Upon this consideration, dilatometer was used in this project to investigate the influence of fluorine and YTZP on the sintering process of the FHA and FHA-YTZP ceramics.

To perform a dilatometer analysis, FHA and FHA-YTZP powders were pressed into bulks with a dimension of 13mm in diameter and 10mm in height. The bulks were then placed into the dilatometer chamber, each side in contact with the detecting probes. The dimension of the bulks were input in the software provided by the machine and the sintering condition such as sintering temperature and ramping rate were set before the sintering started. After sintering, the machine would automatically give the dimension variation with temperature.

3.4.6 Density measurement

The physical dimensions of the sintered samples such as the heights and the diameters after firing were measured using a calliper and the weights of the samples were measured using an electric balance. The bulk density (ρ) was calculated using the following formula:

$$\rho = \text{Weight} / \text{Volume} \quad (3-1)$$

For every sample type, the dimensions and the weights of about 3-4 disks were taken. The bulk density of the individual disk was calculated, and the average was accepted as

the final bulk density.

3.4.7 Corrosion resistance

Corrosion resistance tests were performed by immersing the polished sintered samples in a 5 wt% citric acid solution for 10 minutes. They were then rinsed with distilled water and ethanol before being dried in an oven at 60°C for a few hours. After that, the corroded surfaces were carbon or gold coated and were examined using SEM. The corrosion resistance or chemical stability was judged by the surface morphologies.

3.4.8 Vickers' hardness Test

The equipment used in this experiment was Shimadzu HMV-2000 Microhardness Tester with a load of 500 grams. The holding time of indentation was set at 25 seconds. The samples were first ground and polished until very smooth and shiny surfaces were obtained. After indentation, the diagonal lengths of the diamond-shaped impression and the resultant crack lengths were measured using the microscope attached to the hardness tester. The hardness values were automatically given by the instrument following the formula below:

$$H_v = 1.8544P/(2a)^2 \quad (3-2)$$

where H_v is the Vickers' hardness value with a unit of kg/mm^2 , P the indentation load (kg), and $2a$ the diagonal length of the indentation impression (mm). For every sample

type, the Vickers' hardness was tested for 8-10 times and the average was accepted as the final Vickers' hardness.

3.4.9 Young's modulus

The Shimadzu HMV-2000 Microhardness Tester was used to determine the Young's modulus (E) of the samples. The Young's modulus can be calculated using the following equation:

$$\frac{b'}{a'} = \frac{b}{a} - \alpha \frac{E}{H_K} \quad (3-3)$$

where b'/a' is the impression diagonal ratio after elastic recovery or after indentation, b/a is the dimension ratio of the Microhardness Tester indenter ($= 1/7.11$), α is a constant with a value of 0.45, and H_K is the Knoop hardness obtained from the machine. For every sample type, the Young's modulus was tested for 8-10 times and the average was accepted as the final Young's modulus.

3.4.10 Fracture toughness

The fracture toughness K_{Ic} of the ceramics and the composites was measured using the Vickers' indentation method and using the following equation:

$$K_{Ic} = 0.016 \left(\frac{E}{H} \right)^{\frac{1}{2}} \frac{P}{C^{\frac{3}{2}}} \quad (3-4)$$

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where E stands for the Young's modulus (GPa), H the Vicker's hardness (GPa), P the indentation load (N), C the crack length from the center of the pyramid impression to the crack tip (m). For every sample type, the fracture toughness was tested for 8-10 times and the average was accepted as the final fracture toughness.

Chapter 4 Design of FHA ceramics with preferable stability and microstructure

The objective of this project is to systematically investigate the influence of fluorine content on the thermal and chemical performance of FHA ceramics. FHA powders with different fluorine contents were prepared using the precipitation method, followed by sintering at different temperatures, as described before. The as-prepared samples were characterized using XRD, SEM, TEM, TGA, and dilatometry. The data acquired were analyzed and the optimal fluorine content for FHA ceramics for desirable thermal and chemical performance was obtained.

4.1 Phase analysis of FHA powders by XRD

The mixed solutions of the required ions used for the preparation of HA and FHA powders were initially homogeneous at a molecular level. However, the products from the wet precipitation method were influenced by many experimental parameters such as Ca/P ratio, aging time, and pH. Thus XRD was used to confirm the phases present in the as-prepared powders.

The XRD patterns of the HA, HA02F, HA04F, HA06F, HA08F and FA powders were shown in Figure 4-1. The characteristic peaks observed in the patterns show that crystalline apatites were well developed in all the calcined powders, although the

powders from precipitation (i.e. no calcinations) tended to show a low level of crystallinity. All the six patterns consist of distinct peaks at 26, 32, 40, and 50 degree, which are characteristic of HA phase according to the standard XRD pattern of hydroxyapatite (JCPDS #09-432). No other phases are seen in the XRD patterns. All the XRD patterns of the four powders (from HA02F to HA08F) are similar to those of the HA and FA powders.

Figure 4-1 XRD patterns of HA, FHA and FA powders after calcination at 700°C

By comparing the accurate 2θ positions of the (3 0 0) reflections in the six XRD patterns, gradual shift of these peaks to the right hand side with the increase of the fluorine content could be observed. In other words, the (3 0 0) reflections of the HA, HA02F, HA04F,

HA06F, HA08F, and FA powders appeared gradually at higher two theta angle with the fluorine content, namely, at 32.84, 32.98, 33.06, 33.0, 33.10, and 33.14 degree, respectively. The slight shift of the characteristic (3 0 0) peaks to the right side of the two-theta axis was due to the decrease of the a-axis length of the hexagonal HA crystal lattice. This can be understood by using the Bragg law:

$$\sin\theta = \frac{\lambda}{2d} \quad (4-1)$$

where the interplanar spacing d can be expressed in the following formula for the hexagonal crystal structure of HA:

$$\frac{1}{d^2} = \frac{4}{3a^2}(h^2 + hk + k^2) + \frac{1}{c^2}l^2 \quad (4-2)$$

For the characteristic (3 0 0) reflection, formula 4-1 and 4-2 can be simplified as:

$$\frac{1}{d^2} = \frac{12}{a^2}, \quad \sin\theta = \frac{\sqrt{3}\lambda}{a} \quad (4-3)$$

Thus, when value θ increases, value a decreases. Since the lattice parameter a in FA (0.9375 nm) is slightly smaller than that in HA (0.9441 nm), while the c values are the same for both FA and HA, the F^- substitution for OH^- in the host HA will result in the decrease of value a , which leads to the shift of the (3 0 0) reflections towards higher 2θ values.

From Figure 4-1, it is also seen that the shape of the peaks of FHA is sharper than that of pure HA, which means that the incorporation of fluoride into the HA matrix increased the crystallinity of the host crystals. This increased crystallinity would be responsible for the increased thermal and chemical stability of the FHA ceramics, as will be shown later.

4.2 Morphological observation of powders by TEM

The particle morphologies of the as-precipitated (not calcined) powders were observed using TEM because of its higher resolution than SEM and FE-SEM. The powders were dispersed in ethanol by ultrasonication for 30 minutes before they were subjected to the TEM observation. Figure 4-2 shows the morphologies of the HA, HA02F, HA04F, and HA06F powders. Needle-like apatite crystals, which are about 80nm in length and 20nm in width, are clearly seen. Agglomerates of nanosized particles are found in the micrographs, which may be due to the van der Waal's attraction between particles. From these micrographs, it can be seen that the F^- substitution for OH^- in the host HA did not substantially affect the morphology of the host HA. This observation was in contrary with what was reported by L. J. JHA et al. [75], who claimed that the increasing F^- ion concentration tended to reduce the aspect ratio of the crystallites produced.

Design of FHA ceramics with preferable stability and microstructure

Figure 4-2 TEM micrographs showing the morphologies of HA (a), HA02F (b), HA04F (c), and HA06F (d) powders

On the other hand, L. B. Kong et al. [23] observed spherical apatite particles using SEM. No matter whether SEM or TEM is used, the powder shape should not depend on the observation methods utilized, but rather depend on the precipitation conditions used. By comparing the starting materials and the experimental procedures used by L. J. JHA et al.

with those used by L. B. Kong et al., it is found that the aging process was not used by L. B. Kong et al. Since it has been widely reported that an appropriate aging time should be required for a well developed single phase apatite [62,63], the different morphologies of the HA particles observed by L. B. Kong et al. and L. J. JHA et al. may be ascribed to the different degrees of apatite crystallization due to the different aging times.

4.3 Thermogravity analysis (TGA)

To study the thermal stability of the HA, FHA, and FA powders, thermogravimetric analysis was conducted using the as-prepared (uncalcined) powders in the temperature range from 25°C to 1300°C. Figure 4-3 shows the different degrees of weight loss of the samples with different fluorine contents. It can be seen that pure HA sample had three stages of weight loss; the first stage from 25°C to 200°C was due to the evaporation of absorbed water in the fine powder, the second stage from 800°C to 850°C was due to the release of OH⁻ groups from the HA crystals, and the third stage above 1000°C was related to the further decomposition of HA and hence the large loss of the OH⁻ groups. This observation of weight loss during the heating process was in agreement with the decomposition sequence described by J. Cihlar et al. [150], who reported that the decomposition reactions of HA could be divided into two steps, according to the formula below:

Figure 4-3 TGA data of HA, FHA and FA powders heated to 1300°C in dry air

However, for the HA02F only the first stage and the second stage could be observed. Moreover, for all the FHA samples with fluorine contents higher than that in the HA02F sample, only the first stage could be detected. These observations suggested that when the fluorine content in the HA matrix was high enough, the thermal stability of the HA matrix would be greatly increased or the decomposition of the HA matrix could be effectively retarded. While the increase of thermal stability with the fluorine content was well demonstrated, the weight loss at the first stage varied from one powder sample to another,

as was shown by the large amount of weight loss of the HA02F powder sample and the small amount of weight loss of the HA06F sample. This discrepancy could be explained by the humidity of the air and the uncontrolled storage of the different powder samples, which resulted in the large amount of water absorption of the HA02F powder sample during the storage period.

4.4 Phase analysis of FHA ceramics

XRD was also used to study the thermal stability of the different compositions after the powders were calcined and sintered. Figure 4-4 shows the XRD patterns of HA, HA02, HA04 and HA06F samples sintered at 950°C, 1100°C and 1250°C for 2 hours, respectively. The peaks in Figure 4-4 are similar to those of the starting powders before sintering (Figure 4-1), except for the peaks being sharper for the sintered ceramics. This was mainly because of the better crystallinity of the apatite phase due to the high sintering temperatures. No other phases, e.g., α -tricalcium phosphate (α -TCP), β -tricalcium phosphate (β -TCP), and/or tetra calcium phosphate (TeCP), are identified in Figure 4-4.

Figure 4-4 XRD patterns of HA, HA02F, HA04F, and HA06F samples sintered at 950°C, 1100°C, and 1250°C, respectively

Although the highest sintering temperature of 1250°C in this experiment was higher than the reported decomposition temperature of 1220°C of the HA phase, no obvious decomposition of the HA phase was detected from the XRD patterns. This thermal stability of the apatite phase of these samples could be due to the following two aspects:

1. The temperatures employed for the sintering process together with the short sintering time of 2 hours were not enough to trigger the decomposition from HA to TCP, although the highest sintering temperature, i.e., 1250°C, was slightly higher than the reported HA decomposition temperature of 1220°C.
2. Because the powders were ballmilled with distilled water before they were pressed into green compacts, some residual water may exist in the green compacts, which might shift the reaction equilibrium to the left during the sintering process, and hence retard the decomposition of HA.

However, to investigate the influence of fluorine addition on the thermal properties of the FHA ceramics, a certain degree of decomposition of the HA phase was aimed to compare the behaviour of the FHA ceramics with different fluorine contents during sintering. Therefore, the FHA powders were calcined at 700°C before being pressed into green compacts, followed by sintering at a higher temperature of 1300°C.

The XRD patterns of the FHA ceramics sintered at 1300°C for 2 hours in air are shown in Figure 4-5. As comparing Figure 4-5 to Figure 4-4, not only the characteristic peaks of

FHA are observed, but also new peaks are found at the 2θ angle of 31.2 and 34.65 degree in all the samples. The new peaks were identified to belong to β -TCP. It can be seen that the decomposition of HA to β -TCP was relatively severe in the pure HA sample. Since β -TCP phase is a low temperature stable phase and the β -TCP to α -TCP transformation, or vice versa occurs at 1100°C, the β -TCP phase detected must be derived from the α -TCP phase through the α -TCP to β -TCP phase transformation. Although the degree of decomposition for the HA02F and HA04F samples was relatively lower, the amount of formed β -TCP phase was still noticeable. However, in the HA06F sample and the FHA samples with higher fluorine contents than that in HA06F, the decomposition of the HA phase to β -TCP was dramatically suppressed, as can be seen when comparing the ratio of the intensities of the characteristic peaks of the HA phase and the β -TCP phase.

4.5 Sintering analysis by dilatometry

The sintering shrinkage (i.e., the relative shrinkage) and the sintering shrinkage rate data were acquired by sintering pressed FHA pellets in the dilatometer from 25°C to 1300°C, as shown in Figure 4-6. From the sintering shrinkage rate data, one can see that the onset sintering temperature of HA (Figure 4-6 a) was around 1000°C. In the sintering temperature range from 1000°C to 1100°C, the sintering shrinkage rate or the densification rate increased rapidly. At 1080°C a maximum densification rate was reached. In the temperature range from 1080°C to 1300°C, the densification rate was gradually slowed down.

Figure 4-5 XRD patterns of the FHA ceramics sintered at 1300°C in air

For the HA06F sample, the onset sintering temperature was approximately the same as that of HA. However, in the temperature range from 1000°C to 1180°C, the densification rate of HA06F increased sharply. At 1180°C the highest densification rate was obtained, followed by a gradual decrease in the densification rate.

For the FA sample, the onset sintering temperature was about 1150°C. In the temperature range from 1150°C to 1220°C, the densification rate again increased sharply. At 1220°C

the highest densification rate was obtained, but the sintering process was greatly slowed down thereafter.

In one word, the onset sintering temperature of 1000°C and the maximum densification rate temperature of 1080°C of the HA pellet were significantly lower than those of the HA06F and the FA pellets; with the increase of fluorine content in the FHA ceramics, the onset sintering temperature and the maximum densification rate temperature were dramatically increased. Thus, the introduction of fluorine into the HA matrix had retarded the densification process. This observation could be ascribed to the low ionic diffusion rate in FA pellet due to the strong inter-atomic bonding between the fluorine ions and the other ions into the HA matrix.

(a)

(b)

Figure 4-6 Sintering shrinkage and sintering shrinkage rate data of HA (a), HA06F (b) and FA (c) heated up to 1300°C at 5°C/min (solid line stands for shrinkage rate, dash line stands for relative shrinkage)

4.6 Density results of sintered FHA ceramics

The densities (bulk densities) of HA, HA02F, HA04F, and HA06F ceramics sintered at 950°C, 1100°C, and 1250°C for 2 hours in air, respectively, are presented in Table 4-1.

The relative densities (to theoretical densities) are presented in Figure 4-7, by calculation using the following formula:

Relative density = (Bulk density / Theoretical density(TD)) % (4-6)

Table 4-1 Bulk densities of HA, HA02F, HA04F, and HA06F ceramics sintered at 950°C, 1100°C, and 1250°C, and those of HA, HA02F, HA04F, HA06F, HA08F, and FA sintered at 1300°C in air

Samples	Density (g/cm ³)			
	950°C	1100°C	1250°C	1300°C
HA	2.570	2.900	3.040	3.065
HA02F	2.547	2.893	3.013	3.033
HA04F	2.518	2.830	2.980	3.017
HA06F	2.534	2.830	2.983	3.020
HA08F	/	/	/	3.011
FA	/	/	/	3.010

While the bulk densities of the FHA ceramics were easily determined, the determination of the relative densities of the FHA ceramics was not a simple task. This was because that FHA ceramics were not phase pure and thus the contents of the FHA apatite phase and the β -TCP phase should be determined. This phase content determination was additionally conducted using an external standard method, in which the XRD reflection intensity ratios were correlated with the preset contents of the powder mixtures of the FHA apatite phase and the β -TCP phase. On the other hand, accurate measurements of the theoretical densities of the FHA apatite phase and the β -TCP phase were not done through the crystal lattice analysis due to the large amounts of calculations required. Since the published theoretical densities of pure HA and pure FA ceramics are very similar, 3.16g/cm^3 and $3.10\text{-}3.20\text{ g/cm}^3$, respectively, the theoretical densities of the FHA ceramics were simply taken as 3.13g/cm^3 . Similarly, the reported theoretical density of 3.00 g/cm^3 of the β -TCP phase was taken in this study, regardless of the possible presence of fluorine in the β -TCP phase.

As shown in Figure 4-7, all the sintered samples had the densities over 80% theoretical densities, and the densities of the samples sintered at 1250°C were beyond 95% theoretical density. It can also be seen that the sintering temperature increment from 950°C to 1100°C had a stronger effect on the densification process than the sintering temperature increment from 1100°C to 1250°C . The high degree of densification ($> 90\%$ T.D.) at a low sintering temperature of 1100°C was ascribed to the excellent sinterability of the fine starting powders, which consisted of particles in the nanometer scale.

In the meantime, Table 4-1 shows that the FHA ceramics with lower fluorine contents tended to have higher densities than those with higher fluorine contents, given that they were all sintered at the same temperature and for the same duration. In other word, the introduction of fluorine into the HA matrix tended to retard the densification of the HA matrix.

Figure 4-7 Relative densities of FHA ceramics with different fluorine contents and sintered at 950°C, 1100°C, and 1250°C, respectively

4.7 Morphologies of chemically etched surfaces of FHA ceramics sintered at 950°C, 1100°C, 1250°C, and 1300°C

The different FHA samples sintered at 950°C, 1100°C, and 1250°C were polished using diamond paste and chemically etched by a citric acid solution to reveal the grain size and to evaluate the chemical stability of the sintered FHA ceramics. The surface morphologies of all the samples subjected to immersion in a 5wt% citric acid solution for 10 minutes are presented in Figure 4-8 to Figure 4-10.

From these figures, it can be clearly seen that increasing sintering temperature from 950°C to 1250°C greatly affected the grain size of the samples. For example, the average grain size of HA sintered at 950°C was about 0.9 μm , whereas the average grain size of HA sintered at 1250°C was about 2.8 μm . It was known that open pores powder compacts, which existed at densities lower than 92% theoretical density, inhibited grain growth. In this study, when the HA and FHA ceramics were sintered at 950°C and 1100°C, the micropores in the ceramics were mainly open pores resulting from the low degree of densification, which retarded the grain growth. However, when the HA and FHA ceramics were sintered at 1250°C, closed pores instead of open pores occurred due to the high degree of densification, causing severe grain growth. Based on Figure 4-8 to Figure 4-10, it can be seen that the nanosized feature of the starting particles was lost as a result of the conventional sintering process. It can also be seen from these figures that the fluorine addition tended to increase the grain size of the FHA ceramics. This observation

was in agreement with that reported by E. Adolfsson et al. [106,108].

Comparing the surface morphologies of the sample HA950 and the sample HA06F950 (Figure 4-8), one can see that the surface of HA06F950 is smoother and thus seemed to be less corroded by the citric acid. However, one cannot draw a conclusion that the FHA ceramics with higher fluorine contents had higher corrosion resistance than those with lower fluorine contents. The rough surfaces observed may also be due to the insufficient sintering of the ceramics, resulting in a lot of micropores. To better understand how the fluorine content affects the corrosion resistance of the FHA ceramics, highly densified FHA ceramics was used for the corrosion testing to avoid the influence of incomplete sintering on the surface morphologies of the FHA ceramics.

Therefore, a batch of FHA ceramics was sintered at 1300°C for 2 hours in air and polished, and then etched with a 5 wt% citric acid solution for 10 minutes. The surface morphologies of the HA1300, HA02F1300, HA04F1300, HA06F1300, HA08F1300, and FA1300 samples after the chemical etching are shown in Figure 4-11. The polished surface morphology of the HA1300 sample without chemical etching is also shown in Figure 4-11 for comparison. For the samples with fluorine contents corresponding to $x \leq 0.4$, the surfaces were severely damaged; areas of grains and phases were dissolved. However, for the samples with fluorine contents corresponding to $x > 0.4$, the surfaces appeared to be much smoother; only the grain boundaries were slightly etched. These observations indicated that when the fluorine content in the FHA ceramics reached a

certain high level (e.g., when $x = 0.6$), the corrosion resistance of the ceramics was greatly improved.

The visible pores or defects on the chemically etched surfaces were due to three possible factors: one was the remaining micropores due to incomplete densification; one was the remaining β -TCP phase as a decomposition product, which was dissolved much faster than the pure HA phase; the other one was the intrinsic chemical stability of the FHA especially the FA ceramics. In the current study, the effect of remaining micropores due to incomplete densification could be ignored since the FHA ceramics with all the six compositions had very high densities, as shown in Table 4-1 and Figure 4-11 (a^p). From Figure 4-5, it was noticed that the β -TCP phase increased in amount (judged from the XRD peak heights) from the FA sample to the HA sample. This trend agreed with the increased amount of surface defects on the surfaces from the FA to HA samples, as shown in Figure 4-11. Thus, the β -TCP phase could be the dominant factor causing the surface damage. Nevertheless, the formation of β -TCP was directly related to the fluorine content added. The final issue was the higher intrinsic chemical stability of the FHA and FA samples than that of the pure HA samples, as was confirmed by our previous corrosion tests with the FHA samples sintered at 950°C, 1100°C, and 1250°C, where no β -TCP was formed, as shown in Figure 4-8 to Figure 4-10.

Figure 4-8 SEM micrographs of the chemically etched surfaces of the HA (a), HA02F (b), HA04F (c), and HA06F (d) ceramics sintered at 950°C

Figure 4-9 SEM micrographs of the chemically etched surfaces of the HA (a), HA02F (b), HA04F (c), and HA06F (d) ceramics sintered at 1100°C

Figure 4-10 SEM micrographs of the chemically etched surfaces of the HA (a), HA02F (b), HA04F (c), and HA06F (d) ceramics sintered at 1250°C

Design of FHA ceramics with preferable stability and microstructure

(a^P)

(a)

(b)

Design of FHA ceramics with preferable stability and microstructure

(c)

(d)

(e)

(f)

Figure 4-11 SEM micrographs of the polished surface of the HA(a^p), the chemically etched surfaces of the HA (a), HA02F (b), HA04F (c), HA06F (d), HA08F (e) and FA (f) ceramics sintered at 1300°C

4.8 Morphologies of thermally etched surfaces of FHA ceramics sintered at 1300°C

The FHA ceramics sintered at 1300°C for 2 hours in air were polished and thermally etched at 1250°C for half an hour, the resulting surface morphologies were shown in Figure 4-12. No micropores could be found in each of the six compositions, indicating a very high degree of densification. This observation agreed with the pore-free structure observed in Figure 4-11 a^p, and provided a solid evidence to support the conclusion that the rough surfaces of the chemically etched FHA ceramics could not be ascribed to the formation of micropores due to the incomplete densification.

From Figure 4-12, it is also seen that the pure HA sample had the smallest grain size of

Design of FHA ceramics with preferable stability and microstructure

about 1.8 μm , while the FA sample had the largest grain size of about 6.2 μm . The grain sizes of the FHA ceramics were shown in Table 4-2. It seems that the grain size of the FHA ceramics was strongly influenced by the fluorine content. When the fluorine content in the FHA ceramics increased from 0 to 100%, the grain size grew from 1.8 μm to 6.2 μm . However, the difference in grain size of the fluorine-rich FHA ceramics was not so substantial. For example, the grain size of HA06F ceramics showed only a slight increment of 0.5 μm when compared to that of the HA04F ceramic; whereas the grain size of pure HA was 2.1 μm smaller than that of HA02F.

It was also noticed that the grain sizes of the FHA bioceramics sintered at 1300 $^{\circ}\text{C}$, as shown in Figure 4-12, were consistently larger than those observed in Figure 4-11. This could be attributed to the higher sintering temperature employed and the accessional chemical etching process at 1250 $^{\circ}\text{C}$, which necessitated further grain growth.

Table 4-2 Grain sizes of FHA ceramics with different fluorine contents and sintered at 1300 $^{\circ}\text{C}$

Sample	HA	HA02F	HA04F	HA06F	HA08F	FA
Grain size (μm)	1.8	3.9	4.4	4.8	5.6	6.2

Design of FHA ceramics with preferable stability and microstructure

(a)

(b)

(c)

Design of FHA ceramics with preferable stability and microstructure

(d)

(e)

(f)

Figure 4-12 SEM micrographs of the thermally etched surfaces of the HA (a), HA02F (b), HA04F (c), HA06F (d), HA08F (e) and FA (f) ceramics sintered at 1300 °C

4.9 Discussion

4.9.1 Study of the effect of fluorine on the thermal stability of the FHA bioceramics

The effect of fluorine on the thermal stability of the FHA bioceramics with different fluorine contents sintered by conventional sintering had been studied. Results showed that the thermal stability of the FHA bioceramics increased substantially with the increasing fluorine contents. More specifically, when the fluorine content increased to a certain high level, i.e., when the x in the general FHA formula was greater than 0.6 (HA06F), the FHA bioceramics showed desirable thermal stability up to the sintering temperature of 1300°C, at which temperature most of the HA phase had decomposed to β -TCP for the pure HA sample. Similar observation was also reported by E. Adolfsson et. al. [91, 94, 96] in their studies on the zirconia or alumina toughened HA or FA biocomposites. This phenomenon could be explained by considering the crystal structure of HA. As shown in Figure 4-13, the hydrogen ions (H^+) of HA were arranged in the atomic interstices neighboring to the oxygen ions (O^{2-}), forming OH^- groups and were oriented randomly, which conferred a certain degree of disorder to the crystal structure of HA. Once the OH^- ions were partially substituted by the F^- ions, the existing hydrogen ions of the OH^- groups were bound to the nearby F^- ions because of the higher affinity of the fluoride in respect to the oxygen, producing a quite well-ordered apatite structure, which caused the increase of the thermal and chemical stability of the HA matrix. Therefore, when a certain amount of F^- ions substituted the OH^- groups in the HA matrix, a certain level of chemical and thermal

stability of the FHA ceramics was achieved. Theoretically, an F^- ion concentration of 50% in the FHA should be enough to remove the disorder of the crystal structure of HA and hence stabilize the structure due to the alternating arrangement of F^- ions between each pair of OH^- groups. However, by considering the random substitution of OH^- ions with F^- ions in any OH^- positions, the F^- ion concentration required to stabilize the structure was necessarily higher than 50%. And in this study, the F^- ion concentration was observed to be about 60%. The better stabilized crystallographic structure of the FHA bioceramics due to the introduction of fluorine into the HA matrix had also resulted in the improved chemical stability in acid environments, as shown in chapter 4.7.

Figure 4-13 OH^- and F^- columns in HA, FHA and FA

4.9.2 Study of the effect of fluorine on the sinterability and microstructure of the FHA bioceramics

Through the density measurements of the conventionally sintered FHA bioceramics with different fluorine contents, it was found that the FHA ceramics with lower fluorine contents tended to have slightly higher relative densities than those with higher fluorine contents, given that they were all sintered at the same temperature and for the same duration. In other word, the introduction of fluorine into the HA matrix tended to slightly retard the densification of the HA matrix. It is known that the densification of ceramics during solid-state sintering is governed by lattice and grain boundary diffusion. Of these two diffusion mechanism, the grain boundary diffusion is relatively important to the densification of most ceramics and composites because it is the dominant mass transportation process during sintering; however, mass transportation due to the lattice diffusion can not be underestimated in that lattice diffusion is quite active at high temperatures and also contributes to the densification process. For the FHA bioceramics, the observed lower degree of densification with increasing fluorine contents could be explained by the lowered lattice diffusion resulted from the introduction of fluorine into the HA lattice, which improved the stability of the HA lattice due to the hydrogen bonding formed between the hydroxyl group and the more electronegative fluoride, and hence decreased the lattice diffusion rate, as illustrated in Fig. 6-1. However, since the lattice diffusion was not the dominant mass transportation process during the sintering, the lowered lattice diffusion due to the better stability of the HA lattice had not significantly retarded the densification of the FHA bioceramics with higher fluorine

contents. Only a slight decrease in the relative densities could be noted for the FHA bioceramics with higher fluorine contents from the experimental data.

It was also found that the grain sizes of the FHA bioceramics with higher fluorine contents were larger than those of the FHA bioceramics with lower fluorine contents, given that they were all sintered at the same temperature and for the same duration. This phenomenon could be explained in terms of the different activation energy barrier for grain growth of the FHA bioceramics with different fluorine contents. Since moving away from an equimolar quantity of both hydroxide and fluoride to higher concentrations of fluoride produced a decrease in the activation energy for grain growth due to the better stabilized lattice structure and resultantly decreased movement of fluoride and hydroxide ions within the lattice, the FHA bioceramics with higher fluorine contents were supposed to have lower activation energy barrier for grain growth than those with lower fluorine contents. Therefore, more severe grain growth could be observed in the FHA bioceramics with higher fluorine contents from the experimental data.

4.9.3 Determination of the optimal fluorine content for FHA ceramics for desirable thermal and chemical performance

The major objective of this chapter is to study the influence of fluorine content on the thermal and chemical performance of FHA bioceramics. Based on the XRD, TGA, dilatometric, and microstructural data, the FHA bioceramic with the composition of $\text{Ca}_{10}\text{PO}_4(\text{OH})_{0.8}\text{F}_{1.2}$ (HA06F) was found to possess much improved thermal stability and

Design of FHA ceramics with preferable stability and microstructure

chemically corrosion resistance as compared to pure HA, while it still exhibited desirable sinterability and grain size control. Therefore, the composition HA06F was considered as the optimal FHA bioceramic with preferable thermal and chemical performance' and was used as the substrate material to prepare FHA-YTZP biocomposites for possibly better mechanical performance. The detailed investigation on the thermal and mechanical properties of the HA06F-YTZP biocomposites will be discussed in the next chapter.

Chapter 5 Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

The objective of this project was to investigate the influence of YTZP content on the microstructure and mechanical performance of FHA-YTZP ceramic composites. FHA-YTZP powders with different YTZP contents were prepared using the co-precipitation method, followed by sintering at different temperatures in air or by SPS, as described in chapter 3.3. The as-prepared samples were characterized using XRD, SEM, TEM, TGA, and dilatometry. The data acquired were analyzed and the effect of YTZP content on the microstructure and mechanical performance of FHA-YTZP composites were given.

5.1 Phase analysis of HA06F-YTZP powders by XRD

The XRD patterns of the as-precipitated (not calcined) HA06F5YTZP, HA06F10YTZP, HA06F15YTZP, HA06F20YTZP, HA06F40YTZP and HA06F60YTZP composite powders are shown in Figure 5-1. No other phases except for HA06F and tetragonal zirconia are found according to the standard XRD patterns of HA (JCPDS #09-432), FA (JCPDS #15-876), and t-zirconia (JCPDS #17-923). The observed peaks at 30.30° are representative of t-zirconia and the intensity of the peaks increases with the increasing content of zirconia. Only a very weak peak at 30.30° can be observed in the XRD pattern of the HA06F5YTZP sample due to the low content of zirconia in this sample.

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Figure 5-1 XRD patterns of the as-precipitated HA06F-YTZP composite powders with different YTZP contents

The HA06F10YTZP powders from co-precipitation were calcined at 300°C, 400°C, 500°C, 600°C, and 700°C to investigate the influence of temperature on the crystallization of these composite powders. The XRD patterns are presented in Figure 5-2. From this figure, it can be seen that with the increasing temperature, the composite powders show better degree of crystallinity, which is indicated by the sharp and well-defined peaks. Well-crystallized apatite and zirconia phases started to form from the temperature of 500°C. Moreover, the decomposition of the FHA phase was not triggered at the temperature of 800°C in the presence of zirconia.

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Figure 5-2 XRD patterns of the HA06F10YTZP powders calcined at different temperatures

5.2 Morphological observation of HA06F-YTZP powders by TEM

The morphologies of the HA06F-YTZP composite particles were examined by TEM and shown in Figure 5-3. Needle-like particles with width and length both in the nano region can be observed in this figure together with nanosized spherical particles. From our previous study the needle-like particles were crystallized FHA particles, and the spherical particles with radius around 25 nm were identified to be zirconia particles. It was found that the co-precipitation process of HA06F and YTZP did not substantially change the morphologies of the HA06F particles, as compared with the precipitated HA06F particles observed in Figure 4-2. When the zirconia content increased from 5 wt% to 20 wt%, it was quite difficult to locate isolated zirconia particles since most of the zirconia particles agglomerated due to the affinity of them with each other in the precipitation process. The aggregates grew by the random attachment of small particles in Brownian motion around the prime aggregate formed during the precipitation process. Such aggregates were self-similar with increasing size, and their structure was considered to be fractal.

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(a)

(b)

Figure 5-3 TEM micrographs showing the morphologies of the as-precipitated
HA06F5YTZP (a) and HA06F20YTZP (b) powders

5.3 Thermogravity analysis (TGA)

To study the influence of zirconia content on the thermal stability of the HA06F phase, thermogravimetric data were collected and analyzed using the HA06F20YTZP, HA06F40YTZP, and HA06F60YTZP composite powders in the temperature range of 25°C to 1400°C. Figure 5-4 shows the different degrees of weight loss and weight loss rates of the samples with different YTZP contents. In the first heating stage from 25°C to 600°C, great weight loss was detected in all the compositions due to the evaporation of absorbed water in the three powders. In the second heating stage from 600°C to 800°C, the evaporation of the absorbed water was completed and the OH⁻ groups in the HA06F phase started to decompose and evaporate. At the temperature of 800°C the highest weight loss rate was achieved in the three powders, suggesting that the loss of the OH⁻ groups in the HA06F matrix dominated the weight loss of the three composites. In the temperature range from 800°C to 1000°C, the rate of the loss of the OH⁻ groups slowed down and became constant in the short temperature range from 1000°C to 1050°C. For the HA06F20YTZP composite, the weight loss rate was 0.0008 wt%/°C at 1050°C and slowly increased to 0.0017 wt%/°C in the temperature range from 1050°C to 1400°C due to the subsequent decomposition of the HA06F phase into the β -TCP phase and the loss of the residual OH⁻ groups. For the HA06F60YTZP composite, the weight loss rate was 0.0017 wt%/°C at the temperature of 1050°C and became constant in the temperature range from 1050°C to 1400°C. Based on the above observations, it could be seen that the fluorine in the HA06F-YTZP composites could only stabilize the HA06F phase when the YTZP content was below 20 wt% and when the temperature was lower than 1200°C. For

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

the HA06F20YTZP composite, the decomposition of the HA06F phase was initially suppressed but gradually accelerated, depending on the content of YTZP and when the temperature was higher than 1200°C. However, for the HA06F60YTZP composite, the HA06F phase suffered from dramatic decomposition above the temperature of 1200°C; the fluorine had lost its ability to retard the decomposition of the HA06F phase at this high YTZP content.

(a)

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

(b)

(c)

Figure 5-4 TGA results of the HA06F20YTZP (a), HA06F40YTZP (b), and HA06F60YTZP (c) powders heated up to 1400°C in air (solid line stands for weight while dash line stands for weight loss rate)

5.4 Sintering analysis by dilatometry

The sintering shrinkage (i.e., the relative shrinkage) and the sintering shrinkage rate data were acquired by sintering the pressed HA06F-YTZP pellets in the dilatometer in the temperature range from 25°C to 1400°C, as shown in Figure 5-5. It was found in this figure that the maximum shrinkage rates of the HA06F-YTZP composites with lower YTZP contents were achieved at lower temperatures than those of the HA06F-YTZP composites with higher YTZP contents. For example, the HA06F5YTZP and HA06F10YTZP samples reached their maximum shrinkage rates at the temperature of around 1000°C while the HA06F15YTZP sample and the HA06F-YTZP samples with higher YTZP contents reached their maximum shrinkage rates at the temperature of 1200°C.

However, the above observation did not confirm that the existence of the zirconia phase had retarded the sintering (or densification) of the HA06F-YTZP composites. Since the thermal expansion coefficient (CTE) of HA06F and zirconia remarkably differs from each other, the shrinkage due to the densification of both HA06F and zirconia should be taken into consideration for the HA06F-YTZP composite sintering system.

According to the sintering shrinkage rate data, it was also found that the onset sintering temperatures of all these six samples were about 800°C, despite of the slight difference among individual samples. This onset sintering temperature of the HA06F-YTZP samples was much lower than that of the previous FHA samples, which was shown to be 1000°C

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

in chapter 4 and in Figure 4-6. The noticeable difference in the onset sintering temperature between zirconia-doped HA06F samples and the zirconia-free HA06F samples indicated that the addition of the zirconia phase into the HA06F matrix might have accelerated the sintering process of the HA06F phase although itself was rather difficult to be sintered at the sintering temperature of the HA06F phase.

(a)

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

(b)

(c)

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

(d)

(e)

(f)

Figure 5-5 Sintering shrinkage and sintering shrinkage rate data of HA06F5YTZP (a), HA06F10YTZP (b), HA06F15YTZP (c), HA06F20YTZP (d), HA06F40YTZP (e), and HA06F60YTZP (f) heated up to 1400°C (solid line stands for relative shrinkage while dash line stands for shrinkage rate)

5.5 Microstructure and properties of conventionally sintered HA06F-YTZP composites

5.5.1 Phase analysis of conventionally sintered HA06F-YTZP composites

The XRD patterns of the HA06F-YTZP composites sintered at 1400°C for 1 hour in air are shown in Figure 5-6. In this figure, β-TCP can be observed in all the six patterns due to the decomposition of the HA06F phase. For the HA06F-YTZP composites with YTZP contents lower than 20 wt%, the amounts of β-TCP were not substantial as compared to

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

that of HA06F because of the retardation of the decomposition of the HA06F phase due to the existence of fluorine. However, for the HA06F-YTZP composites with YTZP contents higher than 20 wt%, severe decomposition of the HA06F phase to the β -TCP phase was detected. Almost no HA06F phase was left for the HA06F-60YTZP composite sintered at 1400°C in air. The YTZP contents higher than 20 wt% in the HA06F-YTZP composites seemed to have destroyed the thermal stability of the HA06F phase and accelerated the decomposition of the HA06F phase. This observation agreed with the TGA data (Figure 5-4) that when the YTZP content in the HA06F-YTZP composites was higher than 20 wt%, the fluorine would lose its ability to suppress the decomposition of the HA06F phase at a temperature as high as 1400°C.

Figure 5-6 XRD patterns of the HA06F-YTZP composites sintered at 1400°C

5.5.2 Density results of conventionally sintered FHA-YTZP ceramics

The relative densities of the HA06F5YTZP, HA06F10YTZP, HA06F15YTZP, HA06F20YTZP, HA06F40YTZP, and HA06F60YTZP composites sintered at 1200°C, 1300°C, and 1400°C for 2 hours in air are presented in Table 5-1.

From this table, it can be seen that the sintering temperature has a strong influence on the densities of the HA06F-YTZP samples. When the sintering temperature is 1200°C, all the samples did not have high degrees of densification; the highest relative density at this temperature is 85.3%, which is of the sample HA06F5YTZP, while the lowest relative density is only 72.2%, of the sample HA06F60YTZP. When the sintering temperature increases from 1200°C to 1400°C, the relative densities of the samples of correspondingly same composition increased substantially, especially in the case of temperature increment from 1300°C to 1400°C. For the HA06F-YTZP composites with YTZP contents lower than 20 wt%, relative densities higher than 90% was achieved when these composites were sintered at 1400°C.

It can be also found that the YTZP content strongly affected the relative densities of the HA06F-YTZP composites. The HA06F-YTZP composites with lower YTZP contents had a higher degree of densification as compared to those with higher YTZP contents under the same sintering temperature, and vice versa. For example, under the sintering temperature of 1400°C, the HA06F5YTZP sample had a relative density of 94.6%, while that of the HA06F60YTZP was merely 79.4%.

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

The sintering temperature of YTZP of about 1500°C is known to be much higher than that of FHA, which is normally around 1200°C. The highest sintering temperature of 1400°C employed in this experiment is adequate for densifying the FHA phase, but possibly not enough for densifying the YTZP phase. The density results showed that even at the temperature of 1400°C, the HA06F-YTZP composites with high YTZP contents, i.e., YTZP contents high than 20 wt%, could not be well densified conventionally.

Table 5-1 Relative densities of HA06F5YTZP, HA06F10YTZP, HA06F15YTZP, HA06F20YTZP, HA06F40YTZP, and HA06F60YTZP composites sintered at 1200°C, 1300°C, and 1400°C for 2 hours in air

Samples	Relative density (%)		
	1200°C	1300°C	1400°C
HA06F5YTZP	85.3	85.9	94.6
HA06F10YTZP	84.1	84.3	93.9
HA06F15YTZP	81.5	81.6	91.7
HA06F20YTZP	78.7	77.8	90.5
HA06F40YTZP	74.2	75.5	82.1
HA06F60YTZP	72.2	73.0	79.4

5.5.3 Morphologies of thermally etched surfaces of HA06F-YTZP composites conventionally sintered at 1400°C

The HA06F-YTZP composites sintered at 1400°C for 2 hours in air were polished and thermally etched at 1350°C for half an hour, the resulting surface morphologies are shown in Figure 5-7. From Figure 5-7, it is obvious that the YTZP content of the HA06F-YTZP composites had a strongly negative influence on the densification of the composites. More micropores could be observed in the HA06F-YTZP composites with higher YTZP contents. At the meantime, the surfaces of the HA06F-YTZP composites with higher YTZP contents were much rougher than those with lower YTZP contents. A large number of macropores and cracks could be seen in the HA06F-YTZP composites with YTZP contents higher than 20 wt%, which indicated a very low degree of densification. This observation agrees with the density data of the HA06F-YTZP composites that the HA06F-YTZP composites with higher YTZP contents have lower theoretical densities.

Because of the incapability of thermal etching to reveal the grain structures of the HA06F-YTZP composites with YTZP contents higher than 20 wt%, finer resolution images showing the grain structures of the HA06F-YTZP composites with YTZP contents only lower than 20 wt% are shown in Figure 5-8. The grain size of the HA06F phase (the dark phase) was 3-4 μm , while that of the YTZP phase (the bright phase) was still in the nano region. As compared with Figure 5-3 (a), the shape and size of the YTZP grains did not change much before and after the sintering process, which indicated that the YTZP phase in the HA06F-YTZP composites was not sufficiently sintered at the sintering

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temperature of 1400°C. The existence of agglomerates of small YTZP grains instead of large YTZP grains in the HA06F-YTZP composites with YTZP contents higher than 10 wt% also indicated that the YTZP phase in the HA06F-YTZP composites was not well densified. At the mean time, the grain size of the HA06F phase was substantially smaller than that observed in Figure 4-11 (d). This decrement in the grain size of the HA06F phase might be ascribed to the “pinning effect” of the YTZP phase due to the desirable distribution of it, which was mostly in the grain boundaries of the HA06F grains.

(a)

(b)

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(c)

(d)

(e)

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(f)

Figure 5-7 SEM micrographs of the thermally etched surfaces of the HA06F5YTZP (a), HA06F10YTZP (b), HA06F15YTZP (c), HA06F20YTZP (d), HA06F40YTZP (e), and HA06F60YTZP (f) composites sintered at 1400°C in air

(a)

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

(b)

(c)

(d)

Figure 5-8 SEM micrographs showing the grain morphologies of the HA06F5YTZP (a), HA06F10YTZP (b), HA06F15YTZP (c), and HA06F20YTZP (d) composites sintered at 1400°C in air

5.5.4 Mechanical properties of the HA06F-YTZP composites conventionally sintered at 1400°C

The Knoop hardness, Young's modulus, and fracture toughness of the HA06F-YTZP composites with YTZP contents lower than 20 wt% conventionally sintered at 1400°C for 2 hours are shown in Figure 5-9 to Figure 5-11, respectively. Same mechanical testings were also performed on pure HA06F sample conventionally sintered at 1250°C, as reference. The lack of the mechanical properties of the HA06F-YTZP composites with YTZP contents higher than 20 wt% was due to the insufficient densification of these composites, which subsequently produced microstructurally rough surfaces and resulted in great difficulty in the measurement of the mechanical properties. From these figures, the Knoop hardness and fracture toughness of the HA06F-YTZP composites were noticeably higher than those of the pure HA06F ceramics, although the Young's modulus was slightly lower. The decreased Young's modulus of the HA06F-YTZP composites could be explained in terms of the reaction between the HA06F phase and the YTZP phase, the loose bonding between the HA06F matrix and the YTZP phase, and the existence of microcracks on the surface of the samples. These specific issues observed in the conventionally sintered HA06F-YTZP composites had significantly decreased the Young's modulus of the composites and weakened the strengthening effect of the YTZP phase on the Young's modulus of the HA06F-YTZP composites. However, an elastic modulus too high was not desirable for applications in load-bearing parts for bone and teeth because of the concentration of stress on these restoration parts and their subsequent failure. With the YTZP content being increased up to 20wt%, the Knoop hardness and fracture toughness increased gradually from the initial values of 4.79 GPa and 0.88

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MPam^{1/2} to 6.68 GPa and 2.22 MPam^{1/2}, respectively. However, when the YTZP content increased from 20 wt% to 60 wt%, the Knoop hardness, Young's modulus, and fracture toughness could not be correctly measured because that the testing machines could not generate clear indentation marks on the surfaces of the samples. Nevertheless, considering the rough surfaces observed in Figure 5-7, the difficulty in measuring the mechanical properties of the HA06F-YTZP composites with YTZP contents higher than 20 wt% indicated poor mechanical behaviors of the composites. Since the mechanical properties of a material is strongly effected by the densification and microstructure of the material, the poor mechanical performance of the HA06F-YTZP composites with relatively high YTZP contents was believed to be originated from the insufficient sintering of the composites and the resultantly disordered microstructure.

Due to the lack of die with sufficient size to produce samples large enough for 4-point flexural strength testing, the flexural strength of the HA06F-YTZP samples was not measured in this project. However, review of the published work of other researchers showed that the YTZP content in the HA-YTZP or FHA-YTZP composites had significantly positive effect on the flexural strength, as well as other mechanical properties such as the fracture toughness, of the composites in condition that the composites were dense and no severe decomposition of the FHA phase occurred [117-119,126,141,142,152,153]. H. W. Kim et. al. reported fairly well densified FHA-YTZP composites with well controlled decomposition of the FHA phase in their continuous work on the FHA-YTZP biocomposites. The FHA-YTZP composites were reported to exhibit much improved mechanical properties, such as flexural strength and

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fracture toughness, having values of more than 2-4 times higher than those of pure FHA ceramics [117-119,141,153]. E. S. Ahn also reported an increment of the flexural strength of nanocrystalline hydroxyapatite from 183 MPa to 243 MPa with a low loading (1.5 wt%) of tetragonal zirconia [151]. However, it was found in his work that when the zirconia content increased from 1.5 wt% to 3 wt%, the flexural strength decreased from 243 MPa to 203 MPa. Due to the lack of phase analysis data in his work, it was supposed that certain degree of decomposition of the HA phase and reaction between the HA phase and the zirconia phase occurred during the sintering, which had introduced defects such as microcracks and macropores and thus decreased the flexural strength of the composites since that the flexural strength was very sensitive to structural defects.

Figure 5-9 Knoop hardness vs YTZP content of the HA06F-YTZP composites
conventionally sintered at 1400°C for 2 hours

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Figure 5-10 Young's modulus vs YTZP content of the HA06F-YTZP composites
conventionally sintered at 1400°C for 2 hours

Figure 5-11 Fracture toughness vs YTZP content of the HA06F-YTZP composites
conventionally sintered at 1400°C for 2 hours

5.5.5 Summary

The HA06F-YTZP composites with different YTZP contents were prepared by conventionally sintering at 1400°C for 2 hours, and then were subjected to phase analysis and mechanical testings. It was found in this study that the HA06F-YTZP composite with 20wt% YTZP was preferable due to the stabilization of the hydroxyapatite phase and the pronounced better mechanical properties than pure HA06F ceramics. It was reported in our previous study that fluorine in the FHA ceramics stabilized the hydroxyapatite phase due to a microstructural modification/fixation of the hydroxyapatite lattice. However, in the case of zirconia doped hydroxyapatite composites, diffusion of zirconia into the hydroxyapatite lattice had been reported, which would possibly have detrimental effects on this steady state and introduce certain disorder to the FHA lattice, although the mechanism had not been fully understood. Considering the discrepancy in the sintering and mechanical behavior of the HA06F-YTZP composites with relatively low and high YTZP contents, it was believed that there existed certain equilibrium in the HA06F-YTZP composite system with respect to the fluorine and zirconia contents. In this study, for the HA06F-YTZP composites with YTZP contents lower than 20wt%, the mechanical properties of the composites increased steadily with the increasing YTZP contents although the degree of densification was slowly decreased. On the other hand, for the HA06F-YTZP composites with YTZP contents higher than 20wt%, the mechanical properties of the composites decreased sharply with the increasing YTZP contents due to the substantially decreased degree of densification. Similar phenomenon was observed in the phase purity of the HA06F-YTZP composites. For the HA06F-YTZP composites with YTZP contents lower than 20wt%, the decomposition of the

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hydroxyapatite phase was successfully suppressed, while mass decomposition of the hydroxyapatite phase occurred for those composites with YTZP contents higher than 20wt%.

5.6 Sintering analysis of spark plasma sintered HA06F-YTZP composites

5.6.1 Phase analysis of spark plasma sintered HA06F-YTZP composites

The XRD patterns of the HA06F-YTZP composites with 20, 40, and 60 wt% YTZP prepared by SPS at 1200°C for 10 minutes are shown in Figure 5-12. As shown in this figure, β -TCP could be observed in all these patterns. The amounts of the β -TCP phase in the composites were not initially substantial as compared to those of the HA06F phase, but gradually increased with the increasing YTZP contents, as determined by the ratio of the relative intensities of the HA06F and β -TCP peaks. As compared to the XRD patterns of the HA06F-YTZP composites conventionally sintered at 1400°C for 2 hours, which were shown in Figure 5-6, the decomposition of the HA06F was much more suppressed due to the low sintering temperature and the short sintering time. However, although the initial zirconia phase in the HA06F-YTZP composites was yttria stabilized tetragonal zirconia, monoclinic zirconia was found instead in the HA06F-YTZP sample after SPS heat treatment at 1200°C. Moreover, calcium zirconium oxide was also detected in the HA06F60YTZP sample due to the reaction between the HA06F phase and the unstabilized zirconia phase.

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Figure 5-12 XRD patterns of the HA06F-YTZP composites sintered by SPS at 1200°C

5.6.2 SEM morphologies of spark plasma sintered HA06F-YTZP composites

The microstructure of the HA06F-YTZP composites sintered by SPS at 1200°C for 10 minutes with 20, 40, and 60 wt% YTZP contents are shown in Figure 5-13 and Figure 5-14. From Figure 5-13, it could be clearly seen that the surfaces of the HA06F-YTZP composites were growing rougher and more disordered with the increasing YTZP contents. Micropores with average size of 0.5 – 2 μm could be observed in all the samples due to both the insufficient sintering and the grain pulling-out during the grinding and polishing process. Figure 5-14 presents a higher magnification SEM observation of the HA06F-YTZP composites. Unlike the isolated zirconia particles and the agglomerates of

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

zirconia particles observed in the conventionally sintered HA06F-YTZP composites, as shown in Figure 5-7 and Figure 5-8, the *t*-zirconia grains (the bright phase) in the SPS samples were observed to be well distributed and embedded in the HA06F matrix (the dark phase). The *t*-zirconia grains in the HA06F-YTZP samples prepared by SPS were also found to be much larger than those in the conventionally sintered composites and demonstrated well-defined grain morphologies with an average grain growth from the initial 100 nm to 800nm. The improved and well-defined microstructure indicated better densification results of the HA06F-YTZP composites sintered by SPS than those by conventionally sintering. Considering the concurrently improved phase purity/thermostability of the HA06F-YTZP composites prepared by SPS, the SPS technique were considered to have better ability to produce higher quality HA06F-YTZP composites than the conventional way did. However, the complicated operation process and poor cost-efficiency of SPS have been the main drawbacks preventing the industrial applications of SPS in producing HA06F-YTZP composites.

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

(a)

(b)

Study of HA06F-YTZP composites with preferable phase purity and mechanical properties

(c)

Figure 5-13 SEM morphologies of the HA06F-20YTZP (a), HA06F-40YTZP (b), and HA06F-60YTZP (c) composites sintered by SPS at 1200°C for 10 minutes

(a)

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(b)

Figure 5-14 Grain morphologies of the HA06F-20YTZP (a), HA06F-40YTZP (b), and HA06F-60YTZP (c) sintered by SPS at 1200°C for 10 minutes

5.6.3 TEM study of spark plasma sintered HA06F-YTZP composites

In order to have a better understanding of the microstructure of the spark plasma sintered FHA-YTZP composites, especially the interaction between the FHA phase and the zirconia phase, observation using high resolution TEM (HR-TEM) was carried out on the chosen HA06F-20YTZP sample which was selected as an example. For the HR-TEM observation, the sintered body of the HA06F-20YTZP composite was first grounded carefully into a fine powder using a jade pestle. Then the powder was dispersed in an ethanol solution by ultrasonification, and the as-prepared solution was slowly dipped onto a carbon grid. After drying, the carbon grid was subjected to high resolution TEM observation. Figure 5-15 shows a local area of the HA06F-20YTZP sample spark plasma sintered at 1200°C for 10 minutes. The bright large grain belonged to HA06F whereas the dark small grains (300 – 400 nm) were zirconia. Apparently a defined neck structure could be identified between the two zirconia grains, which was different from the observation of the conventionally sintered HA06F-20YTZP composite, where no such a neck structure was developed. Specifically speaking, isolated zirconia grains and agglomerates of individual zirconia grains existed in the HA06F-YTZP composites prepared by conventional sintering at 1400°C, indicating a low degree of sintering of the zirconia particles. The well-defined neck structure between two zirconia grains in the spark plasma sintered HA06F-20YTZP suggested a high degree of sintering of the zirconia particles, which also agreed with the results shown in section 5.6.2.

To study the interfacial structure of the HA06F phase and the YTZP phase of the HA06F-20YTZP sample, observation at a higher magnification of the contact area

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between the FHA grain and the zirconia grain was performed and shown in Fig 5-16. It can be clearly seen that there was no third phase or interfacial layer in the grain boundary between the FHA phase and the zirconia phase as the two phases were in direct contact. This observation agreed with the XRD pattern of the HA06F-YTZP sample, which showed that no reaction between the FHA phase and the zirconia phase was presented, although a small amount of the FHA phase had decomposed to β -TCP, as shown in Figure 5-12. The FHA-YTZP composite of the current study behaved differently from the HA-YTZP composite, reported by H. Guo et al. [146], where a CaZrO_3 layer with an average thickness of less than 10 nm was observed on the HA/zirconia interface of the HA-YTZP composite spark plasma sintered at 1200°C for 5 minutes. In other words, there was no evidence of a third phase or interfacial layer in our study, although the current sintering time of 10 minutes and the zirconia content of 20 wt% were considerably higher than those used by H. Guo et al., which would potentially accelerate the reaction between HA and zirconia,. The difference was due to the fact that FHA rather than HA was used in the present study. The lack of the CaZrO_3 layer as a reaction product suggested a low level of decomposition of the FHA phase and the reaction between the FHA and the zirconia phase, which agreed with the result that fluorine addition could make the HA phase stable thermally.

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Ha-ZrO2 interfaceLow-25.tif
ZrO2-HA
Print Mag: 39400x @ 51 mm
14:11 10/05/06
TEM Mode: Imaging

100 nm
HV=200kV
Direct Mag: 20000x
Tilt:-.2
AMT Camera System

Figure 5-15 HR-TEM bright field image of the HA06F-20YTZP sample spark plasma sintered at 1200°C for 10minutes

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Figure 5-16 HR-TEM bright field image of the HA06F/YTZP interface of the HA06F-20YTZP sample spark plasma sintered at 1200°C for 10minutes

5.6.4. Mechanical properties of spark plasma sintered HA06F-YTZP composites

The Knoop hardness, Young's modulus, and fracture toughness of the HA06F-YTZP composites with 20 wt%, 40 wt%, and 60 wt% YTZP as the phase contents and sintered by SPS at 1200°C for 10 minutes are shown in Table 5-2. It can be seen that as the YTZP content of the HA06F-YTZP composites increased from 20 wt% to 40 wt%, both the Knoop hardness and the Young's modulus increased from 7.54 GPa to 8.23 GPa and from 136.78 GPa to 148.19 GPa, respectively. Similarly, the fracture toughness of the HA06F-YTZP composites with 20 wt% and 40 wt% YTZP increased from 2.60 MPam^{1/2} to 3.37 MPam^{1/2}. However, at the phase content of 60% YTZP, a dramatically decrease in the fracture toughness was found and the fracture toughness of 2.21 MPam^{1/2} was even lower than that of the HA06F-20YTZP sample. This variation of fracture toughness with the YTZP content could be due to the significant amount of m-zirconia phase instead of t-zirconia phase present in the spark plasma sintered sample, as shown in Figure 5-12. The loss of the t-zirconia phase in the sample obviously eliminated the martensitic transformation toughening mechanism of the zirconia phases. Nevertheless, the mechanical properties of the spark plasma sintered HA06F-YTZP composites were noticeably higher than those of the conventionally sintered HA06F-YTZP composites, which was attributed to the higher degree of densification of the composites prepared by the spark plasma sintering.

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Table 5-2 Mechanical properties of the HA06F-YTZP composites spark plasma sintered at 1200°C for 10 minutes, and mechanical property of the conventionally sintered HA06F-20YTZP* composite at 1400°C.

Samples	Knoop hardness (GPa)	Young's modulus (GPa)	Fracture toughness (MPam ^{1/2})
HA06F-20YTZP	7.54 ± 0.31	136.78 ± 5.61	2.60 ± 0.14
HA06F-40YTZP	7.91 ± 0.41	142.33 ± 7.40	3.37 ± 0.24
HA06F-60YTZP	8.23 ± 0.40	148.19 ± 7.26	2.21 ± 0.21
HA06F-20YTZP*	6.68 ± 0.32	101.6 ± 6.40	2.21 ± 0.18

5.7 Discussion

5.7.1 Study of the effect of zirconia on the microstructure and sinterability of the HA06F-YTZP biocomposites

It was shown in the dilatometric analysis that the maximum shrinkage rate or densification rate was achieved at noticeably higher temperatures for the HA06F-YTZP composites with higher zirconia contents, which indicated that the HA06F-YTZP composites with higher zirconia contents required higher temperature to be sintered than those with lower zirconia contents did. This indication could be explained in that the sintering temperature of zirconia of about 1500°C was much higher than that of FHA, which was normally around 1200°C; and therefore, the densification of the HA06F-YTZP composites with higher zirconia contents would require a much higher temperature than that of the composites with lower zirconia contents. However, a too high sintering

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temperature would substantially trigger the decomposition of the HA06F phase and hence the reaction between the β -TCP phase and the zirconia phase to form CaZrO_3 , which would introduce structural defects such as pores, microcracks to the HA06F-YTZP composite bodies. From the density measurements of the HA06F-YTZP composites conventionally sintered at different temperatures, it could be found that the densities of the HA06F-YTZP composites with higher zirconia contents were noticeably lower than those of the composites with lower zirconia contents at any given temperature, which indicated a lower degree of densification. The lower degree of densification had also resulted in the rougher surface microstructure of the HA06F-YTZP composites with higher zirconia contents, which was associated with the existence of micropores and microcracks all over the composites' surfaces. At higher magnification, it was found that the HA06F matrix was sufficiently densified with an average grain size of 3-4 μm while the zirconia phase remained narrowly unsintered. The shape and size of the zirconia grains did not noticeably change before and after the sintering process. Agglomerates of small zirconia particles instead of the existence of large sintered zirconia grains were also evidenced in the HA06F-YTZP composites. Due to the initially fine particle size of the zirconia phase, agglomeration of the nanosized zirconia particles was inevitable because of their high specific surface areas. Moreover, interagglomerate pores were formed during the pressing process. While small interparticle pores are easily closed during sintering, large interagglomerate pores need high sintering temperatures or long sintering times to be eliminated. In this study, the existence of agglomerates of zirconia particles after the sintering process had suggested either an insufficient sintering temperature or an insufficient sintering time, or both. This was reasonable considering the conventional

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sintering temperature of 1500°C or higher of the zirconia phase and the highest sintering temperature of 1400°C employed in the study. Therefore, although the fine particle sizes of the HA06F phase and the zirconia phase prepared from a co-precipitation method had provided high surface energy and high diffusivity because of the existence of a high density of short circuit diffusion paths brought by a very large fraction of atoms at the grain boundaries, the severe degree of agglomeration of the zirconia phase had substantially retarded the densification of it during the sintering process in this study.

Taking this into consideration, spark plasma sintering was employed in attempt to eliminate the large interagglomerate pores and better sinter the HA06F-YTZP composites, especially to sinter the zirconia phase dispersed in the HA06F matrix. The spark plasma sintering process involves first compressing the starting powder materials and then applying ON/OFF pulse-controlled power from a direct current pulse generator to concentrate a high-density energy in the areas of necks between particles in order to achieve densification. The pressure exerted on the HA06F-YTZP composites before and during the sintering process was supposed to be helpful to the elimination of large interagglomerate pores due to the resultantly plastic deformation of the composites; while the high-density energy applied in the areas of necks between particles during the sintering process was desirable in that the sintering process always started with the formation of neck-structure between particles and the mass transportation around the necks through different mechanism. Microstructure observation showed that the zirconia grains in the HA06F-YTZP composites were much larger than those in the conventionally sintered composites and demonstrated well-defined grain morphologies with an average

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grain growth from the initial 100 nm to 800 nm. Moreover, unlike the isolated zirconia particles and the agglomerates of zirconia particles observed in the conventionally sintered HA06F-YTZP composites, the zirconia grains in the spark plasma sintered composites were observed to be well distributed and embedded in the HA06F matrix. An example of the neck-structure between two zirconia grains was also evidenced in TEM observation. These phenomena had suggested better densification results of the HA06F-YTZP composites sintered by spark plasma sintering than those by conventionally sintering.

5.7.2 Study of the mechanical properties of the HA06F-YTZP biocomposites

The mechanical properties such as hardness, elastic modulus, and fracture toughness of ceramic composites are strongly influenced by their microstructures in terms of porosity and grain size, of which the major effect of the structure in most ceramics is the result of porosity. Pores obviously decrease the cross-sectional area on which the load is applied but also act as stress concentrators (For an isolated spherical pore the stress is increased by a factor of 2.). It is shown by Ryskewitsch that the strength of porous ceramics is decreased in a way that is nearly exponential with porosity:

$$\sigma = \sigma_0 \exp(-nP) \quad (5-1)$$

where n is in the range of 4 to 7 and P is the volume fraction porosity. That is to say, the strength is decreased to a value of half that observed for the pore-free material with about

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10% porosity. The porosity in a material necessarily depends on the particle (and grain) size and morphology, and the degree of densification of the material. The particle (and grain) parameters do not only have their influence on the porosity and hence on the mechanical properties of a material, but they themselves also have their effects on the hardness, elastic modulus, fracture toughness, and other mechanical properties of the material. Among these mechanical properties, elastic modulus does not actually depend on particle size, unless the particle size is large enough to trigger the onset of microcracking. However, elastic modulus clearly depends on the volume fraction of 2nd phase and its elastic properties. Generally a rule of mixture is often suitable for a first-order estimate of many composites, especially for those with constituents whose modulus does not differ substantially, e.g. by a few fold or less:

$$E_{UC} = \phi E_P + (1-\phi)E_M \quad (5-2)$$

where ϕ = the volume fraction of 2nd phase, E_P = the Young's modulus of the 2nd phase, and E_M = the Young's modulus of the matrix phase. According to this formula, the Young's modulus of the HA06F-YTZP composites should be increasing with the increasing zirconia contents. However, for the conventionally sintered HA06F-YTZP composites, the Young's modulus of the composites was found to be lower than that of pure HA06F. This could be explained in terms of the lower degree of densification of the HA06F-YTZP composites with higher zirconia contents, which generated porosity and microcracks and hence deteriorated the Young's modulus of the composites. For the spark plasma sintered HA06F-YTZP composites, the Young's modulus of the composites were

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found to be increasing with the increasing zirconia contents, due to the better densification of the composites, and the resultantly lower porosity and less cracks. Although some micropores could still be observed in the spark plasma sintered composites, the decrease of the Young's modulus of the composites due to the existence of porosity was not substantial as compared with the increase of the Young's modulus from the incorporation of large amount of the zirconia phase. Formula (6-2) is also applicable to estimate the microhardness of the HA06F-YTZP composites. The hardness of the HA06F-YTZP composites sintered by both conventional sintering and spark plasma sintering showed the tendency to increase with the increasing zirconia contents, regardless of the degree of densification. This was probably because the incorporation of the high hardness zirconia phase had counteracted the effect of micropores and cracks on the hardness of the composites.

Normally, the fracture toughness of ceramic composites at and near room temperature varies noticeably with the volume fraction of 2nd phase and the coarseness of it and the matrix grain size. However, for the zirconia toughened ceramic composites, the variation of fracture toughness due to these parameters is not as substantial as that resulted from the transformation toughening mechanism of the zirconia phase, in which the martensitic tetragonal to monoclinic crystal phase transformation of zirconia occurs. The effectiveness of this process comes from first the fact that the transformation is diffusionless, so it can occur rapidly, i.e. in response to crack tip stress effects. It arises secondly from the unusual character of the transformation in the lower temperature, monoclinic phase is less dense than the intermediate tetragonal phase. The most

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fundamental effect of transformation toughening is when trapped tetragonal zirconia particles or grains transform due to crack tip stresses relaxing the matrix constraint on their transformation. The resultant transformation results in compressive strains around transformed zirconia particles or grains due to the shape and volume increase of the resultant monoclinic phase over the original metastable tetragonal phase. These compressive strains from the transformation zone that results around the crack tip and along its faces thus partially counteract or shield the crack from the normal stress levels, making it more difficult for it to propagate. In this study, since the grain sizes of the HA06F phase and the zirconia phase did not vary substantially with composition, the fracture toughness of the HA06F-YTZP composites prepared by both conventional sintering and spark plasma sintering increased with the increasing zirconia contents, regardless of the different degrees of densification. However, the fracture toughness of the HA06F-YTZP composites sintered by spark plasma sintering was found to be noticeably higher than that of the conventionally sintered composites. This was believed to be due to the better densification and distribution of the zirconia phase, which was firmly bonded to the HA06F matrix.

Chapter 6 Conclusions

In this thesis, fluoride substituted hydroxyapatite (FHA) ceramic with different fluorine contents and zirconia doped FHA (FHA-YTZP) ceramic composites with different zirconia contents were synthesized and studied. The objective of the work on FHA ceramic is mainly to study the influence of fluorine content on the thermal and sintering properties of hydroxyapatite; while the purpose of the work on FHA-YTZP ceramic composites is to study the effect of zirconia content on the thermal stability of hydroxyapatite, as well as on the sintering and mechanical properties of FHA-YTZP composites, by conventional sintering and spark plasma sintering.

Base on the experimental data and analysis, the following conclusions were drawn for the work on FHA ceramic.

1. Needle-like FHA crystals, which are about 80nm in length and 20nm in width, with a relatively low level of crystallinity, were developed by a modified wet precipitation method.
2. By comparing the accurate 2θ positions of the (3 0 0) reflections in the XRD patterns, a gradual shift of these peaks to higher 2θ angles with the increase of the fluorine content was detected, which confirmed the incorporation of fluorine into the hydroxyapatite matrix.
3. Thermogravimetry data indicated that when the fluorine content in the HA matrix was high enough, the thermal stability of the HA matrix would be greatly increased or the decomposition of the HA matrix could be effectively retarded.

Conclusions

4. The XRD data of FHA ceramics sintered at 1300°C showed that in the HA06F sample and the FHA samples with higher fluorine contents than that in HA06F, the decomposition to form β -TCP was dramatically suppressed, which severe decomposition of hydroxyapatite to β -TCP were spotted in the FHA ceramics with lower fluorine contents that that in HA06F.

5. From dilatometric analysis, it was found that with the increase of fluorine content in the FHA ceramics, the onset sintering temperature and the maximum densification rate temperature were dramatically increased, which suggested that the introduction of fluorine into the HA matrix had retarded the densification process. This observation was also confirmed by the density and microstructural measurements. Despite of the retardancy of fluorine to the densification of hydroxyapatite, all the FHA samples sintered at 1250°C in air had the densities over 95% theoretical densities, which indicated a very high level of densification.

6. Chemical etching experiments on the FHA ceramics sintered at 1300°C showed that when the fluorine content in the FHA ceramics reached a certain high level (e.g., when $x = 0.6$), the corrosion resistance of the ceramics was greatly improved.

7. Thermal etching experiments on the FHA ceramics sintered at 1300°C showed that the fluorine content has slightly increased the grain size of FHA ceramics. When the fluorine content in the FHA ceramics increased from 0 to 100%, the grain size grew from 1.8 μm to 6.2 μm .

The following conclusions were drawn from the continuous work on the HA06F-YTZP composites.

Conclusions

1. Calcination of the precipitated HA06F-YTZP powders showed that well-crystallized apatite and zirconia phases started to form from the temperature of 500°C. Moreover, the decomposition of the FHA phase was not triggered at the temperature of 800°C in the presence of zirconia.

2. From TEM observation of the precipitated HA06F-YTZP powders, it was found that the co-precipitation process of HA06F and YTZP did not substantially change the morphologies of the HA06F particles. Severe agglomeration of zirconia particles were also spotted due to the affinity of them with each other in the precipitation process.

Based on the TGA analysis, it was concluded that the fluorine in the HA06FYTZP composites could only stabilize the HA06F phase when the YTZP contents were below 20 wt% and when the temperatures were lower than 1200°C. For the HA06F20YTZP composites, the decomposition of the HA06F phase was initially suppressed but gradually accelerated, depending on the content of zirconia and when the temperatures were higher than 1200°C. However, for the HA06F60YTZP composites, the HA06F phase suffered from dramatic decompositions above the temperature of 1200°C; the fluorine did not seem to retard the decomposition of the HA06F phase any more at the high YTZP content. This observation also agreed with the XRD patterns of the HA06FYTZP composites.

3. The measurements of sintering shrinkage and sintering shrinkage rate of the HA06F-YTZP samples from the temperature range from 25°C to 1400°C showed that the maximum shrinkage rates of the HA06FYTZP composites with lower YTZP contents were achieved at lower temperatures than those of the HA06FYTZP composites with higher YTZP contents did, which indicated insufficient densification of the YTZP phase at this temperature range. Density measurements and microstructural observation also agreed with

this indication.

4. Mechanical testings including Knoop hardness, Young's modulus, and fracture toughness showed that with the YTZP content being increased up to 20wt%, the Knoop hardness and fracture toughness increased gradually from the initial values of 4.79 GPa and 0.88 MPam^{1/2} to 6.68 GPa and 2.22 MPam^{1/2}, respectively. However, when the YTZP content increased from 20 wt% to 60 wt%, the Knoop hardness, Young's modulus, and fracture toughness could not be correctly measured because that the testing machines could not generate clear indentation marks on the surfaces of the samples. The difficulty in measuring the mechanical properties of the HA06F-YTZP composites with YTZP contents higher than 20 wt% indicated poor mechanical behaviors of the composites, probably due to the insufficient sintering of the composites and the resultantly disordered microstructure.

5. Based on the XRD analysis, the microstructural observation, and the mechanical testings of HA06F-YTZP composites sintered by SPS, it was found that the SPS technique seemed to have superior ability to produce better densified FHA-YTZP composites with higher purities and mechanical properties than the conventional sintering did. However, the complicated operation process and poor cost-efficiency of SPS have been the main drawbacks preventing the industrial application of SPS technique in producing HA06F-YTZP composites.

Based on the study of the FHA bioceramics and HA06F-YTZP bioceramic composites, the following conclusion could be drawn:

Conclusions

The HA06F bioceramic was found to have superior corrosion resistance and thermal/chemical properties as compared with pure hydroxyapatite; and the spark plasma sintered HA06F-YTZP composites were found to possess noticeably higher microhardness and Young's modulus than human cortical bone, while the fracture toughness of these composites was narrowly the same with human natural bone. Since the above mentioned properties are all of major importance for materials used as the articulating surfaces in total joint replacement, the HA06F-YTZP composites were found to be a promising potential material in both orthopedic and hip joint applications which require high mechanical properties. However, since the Young's modulus of these HA06F-YTZP composites, even of those poorly sintered under conventional sintering conditions, was too much higher than human natural bone, the HA06F-YTZP composites alone were not suitable for other load-bearing applications because that an implant with too high modulus of elasticity will carry almost all the load and prevent the bone near it from being properly loaded. The so-called "stress shielding" weakens bone in the region where the applied load is lowest and make the bone which is unloaded undergo a biological change that leads to bone resorption. Therefore, the HA06F-YTZP composites discussed in the thesis were not very suitable for load-bearing applications that do not have critical requirements of the mechanical properties. Nevertheless, from a point of view of the material itself, the HA06F-YTZP composite system could still be applicable in biomedical applications as coating material or porous material to control the mechanical properties.

Chapter 7 Recommendation for future work

Some studies on the thermal behavior, densification behavior, microstructure, and mechanical properties of the FHA ceramics and the FHA-YTZP composites prepared by both conventional sintering and spark plasma sintering were done for the PhD thesis. Further research can be carried out in the following areas to have a better understanding of the ceramics and composites.

1. Systematical high resolution TEM study of the FHA-YTZP composites prepared by conventional sintering can be done to observe the interaction between the FHA and the YTZP phase during the sintering process so that the reaction mechanism and structural evolution of the FHA-YTZP composite system during the sintering process could be further understood and optimum processing conditions might be developed for improving the densification of the composite system under the conventional sintering conditions.
2. Powder processing starting from the synthesis of powders to the formation of compact green bodies is believed to be very important to produce ceramics with both high density and phase purity. However, systematic studies on the influence of powder morphology, powder distribution and powder packing process have not been done yet. Further research can be focused on this area to develop a better powder processing approach for higher quality FHA-YTZP composites.

Recommendation for future work

3. Although some mechanical properties such as microhardness, elastic modulus, and fracture toughness of the FHA-YTZP composites were collected and analyzed in the thesis, further mechanical evaluation of the FHA-YTZP composites including Poisson ratio, bending strength, and Weibull modulus is suggested for a systematical study of the effect of the zirconia phase on the FHA-YTZP composites. The Poisson ratio could be measured by a non-destructive ultrasonic pulse method, while the bending strength could be measured by the three-point bending method. The results of bending strength tests could be analyzed statistically using the Weibull's distribution [161], from which the Weibull modulus could be determined to evaluate the degree of reliability of the FHA-YTZP composites.

4. It is well accepted that hydroxyapatite and fluorohydroxyapatite possess superior bioactivity which allows them to form direct bonding with bone tissue, whereas zirconia is nearly bio-inert. However, the biological behavior of the FHA-YTZP composites has still not been studied. Therefore, in vitro and in vivo studies, including cell culture and animal implantation, on the effect of zirconia on the biological behavior of the FHA-YTZP composites should be done in the future for the better understanding of the potential of the composite system.

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Nomenclature

HA	Hydroxyapatite	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$
FA	Fluoroapatite	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$
FHA	Fluorohydroxyapatite	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{F}_{2x}$ $0 < x < 1$
HA02F		$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{1.6}\text{F}_{0.4}$
HA04F		$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{1.2}\text{F}_{0.8}$
HA06F		$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{0.8}\text{F}_{1.2}$
HA08F		$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{0.4}\text{F}_{1.6}$
YTZP	Yttria stabilized tetragonal zirconia	
HA06F-xYTZP	x stands for the weight percentage of YTZP in the composite	
TCP		$\text{Ca}_3(\text{PO}_4)_2$
SPS	Spark Plasma Sintering	
XRD	X-Ray diffractometer	
SEM	Scanning Electron Microscopy	
FE-SEM	Field Emission Scanning Electron Microscopy	
TEM	Transmission Electron Microscopy	
HR-TEM	High Resolution Transmission Electron Microscopy	
TGA	Thermogravity analysis	

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