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Liu, Jianli

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Porous Alumina Ceramics with Bioactive Coating for Potential Biomedical Applications

Liu Jianli

School of Materials Science and Engineering

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Summary

In this thesis, a novel vacuum infiltration technique was developed to fabricate porous alumina ceramics. The preparation and characterization of porous alumina ceramics with a bioactive glass coating was reported. The obtained porous materials were expected to find implantation applications including bone replacement and bone regeneration, because they would have the ability to induce bone ingrowth and bone bonding, and maintain sufficient mechanical strengths to support the physiological loads. The project was focused on the relationships between the processing, microstructure and properties of the porous alumina ceramics.

Highly porous alumina/zirconia ceramics were successfully prepared using porous expanded polystyrene (EPS) bead templates as the pore former. A vacuum infiltration process was developed to prepare the porous bodies, in which ceramic slurries were allowed to penetrate into the pore spaces of the porous EPS template. After drying, the ceramic particle-pore former compacts were fired in air to burn out the pore formers and densify the ceramic struts. Finally, the porous structure, which was negatively duplicated from the pore structure of the porous EPS bead, was obtained.

The prepared porous alumina ceramics were featured with controllable pore sizes ranging from 1.21mm to 2.63mm, high total porosities about 60.84%-65.93%, high open porosities above 48.32%, and excellent pore interconnectivity. The mechanical properties of all the porous ceramics decreased with the increase of the porosity. With the pore sizes of porous alumina ceramics increasing from 1.21mm to 2.63mm, the compressive strength decreased

Chapter 1 General Introduction

1.1 Background

Bone is the substantial unit of human skeletal system which functions as load bearing, protection of most vital internal organs and storage of minerals. Pathologies of bone have substantial impacts on the health and quality of life of the population. The revolution of replacement of bone tissues by transplants and implants has led to a remarkable increase in the quality of life for millions of patients. The surgical methods involves: autografting (using patient's own bone), allografting (using donor's bone), xenografting (using animal's bone), synthetic graft (biomaterials) and tissue engineering (biomaterials and cell). The former three methods all use the natural materials, but are limited by the scarce supply of the grafts. Besides, great concerns exist in the immune response and infection. As a result, a synthetic graft method was developed to use biomaterials with desired shapes and forms to serve as the implantable grafts. Due to the plenty of supply and excellent biocompatibility of biomaterials, the synthetic grafts are still widely used in clinical surgery up to now. From 1970s, with the development of biology, a novel method, tissue engineering, has become emerging and potential method for treating damaged and diseased bones. In this method, the well shaped synthetic materials and the cells are combined to regenerate tissues or organs either *in vitro* or *in vivo*.

The ceramic materials used for biomedical and prosthesis application are called bioceramics. In 1960s, a wide range of new and exciting bioceramics have emerged, and the number of professionals working in the field has grown enormously. Bioceramics have been used extensively as bone implant materials due to their structural and

compositional stability. They can be classified into three main categories: bioinert ceramics (Al_2O_3 and ZrO_2), bioactive ceramics (hydroxyapatite (HA), bioactive glasses and glass-ceramics), and biodegradable ceramics (calcium phosphate ceramics and bone cement). A summary for three types of bioceramics and their reaction with host tissue is shown in Table 1-1.

Table 1-1 Summary for the types of bioceramics and their reaction with host tissues

Types of biocearmics	Typical bioceramics	Reaction with host tissues
Bioinert	Al_2O_3 and ZrO_2	Stable in human body. Tissue forms a non-adherent fibrous capsule around the implant
Bioactive	HA, bioactive glasses and glass-ceramics	Tissue forms an interfacial bond with the implant
Biodegradable	calcium phosphate ceramics and bone cement	Materials dissolve and tissue replace the materials

Recent investigations have opened new possibilities to use porous bioceramic scaffolds to guide the tissue development. The porous configurations enhance bone regeneration by facilitating cell migration, proliferation and differentiation, and provide strong fixation or stabilisation of the implants by means of bone ingrowth. For the bone ingrowth, the porous scaffolds must have the certain architecture of pores. For example, the minimum pore size for bone ingrowth is about 150-200 microns. The pores must be interconnected in order to maintain the vascular system needed for continued bone development within the pore spaces. Many other factors also affect bone ingrowth into the pore spaces, such as porosity, pore size and shape, time of implantation, biocompatibility, implant stiffness, micromotion between the implant and adjacent bone. Since dense bioceramics have much higher Young's moduli than those of bones, porous ceramics with a high porosity can

have low Young's moduli, which can be close to those of bones. Nevertheless, the increase in porosity is undoubtedly associated with the decrease in mechanical strength.

Although porous bioceramics have great advantages of tissue ingrowth, they have poor mechanical properties due to the existence of large amount of pores, which limits their load-bearing applications. Therefore, it is necessary to design a porous structure with both suitable porosity and matched mechanical properties. In this regard, a porous bioceramic composite scaffold with a strong porous substrate and a layer of bioactive coating can fulfil the requirements.

However, the realisation of such a complex and multi-functional implant requires the understanding of the structure-property relationship of the selected material system. It is essential to develop a methodology to optimise the porous structure and the mechanical strength. The effects of porosity and pore size on the mechanical properties, such as Young's modulus, compressive strength, need to be studied. If a coating is applied on the porous structures, the effect of coating on the bioactivity and mechanical strength needs to be understood.

1.2 Motivations, objectives and scopes

In the previous studies, the biomedical applications of porous ceramics were osteointegration of dental implant, fillers of osseous cavities, and implants for improved biocompatibility, long-term fixation and stress transfer for the cementless skeletal fixation by bone ingrowth. Various fabrication methods were reported to fabricate porous ceramics such as gas foaming, coral replamineform, combustible pore former, and foam relic process etc. However, limitations exist in these methods. The gas foaming is not

Chapter 1 General Introduction

controllable in pore shape and distribution. Coral replamineform is limited by the high cost of natural coral. Combustible pore former method can't obtain interconnected pore structure to suit bone ingrowth. The relic process is equipment dependent. More recently, porous ceramics are used as matrices for tissue engineering as well as scaffolds to carry cells and tissue. Thus, porous ceramics are greatly demanded. They should have interconnected macropores (bigger than 150 μm) for cell penetration, tissue ingrowth and vascularisation. Then they should provide sufficient mechanical properties for some applications involving load bearing by tailoring the pore size and the porosity of the porous structure. Therefore, it is significant to develop a new methodology to prepare the desired porous ceramics for the biomedical application.

In current study, a vacuum infiltration method for preparing porous alumina/zirconia scaffolds was developed. Compared to the other methods, the vacuum infiltration method has it advantages of low cost, easy operation, the ability to tailor the pore size and distribution and porosity of the porous structure. Secondly, the alumina/zirconia composites were used as substrate materials for porous scaffold to achieve sufficient mechanical properties. The effects of zirconia additive on the sintering, the microstructure and the mechanical properties of the alumina were studied. Finally, a porous bioceramic composite scaffold with a strong porous substrate and a layer of bioactive glass coating was developed to fulfil the demanding requirements for tissue engineering.

This project focused on the preparation and characterization of porous ceramic scaffolds with controlled porous structures, suitable mechanical properties and desirable bioactivity. The objectives and scopes of the research were:

1. To develop alumina based ceramics that would be biocompatible, mechanically strong and suitable for strong porous structures.
2. To develop a new method for the preparation of porous ceramic scaffolds. The targeted scaffolds should have controllable pore sizes, high porosities, high pore interconnectivities and suitable mechanical properties.
3. To optimize the processing parameters for porous ceramic structures and to investigate the effect of pore size and porosity on the mechanical properties of the porous ceramic structures.
4. To synthesize and characterize the sol-gel derived bioactive glasses and study the microstructural development of the bioactive glass powder compacts.
5. To modify the porous alumina based ceramics with bioactive layers of the bioactive glass so that both mechanical strength and bioactivity would be obtained for bone ingrowth and bone bonding.

1.3 Organization of the report

The report begins with the general introduction of background, objective and scope of the project, which are presented in Chapter 1. The previous studies and other background information relevant to the project are summarized in Chapter 2. The experimental procedures of the work are covered in Chapter 3, and the results are presented and discussed in Chapter 4-Chapter 7. Finally, the conclusion and the future work are presented in Chapter 8 and Chapter 9, respectively.

Chapter 2 Literature Review

2.1 Bone tissue

Since the biomaterials concerned are for bone replacement and regeneration, it is essential to have some background about the structure and the properties of bone. Lots can be learnt from the natural bone for the biomaterials design. The composition, the structure, and the mechanical properties of bones are reviewed in the following sections.

2.1.1 Composition of bones

Bone is the substantial unit of human skeletal system which functions as load bearing, protection of most vital internal organs and storage of minerals [1]. The main constituents of bone are collagen, calcium phosphate, and water [2]. The collagen, the main polymer component, is a protein abundant in the bodies of mammals. Calcium phosphate is the main ceramic component. Crystallized hydroxyapatite, $\text{Ca}_{10}(\text{HPO}_4)_6(\text{OH})_2$, is the major substance of bone mineral. Amorphous calcium phosphates, such as $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$, are also present. There are many substitutions in the molecules of calcium phosphates: K, Mg, Sr, and Na for Ca, carbonate for phosphate, and fluorine for OH [3]. Some of these substitutions are thought to play significant roles in the structure and mechanical properties of the bone mineral.

2.1.2 Structure of bones

Bone is a porous material composed of a solid matrix containing voids of varying sizes which are filled with soft tissues [1,4,5]. These soft tissues include various bone cells and their blood supply as well as bone marrow. The porosity of bone varies from 5%~95%.

According to the porosity, two kinds of bone are divided: compact bone (of low porosity) and cancellous bone (of high porosity). The major part of a long bone is shown in Figure 2-1.

The collagen fibers are arranged into lamellar sheets of 3-7 micron thick to form the bone matrix. Osteons exist only in the compact bone. These are tubular structures of 200 microns in diameter, with concentric lamellae arranged about a central Haversian canal containing a blood vessel.

Figure 2-1 Major part of a long bone [6].

2.1.3 Mechanical properties of bones

As a ceramic-organic composite, bone has a high toughness and a relatively high modulus. The high toughness is related not only to the presence of collagen, but also to the complicated fibrous microstructure. It is reported [7] that bone is a tough material at low strain rates but fractures more like a brittle material at high strain rates. Besides, the

stiffness of the bone increases with increasing mineral content. Studies [8] on the fracture surface of bone showed that its plywood structure is the main reason for the excellent toughness, as it can stop cracks from propagation.

The mechanical properties of the compact bones and the sponge bones are summerized in Table 2-1. The mechanical properties of bone depend largely on the humidity, mode and direction of applied load, and kind of bone. For the sponge bones, the mechanical properties significantly increase with increasing bone density. Moreover, the level of bone mineralization also influences the mechanical properties of bone.

Table 2-1 Mechanical properties of the compact bone and the sponge bone [2-6]

	Compact bone		Spongy bone
	Parallel to bone axis	normal to bone axis	
Compressive strength (MPa)	170-193	133	1-100
Flexural strength (MPa)	160	/	10-20
Young's modulus (GPa) (Compression)	17.0-18.9	11.5	1-2
Fracture toughness (MPa m ^{1/2})	2-12	/	/

2.2 Bone tissue engineering

The potential application of current project is bone tissue engineering, thus it is necessary to have understanding of bone tissue engineering. Here, the review of tissue engineering and bone tissue engineering is included.

Orthopedic surgeons are frequently faced with defects in bone resulting from disease or trauma [9,10]. The revolution of replacement of tissues by transplants and implants has led to a remarkable increase in the quality of life for millions of patients as show in Table 2-2.

Table 2-2 Evolution of replacement of tissue by transplants and implants [11,12]

Method	Source of grafts	Concerns
Autografting	Tissues from the patient	limited supply pains and infections in the donor site
Allografting	Tissues or organs from a donor	shortage in donor availability immune response
Xenografting	Tissue of other species (animals)	immune response and viral infections
Synthetic prosthesis	Artificial biocompatible devices	Stability and biocompatibility

In 1970s, tissue engineering has emerged as a potential alternative to the current therapies for tissue regeneration [13,14]. It focuses on the combination of biomaterials and cells to enhance the regeneration of natural tissues. Its aims are not only the restoration of structure, but function, metabolic and biochemical behaviour, and biomechanical performance [15,16]. In this approach, new tissues are generated by transplantation of cells using biomaterials or by inducing tissue to grow from the surrounding tissue into the biomaterials.

The procedure of bone tissue engineering is illuminated by Figure 2-2. Biomaterials are fabricated in the shape of three-dimentional matrices, and then they are seeded with living osteoblast and bathed with growth factors in a bioreactor to allow osteoblast to recreate their intended tissue functions. After implantation, the 3-dimentional matrix dissolves

or is encapsulated in the new bone tissue, and the newly grown bone tissue eventually blends with its surroundings.

Figure 2-2 Procedure of bone tissue engineering [15].

Recent investigations in tissue engineering are to construct vital autologous tissues *in vitro* using appropriate biomaterials to guide the tissue development [17,18]. Two elements are involved in bone tissue engineering: cells and three-dimensional (3-D) scaffolds [19].

Cells

Tissue engineering produces tissue in culture by cells seeded (grown) in various porous absorbable matrices. It is based on the fact that various cell types, such as bone cells, can proliferate and maintain their phenotype when cultured in primarily two-dimensional substrates, three-dimensional porous matrices, or gels *in vitro* [20]. The cells used in bone tissue engineering are usually fresh bone marrow cells from femora and tibiae.

Three-dimensional scaffolds

Scaffolds made of biomaterials play important roles during the process of tissue regeneration. A scaffold can structurally reinforce the defect site so as to maintain the

shape of the defect and prevent distortion of the surrounding tissue. A scaffold then serves as a barrier for the ingrowth of unwanted surrounding tissue that may impede the process of regeneration, and for migration and proliferation of cells *in vivo* or for cell seeding *in vitro* [21].

2.3 Slip casting

Slip casting is a method for powder-based shaping of advanced ceramics [22]. It is a filtration process, in which a powder suspension (or slip) – usually a water based suspension is poured into a plaster mould, which by its porosity creates capillary forces and removes liquid from the suspension (slip). When the liquid is sucked into the plaster mould, the powder particles are forced towards the mould walls and a consolidated layer is gradually built up. When a desirable layer thickness has been obtained, the casting process is stopped either by having the excess slip removed or to form a solid body. The slip casting process is schematically illustrated as Figure 2-3.

Figure 2-3 Schematics of slip casting process

The advantages of slip casting as a forming method are mainly that complex geometries can be shaped, and good material homogeneity is generally achieved. Furthermore, the mould material is cheap. The disadvantages are that a large-scale production requires

many moulds and large areas, coupled with the fact that the plaster moulds have a limited durability, as plaster of Paris erodes/corrodes in water processing. To get around these problems a method called pressure slip casting or pressure casting [23] has been developed. Instead of plaster moulds, moulds of polymeric materials are used and externally pressure is applied to drive the filtration process. As much higher pressure (<40 bar or 4.0 MPa) is applied, this gives much faster casting cycles than in slip casting where the capillary forces correspond to a pressure of 1–2 bar (0.1–0.2 MPa).

2.3.1 Theory background

Many studies [24,25] had pointed out that the rheological properties of ceramic slurries are closely related to the quality of the final product. In the slip casting process, the ceramic powder should be well dispersed in an aqueous medium [26,27]. The aqueous suspensions have to fulfill several requirements. The particles should not settle too fast under the effect of gravity, because otherwise segregation occurs and causes density inhomogeneities in the cast bodies [28]. Therefore, the size of ceramic particles used in slip casting is traditionally limited at the range of 0.1–1 μm [29]. In addition, the slurries also need to have a high solid content to achieve reasonable casting rates and reduce energy consumption in the subsequent drying stage [30,31]. The combination of a high solid loading and small particles leads to a viscosity increase because of the increased particle-particle interactions and, consequently, to difficulties in slurry handling. This tendency can be reduced with the addition of an appropriate dispersant which alters the powder surface properties so that repulsive forces become dominant and the particles can be separated in the suspension.

In an aqueous suspension, the nature of the force acting between individual particles governs the properties of the mixture.

1. Electrical double layer (EDL)

Most substance acquire a surface electrical charge when brought into contact with a polar medium (e.g. water), resulting form one or more mechanisms involving ionization, ion adsorption or ion dissolution. [32,33,34]. In aqueous solutions proton equilibria is especially important. The surface charge influences the spatial distribution of nearby ions in the surrounding solution, attracting ions of opposite charge but repelling ions of similar charge to that of the surface. This leads to the formation of the electrical double layer (EDL) which consists of the surface charge and a neutralizing excess of counter-ion and, further from the surface, co-ions distributed in a diffuse manner in the polar medium. Figure 2-4 shows the electric potential distribution in an electrical double layer (EDL) surrounding a charged particle. The EDL is of importance because the interaction between charged particles is governed by the overlap of their diffuse layers.

Figure 2-4 Electrical double layer surrounding a charged particle.

2. DLVO theory

Deryagin, Landau, Vrij and Overbeek (DLVO) quantitatively takes account of the interaction of double electric layers (DEL) and the electrostatic repulsion between particles to analyze the repulsion forces and the attraction depending on the distance

between particles. DLVO theory was developed to study the stability of colloid system [33,34].

In DLVO theory, the energy of interaction between two neighboring particles with overlapping double layers (as shown in Figure 2-5) is predicted.

Figure 2-5 Model of the energy interaction between two neighbouring particles with overlapping double layers.

The repulsive energy (V_R) is given by

$$V_R = 2\pi\epsilon\zeta^2 a \exp(-\kappa h) \quad (2-1)$$

where a is the radius of particles, ϵ is the dielectric constant of the medium, ζ is the zeta potential (the electrical potential of particle between the stern plane and the particle surface), κ is the reciprocal of the thickness of the double electrical layer and h is the distance between the surface of particles. The repulsive force gives the positive effect on the dispersing of colloid system.

Between two adjacent particles, the Van Der Waals attraction force tends to encourage spontaneous aggregation when the distance of separation between particles became very small. The attraction force of dispersion attraction between particles is described as:

$$V_A = -\frac{A_{12}a}{12h} \quad (2-2)$$

where A_{12} is the appropriate Hamaker constant for the system of two particles separated by a second liquid medium, h is the distance between the surface of particles.

Therefore, the net energy of interaction (V_T) is presented by adding together the repulsive and attractive force approximated by equation 2-1 and equation 2-2.

$$V_T = V_A + V_R \quad (2-3)$$

DLVO theory gives the basis of colloid stability for simple aqueous dispersions. The net energy of interaction between particles predicts the aggregation at very close distance of separation (in a deep energy well known as the primary minimum) and the possibility of weak or reversible aggregation in a secondary minimum.

2.3.2 Stabilisation mechanisms of dispersant in ceramic slurries

In practice, fine ceramic particles tend to aggregate in the aqueous medium. Some polymers are usually used as dispersants to stabilize the ceramics slurries [35]. Studies have proved that the addition of a dispersant can dramatically reduce the viscosity of slurries even with very high solid contents. These dispersants usually consist of a hydrocarbon chain and a polar ionic part, such as COO^- and function via an electrostatic repulsion mechanism and steric hindrance mechanism. The mechanisms are necessary to be discussed.

1. Electrostatic repulsion mechanism

Many studies showed that ceramic powders could be dispersed by dispersants through an electrostatic stabilization mechanism. As the DLVO theory states, a stable suspension can be obtained when there is a sufficient high surface charge density to generate a strongly repulsive force among particles. It is well known that an oxide powder dispersed in water can adsorb water molecules and form a hydration layer. The hydration layer will become charged as shown in Equations 4-1 and 4-2, where Me is a metal ion [36]:

Acidic condition

Basic condition

Therefore, the surface charge of the ceramic powder was affected by the H^+ and OH^- ions adsorbed on the particle surface. The MeO^- charge contributed to the dispersion of the slurries [37].

P. C. Hider, et al. [38] showed the adsorption process of ammonium polymethacrylate on the alumina surface and consequently the powder was negatively charged. When dissolved in water, the negatively charged carboxyl groups were obtained through hydration dissociation, as shown in the following equation 2-6:

The negatively charged carboxyl group dissociated from ammonium polymethacrylate was adsorbed on the alumina surface. Both MeO^- and RCOO^- on the particle surface generated a repulsive force which overcame the Van Der Waals attraction.

2. Steric hindrance mechanism

The steric interaction arises if adsorbed molecules (e.g. polymers) are present on the surface of particles. In this case, the particles host a significant coverage of a polymer, segments of the polymer molecule may protrude into solution; thus as particles approach one another the hydrocarbon chain may overlap. The hydrocarbon chains are often hydrated so any overlap would cause dehydration and an increase in free energy, which is thermodynamically unfavorable and therefore tends to stabilize the suspension.

2.4 Bioceramics

Compared with metal or polymer materials, ceramic materials are featured with superior mechanical properties (e.g. hardness, compressive resistance, and wear resistance) and chemical properties. Dozens of various ceramic compositions have been tested for biocompatibility and have been found suitable for use as materials of constructions for surgical implants. These ceramics are called bioceramics. In the following section, bioceramics will be reviewed.

According to the tissue response manners and the attachment types [39], ceramic materials for musculoskeletal prostheses are generally divided into three types: (1) bioinert ceramics, such as alumina or zirconia, that are stable in the body and can develop a non-adherent fibrous capsule at the tissue-implant interface. (2) bioactive ceramics, such as hydroxyapatite (HA) and bioactive glasses. These ceramics can form an interfacial bond with surrounding tissue. And (3) bioresorbable ceramics, including tricalcium phosphate (TCP) and bone cement. They can dissolve in the biological environment and finally are replaced by the surrounding tissues.

2.4.1 Alumina

High-density, high-purity ($>99.5\%$) α - Al_2O_3 has been widely used in load-bearing hip prostheses and dental implants. That is due to its combination of excellent corrosion resistance, biocompatibility, high wear resistance and strength [40,41]. Most Al_2O_3 devices in clinical application are very fine-grain polycrystalline α - Al_2O_3 produced by pressing and sintering at temperatures of about 1600°C . In order to aid sintering and limit grain growth, a very small amount of magnesia ($<0.5\text{ wt}\%$) can be added [42].

Alumina is a typical bio-inert material. It undergoes little or no chemical change during a long-term exposure to the physiological environment and develops a non-adherent fibrous capsule at the tissue implant interface. The non-direct attachment of alumina implant to the surrounding tissue is not mechanically strong, so that loosening leading to clinical failure occurs easily. Therefore, alumina implants are usually implanted with a very tight mechanical fit and loaded primarily in compression.

The strength, fatigue resistance and fatigue toughness of polycrystalline α - Al_2O_3 greatly depend on its grain size and purity. Studies [43] revealed that alumina with an average grain size of $<4\text{ }\mu\text{m}$ and $>99.7\%$ purity exhibits good flexural strength and excellent compressive strength. The specific physical and mechanical properties of alumina as compared to those of zirconia are shown in Table 2-3.

Because the Young's modulus of alumina (400 GPa) is much higher than that of human bone (17.0-18.9 GPa for compact bones and 1-2 GPa for porous bones), stress shielding may occur after implanting of alumina devices [44]. The modulus mismatch between an implant material and the host tissue will prevent the bone from being loaded properly, and cause bones to resorb at the implant-bone interface, which leads to implant instability and

eventual failure. Therefore, methods for reducing the Young's modulus of alumina should also be studied, such as the methods of surface coatings and porous materials.

Table 2-3 Physical and mechanical properties of alumina and zirconia (at 25 °C) [41, 43,45]

Properties	Alumina	TZP	Mg-PSZ
Crystallography	Hexagonal	Tetragonal	Tetragonal and cubic
a-axis (nm)	0.476	0.364	/
c-axis (nm)	1.30	0.527	/
Melting point (°C)	2040	2680	/
Density (kg/m ³) x10 ³	3.98	6.08	5.72
Vickers hardness (HV)	2400	1200	1120
Thermal coefficient of expansion (K ⁻¹)	6.6 x10 ⁻⁶	11 x10 ⁻⁶	/
Compressive strength (MPa)	4250	2000	1850
Young's modulus (GPa) (compression test)	400	150	208
Fracture toughness (MPa m ^{1/2}) (three point bending)	4-6	6-15	8

2.4.2 Zirconia

Zirconia is another exceptionally inert bioceramic [46]. Zirconia ceramics have advantages over alumina ceramics for higher fracture toughness and higher flexural strength and lower Young's modulus. Zirconia ceramics suggested for surgical implants fall into two basic types: Tetragonal zirconia stabilized with yttria (TZP) [47] and

partially stabilized zirconia (PSZ) [48]. Properties of zirconia are compared with alumina in previous section (Table 2-3).

Stabilization of zirconia phases

Zirconia ceramics can exhibit three well-defined polymorphs, namely, monoclinic (M), tetragonal (T) and cubic (C) phase as shown in Table 2-4 [49,50]. Pure zirconia is monoclinic at room temperature. The phase changes with the temperature: M→T at 1170°C and T→C at 2370 °C. On cooling, T→M phase transformation takes place with a volume expansion of approximately 3-4 %. Stresses generated by the expansion originate cracks in pure zirconia ceramics. Addition of various metal oxides (CaO, MgO, CeO₂ and Y₂O₃) can remove the disruptive transformation by partially or fully stabilizing the cubic phase or the tetragonal phase at low temperature.

Table 2-4 Outline of the salient properties of zirconia

Phase	Transformation temperature (°C)	Unit cell constants (nm)	Space group	Density (kg/m ³)
Monoclinic	1170	a = 0.5156 b = 0.5191 c = 0.5304 β = 9.890	P2 ₁ /c	5560
Tetragonal	2370	a = b = 0.5094 c = 0.5177	P4 ₂ /nmc	6100
Cubic	/	a = b = c = 0.5124	Fm3m	6090

For instance, Y₂O₃ is the most widely used additive. The phase diagram of the Y₂O₃-ZrO₂ system is shown in Figure 2-6. Tetragonal zirconia polycrystalline (PZT) materials, containing approximately 2-3 mol% Y₂O₃, are completely constituted by tetragonal grains with size of the order of hundreds of nanometers. Partially stabilized zirconia (PSZ) materials have microstructures at room temperature generally consists of cubic zirconia as

the major phase, with monoclinic and tetragonal zirconia precipitates as the minor phase. The mechanical strength of PSZ was improved by a homogeneous and fine distribution of the monoclinic phase within the cubic matrix [51].

Figure 2-6 $\text{Y}_2\text{O}_3\text{-ZrO}_2$ phase diagram (m_{ss} : monoclinic phase; t_{ss} : tetragonal phase; C_{ss} : cubic phase) [52].

Transformation toughening

Report [53] showed that the T-M phase transformation could improve their mechanical strength and toughness of zirconia ceramics. They observed that tetragonal metastable precipitates finely dispersed within the cubic matrix were able to be transformed into the monoclinic phase when the constraint exerted on them by the matrix was relieved, i.e. by a crack advancing in the material. In that case, the stress field associated with expansion

due to the phase transformation acts in opposition to the stress field that promotes the propagation of the crack. An enhancement in toughness is obtained, because the energy associated with crack propagation is dissipated both in the T-M transformation and in overcoming the compression stresses due to the volume expansion. A schematic representation of this phenomenon is given in Figure 2-7.

Figure 2-7 Representation of stress-induced T-M transformation toughening process [54].

Mechanical properties of the TZP

TZP ceramics are the materials selected by almost all the manufactures that are introducing zirconia ball beads into the market. As shown in Table 2-3, TZP has higher mechanical strength and fracture toughness than those of alumina, while its Young's modulus and hardness are lower.

2.4.3 Alumina and zirconia composites

In the past twenty years, ceramic composites have been widely studied and developed. The mechanical properties and biological properties of the ceramic composites can be

tailored. Alumina/zirconia composites are typical bioinert materials. Literatures about the alumina zirconia composites are reviewed.

In general, alumina zirconia composites can only be densified above 1550 °C by solid-state sintering [55]. It is reported [56] that for ZrO₂ doped sapphire single crystals from 1200 °C to 1600 °C, a zirconia solubility in alumina was detected as 0.004 - 0.027 wt% while the alumina solubility in zirconia for Al₂O₃ doped yttria-stabilized zirconia (YSZ) single crystal. The higher sintering temperature of the alumina/zirconia composites relative to their constituents is because the densification is significantly retarded by the presence of ZrO₂ inclusions [57,58].

Many reports have shown that alumina/zirconia composites exhibit higher performance than single-phase alumina or TZP ceramics [59,60]. It was reported [61] that the addition of zirconia particles effectively hindered the alumina matrix grain growth corresponds to the mechanism of controlling the matrix coarsening rate by grain boundary pinning due to second phase particle. The main toughening and strengthening mechanisms are zirconia phase transformation and microcracking [55]. Zirconia toughened alumina composite consist of an alumina matrix in which there are embedded zirconia particles, either unstablized or stabilized. Under stress, tetragonal zirconia undergoes into the more stable monoclinic phase. This phase transformation is accompanied by a volume increase (about 4 %) that induces compressive stresses around a propagating crack and develops the toughening effect [62]. Many researchers have studied the mechanical properties of zirconia toughened alumina ceramics. Casellas *et al.* [61] reported the addition of ZrO₂ to an alumina matrix resulted in a hardness decrease and a fracture toughness increase, and fracture toughness increases with ZrO₂ particle coarsening. Kaya *et al.* [63] developed high strength and toughness zirconia toughened alumina with a helical spring shape from

a sol-gel derived paste. Huang *et al.* [55] studied the influence of zirconia content and sintering temperature on the microstructure and the mechanical properties of zirconia toughened alumina.

A common approach for estimating the materials properties of composite is to apply a rule of mixtures. Some relationships can be used to approximate thermal or mechanical properties of a composite material in terms of the individual properties and relative amount of the constituents. The classical linear rule of mixtures (Voight estimate) [64] for two constituent materials is:

$$P = V_{\alpha}P_{\alpha} + V_{\beta}P_{\beta} \quad (2-7)$$

Where P is a typical property, V the volume fraction and the subscripts α and β used to distinguish the two constituents.

The rule of mixtures was applied to the alumina/zirconia composites. Lange [65] reported that both Young's modulus and hardness of ZTA composites containing particles of zirconia stabilized with 2 mol% Y_2O_3 obeyed a linear rule of mixtures. Thus, in present work, the related properties of the alumina/zirconia composite, such as relative density, Young's modulus were calculated using the linear rule of mixtures on the basis of the intrinsic properties of the two constituents.

2.4.4 Bioactive glasses and glass-ceramics

Certain compositions of glasses and glass-ceramics have been shown to bond to bone [66]. They exhibited rapid rate of surface reaction after implanted, which leads to fast tissue bonding [67]. Earlier studies showed that bioactive glasses such as 45S5 bioglass® and

glass-ceramics attached to bone by a chemical bond, a dense layer of nanometer-scale hydroxy-carbonate apatite (HCA) crystal layer. This layer was formed through a process consisting of forming a soluble silica-rich gel and mineralizing [68]. Some clinically used glasses and glass ceramics are listed in Table 2-5.

Table 2-5 Composition and mechanical properties of bioglasses and glass ceramics used clinically [69]

Property	Bioglass 45S5	S45PZ	Glass-ceramic Ceravital	Glass-ceramic Cerabone A/W	Glass-ceramic Imaplant L1	Glass-ceramic Bioverit	Sintered hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (~99.2%)	Sintered β - $3\text{CaO}\cdot\text{P}_2\text{O}_5$ (~99.7%)
Composition (wt%)								
Na ₂ O	24.5	24	5–10	0	4.6	3–8		
K ₂ O	0		0.5–3.0	0	0.2	3–8		
MgO	0		2.5–5.0	4.6	2.8	2–21		
CaO	24.5	22	30–35	44.7	31.9	10–34		
Al ₂ O ₃	0		0	0	0	8–15		
SiO ₂	45.0	45	40–50	34.0	44.3	19–54		
P ₂ O ₅	6.0	7	10–50	16.2	11.2	2–10		
CaF ₂	0			0.5	5.0	3–23		
B ₂ O ₃	0	2						
Phase [†]	Glass	Glass	Apatite Glass	Apatite β -Wollastonite Glass	Apatite β -Wollastonite Glass	Apatite Phlogopite Glass	Apatite	Whitlockite
Density (g/cm ³)	2.6572			3.07		2.8	3.16	3.07
Vickers hardness (HV)	458 ± 9.4			680		500	600	
Compressive strength (MPa)			500	1080		500	500–1000	460–687
Bending strength (MPa)	42 [‡]			215	160	100–160	115–200	140–154
Young's modulus (GPa)	35		100–150	218		70–88	80–110	33–90
Fracture toughness, K_{IC} (MPa·m ^{1/2})				2.0	2.5	0.5–1.0	1.0	
Slow crack growth, n (unitless)				33			12–27	

[†]Reference 15. [‡]Apatite is $\text{Ca}_{10}(\text{PO}_4)_6(\text{O,F})$, β -wollastonite is $\text{CaO}\cdot\text{SiO}_2$, phlogopite is $(\text{Na,K})\text{Mg}_3(\text{AlSiO}_{10})\text{F}_2$, and whitlockite is β - $3\text{CaO}\cdot\text{P}_2\text{O}_5$. [§]Tensile.

According to the composition, the reported bioactive glasses and glass-ceramics could be divided to three types: (I) silicon-phosphate glasses (SiO_2 - P_2O_5 - CaO (MgO , Na_2O , F , K_2O) base system) [70,71], (II) silicate glasses (SiO_2 - MgO (Na_2O , K_2O , F) base system) [72] and (III) phosphate glasses (P_2O_5 - CaO (Na_2O , MgO , K_2O) base system) [73,74]. Glass-ceramics were derived from the different base glasses. The compositions and phases of three types of glasses and glass-ceramics were summarized in Table 2-6. Mechanical properties reported by Hench [39] are listed in Table 2-7. It shows that the mechanical properties of type I and type II are higher than those of type III. Moreover, implants made of type I and type III showed good bioactive behaviour [75], while type II is a biocompatible glass ceramic with lower bioactivity. In the case of bone tissue

Chapter 2 Literature Review

engineering, both the mechanical and the biological properties are demanded. Thus, silicon phosphate glasses and glass-ceramics are chosen as the studied materials in this project.

Table 2-6 Three types of bioactive glasses and their glass-ceramics

Base glasses	Composition	Phases in glass-ceramics
silicon-phosphate glasses (Type I)	$\text{SiO}_2\text{-P}_2\text{O}_5\text{-CaO}$ (MgO, Na_2O , F, K_2O)	Mica-apatite phase and three glassy phases
silicate glasses (Type II)	$\text{SiO}_2\text{-MgO}$ (Na_2O , K_2O , F)	Mica-apatite phase (main crystal), secondary crystal and two glassy phases
phosphate glasses (Type III)	$\text{P}_2\text{O}_5\text{-CaO}$ (Na_2O , MgO, K_2O)	Apatite and other phosphate crystals and no phase separation in the base glass

Table 2-7 Mechanical properties of three types glass-ceramics [39]

	silicon-phosphate glasses	silicate glasses	phosphate glasses
Thermal expansion coefficient (20-400 °C) (K^{-1})	$8\text{-}12 \times 10^{-6}$	$7.5\text{-}12 \times 10^{-6}$	$14\text{-}18 \times 10^{-6}$
Bending strength (MPa)	140-180	90-140	60-90
Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$)	1.2-2.1	1.2-1.8	0.6
Young's modulus (GPa)	70-88	70	45
Compressive strength (MPa)	500	450	/
Vickers hardness, HV	5000	Up to 8000	/

Bioactive glasses have low mechanical strength and fracture toughness due to an amorphous three-dimensional glass network. Therefore, bioactive glasses usually function as a coating material [76,77]. Glass-ceramics [48,78,79] is the half crystallized bioglass materials have been used as implants and the correction of dental defects and the replacement of subperiosteal teeth.

Hench [40] has worked out the reactions involved in the bioglasses under conditions either in vivo or in vitro.

- Stage 1. Rapid exchange of cation such as Na^+ or Ca^{2+} with H_3O^+ from the solution.
- Stage 2. Loss of soluble silica in the form of $\text{Si}(\text{OH})_4$ to the solution as a result of the breakage of Si-O-Si bonds and formation of Si-OH at the glass-solution interface
- Stage 3. Condensation and repolymerization of a porous SiO_2 rich-layer on the surface depleted in alkali and alkaline earth cations.
- Stage 4. Migration of Ca^{2+} and PO_4^{3-} to the surface through the SiO_2 -rich layer, forming a $\text{CaO-P}_2\text{O}_5$ -rich film on the top of SiO_2 -rich layer, followed by growth of the amorphous calcium phosphate (CaP) by incorporation of soluble calcium and phosphates from solution.
- Stage 5. Crystallization of the amorphous CaP to form a hydroxycarbonate apatite (HCA).

The mechanism of apatite formation is interpreted as follows: the calcium ion dissolves from the surface of the glasses and increase the ion activity product of the apatite in the surrounding fluid, whereas the disrupted silica network on the surface forms into a sediment of hydrated silica, which provides favorable sites for apatite nucleation. The apatite nuclei then grow spontaneously consuming calcium and phosphate ions from the surrounding fluid.

2.4.5 Hydroxyapatite

Hydroxyapatite is a compound with a definite composition, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and in a hexagonal structure [80]. It is the inorganic mineral phase of natural vertebrate hard tissue (60-70 % in bone and 98 % in dental enamel). Due to its similar mineral phase of bone and teeth, synthetic hydroxyapatite is accepted as a potential biomaterial for use in orthopedics, bone grafts and dentistry. It can be rapidly integrated into the human body, and finally form chemical bonds with bone. Studies [81] have found that some carbonate apatite crystals are formed on the surface of HA after implantation through epitaxial growth. The formation of these microcrystals is believed to be a dissolution-precipitation process.

Dense HA is stiffer and stronger than bone, as the Young’s modulus, compressive strength, and flexure strength of dense HA are greater than those of human bone, dentin and enamel [2]. Mechanical properties of dense HA are tabulated in Table 2-8. The scatter of data is caused by statistical nature of strength distribution, influence of remaining microporosity, grain size, impurities etc.

Table 2-8 Mechanical properties of dense HA [82]

Properties	
Bending strength (MPa)	38-250
Compressive strength (MPa)	120-900
Tensile strength (MPa)	38-300
Young’s modulus (GPa)	35-120
Slow crack growth coefficient	26-80
Fracture toughness ($\text{MPa m}^{1/2}$)	0.77-1.77 [83]

In practice, the mechanical properties of HA are poor, because they are greatly influenced by the properties of apatite powder and sintering conditions. The mechanical properties

decrease with increasing porosity. Therefore, hydroxyapatite is seldom used in a bulk form for load bearing applications such as orthopaedics. Coatings of hydroxyapatite are potential as the biocompatibility and the bone bonding property of the coatings can be utilized and the mechanical properties of substrates such as Al_2O_3 and some biocompatible alloys can be combined. While the matrix materials have the required mechanical properties, they benefit from the hydroxyapatite coatings, which provide an surface for bone to bond to, anchoring the implant and transferring load to the skeleton [84].

2.4.6 Biodegradable ceramics

Biodegradable ceramics are the ones which resolve in biological environment. Calcium phosphates are important biodegradable ceramics. Listed in Table 2-9 are some biodegradable calcium compounds.

Table 2-9 Some calcium phosphate compounds [85]

Chemical name	Abbr.	Chemical formula	Phase	Ca/P
Amorphous calcium phosphate	ACP	/	/	/
Dicalcium phosphate	DCP	CaHPO_4	Monetite	1.00
α -tricalcium phosphate	α -TCP	$\text{Ca}_3(\text{PO}_4)_2$	/	1.50
β -tricalcium phosphate	β -TCP	$\text{Ca}_3(\text{PO}_4)_2$	Whitlockite	1.50
Pentacalcium hydroxyapatite	HA	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	Hydroxyapatite	1.67
Tetracalcium phosphate monoxide	TTCP	$\text{Ca}_4\text{O}(\text{PO}_4)_2$	hilgenstockite	2.00

Tricalcium phosphate (TCP) has a nominal composition of $\text{Ca}_3(\text{PO}_4)_2$. TCP is found in two different phases, i.e. α -TCP and the more stable β -TCP. One advantageous

characteristic of TCP is its high biodegradation rate in vivo. Some studies have observed the different degrees of in vitro dissolution behavior of calcium phosphate ceramics, and found that the dissolution rate increases in the order of TTCP > α -TCP > β -TCP > HA > FA (fluorine substituted apatite) [40]. Table 2-10 compares the solubility of several calcium phosphate coating in various buffers. The mechanism of biodegradation seems in three aspects:

- 1) Physicologic dissolution [86]: when placed in an acidic environment, TCP dissolves *in situ*. This may be influenced by the environmental pH value and the crystalline structure.
- 2) Physical disintegration [17]: solution tends to attack poorly developed grain boundaries, which greatly increases the dissolution rate. When materials are in porous configuration, the rate of dissolution increases as the materials contain a larger amount of exposed surface area.
- 3) Biological factors [87]: after implantation, osteoclast cells attached to the surface of TCP, and cellular breakdown by macrophages will cause materials to dissolve.

TCP appears to be the most suitable bioceramics for bone tissue regeneration due to its biodegradation, which permits tissue infiltration and replacement. As the material dissolves, new bone fills the volume once occupied by the TCP implant. However, a disadvantage of TCP is the serious strength reduction that occurs during the dissolving process. Moreover, attention should be paid to the dissolution rate to match bone growth rate.

Table 2-10 solubility of different calcium phosphate coatings in Citrate buffer and Gomori's buffer [39]

	Citrate		Gomori's	
	Ca ⁺	P ⁻	Ca ⁺	P ⁻
FA45	325	150	150	56
HA45	400	184	330	127
TCP	400	118	450	75
TTCP	500	152	800	275

FA45 and HA45 are fluorapatite and hydroxyapatite with powder particle distribution of 1-45 μm , respectively

2.4.7 Current ceramic implant

Up to now, numerous studies have been conducted in the area of bone tissue engineering. A variety of ceramic materials have been used [88,89] and the scaffolds have been designed into different porous structures. They serve functions in bone defect repair, spinal fusion, total hip replacement, dental surgery and some load-bearing applications.

The applications of porous alumina implants include knee prostheses, alveolar ridge (jaw bone) and maxillo-facial reconstruction, ossicular middle ear bone substitutes [90,91], pot-type dental implants [92,93]. Hydroxyapatite and bioactive glass have superior bioactivity, but low mechanical properties. They are usually used as the coating materials on the porous alumina or porous metal implants [94]. Porous calcium phosphate implants have been extensively used as hard tissue repair and replacement due to their excellent biocompatibility, ability of bonding with bone directly, and bioresorption in vivo [95].

Although there is growing excitement in the field of bone tissue engineering, it is still in its infancy. It is difficult to synthesize fully bioresorbable implants, and new processing techniques are required to provide reproducible patterns of 3-D architectures at the

micrometer and possibly the nanometer scale. Furthermore, an understanding of the parameters that control the cell-material interactions is needed to provide optimal conditions for the attachment, growth, differentiation, and 3-D organization of individual cells into viable tissues.

2.5 Porous bioceramics

Bioceramics are fabricated into three-dimensional structures in the applications of bone tissue engineering, such as osteointegration of dental [96], fillers of osseous cavities, skeletal fixation by bone ingrowth [97]. Porous structures provide the necessary support for cells to proliferate and maintain their differentiation. The interconnected pores permit tissue in-growth and thus anchor the scaffold to the surrounding bone, preventing loosening of the implant. The porosity also allows the formation of vascular canals that can ensure the blood and nutrition supply for the bone. It has been shown that the pore sizes should be at least 150 μm for the health of ingrown bone. Moreover, most ceramics exhibit much higher strengths and moduli than human bone. To avoid the risk of stress shielding, the bioceramic implants are shaped into porous ones to match the mechanical of host bone tissue. The structural and mechanical properties and the preparation of porous ceramics are reviewed in the following section.

2.5.1 Structural properties of porous ceramics

A porous ceramic is illustrated in Figure 2-8. Porous ceramics are the integration of pores and ceramic struts (solid parts among pores)

Figure 2-8 Sketch of a porous ceramic [98].

The important parameters of porous ceramics are porosity (P), density (ρ), pore size (mean, hydraulic radius/diameter, pore size distribution), pore connectivity, pore shape, pore surface roughness, and others [99,100]. Porosity and density describe the fractions of pore volume and solid volume in a porous structure. The definitions of various porosities are listed in Table 2-11. They are usually obtained by density-based measurement [101,102]. Reports showed that porosities greatly influence the mechanical properties of porous ceramics [75,103,104]. A typical porosity-strength curve is shown in Figure 2-9. Pore size, pore size distribution and pore shape are important for tissue ingrowth. According to pore size, pores are divided as micropores ($< 10 \mu\text{m}$) and macropores ($> 50 \mu\text{m}$). Tissue can only grow into the macropores with pore size $> 150 \mu\text{m}$. Pores in porous ceramics can be isolated pores (closed pores) or connected pores (open pores). Pore connectivity is a feature of a pore network. It can be described by the fraction of open porosity in the total porosity.

Table 2-11 Definitions of important parameters in porous materials

Parameters	definition
Total porosity	Total pore volume/bulk volume
Open porosity	Open pore volume/ total pore volume
Closed porosity	Closed pore volume/ total pore volume
Pore interconnectivity	Open pore volume/ total porosity

Figure 2-9 Effect of porosity on compression strength of porous alumina ceramics [105,106].

2.5.2 Mechanical properties of porous ceramics

The basic mechanical properties of porous ceramics include Young’s modulus, hardness, strength and fracture toughness. The importance of mechanical properties of porous ceramics lies in the fact that bone and teeth to be replaced by the porous structures have a certain level of mechanical properties. It is a practical issue to achieve optimal balance between the porosity and the mechanical properties. Therefore, it is critical to understand

mechanisms of failure of these materials and the relationships between the properties and the porous parameters.

Various methods have been used to characterize various porous ceramics mechanically. Strengths (compressive, tensile and bending), Vicker’s hardness, Young’s modulus, Fracture toughness et al. were characterized in most studies. The mechanical properties and their characterization methods are summarized in Table 2-12.

Table 2-12 Important mechanical properties of porous ceramics and their characterization methods

Mechanical properties	Characterization methods
Compressive/tensile strength	Compression/tension test [102]
Bending strength	Three/four point bending (notched /unnotched) [103]
Vicker’s hardness	Vicker’s hardness test [100]
Young’s modulus	Compression/tensile test [102] Ultrasonic test [104]
Fracture toughness	Three/four point bending (notched /unnotched) [103] Vicker’s hardness test [100]

The mechanical properties of porous ceramics are dependent on the porous structural parameters, such as porosity, pore size, pore shape, etc. Some researchers have been devoted to setting up theoretical models to explain the relationships between the above two. Rice [107] developed a physical property-porosity model based on minimum solid areas (MSA). The MSA concept is illustrated in Figure 2-10. For a homogenous solid (a) the minimum and average solid cross section are the same. However it is clear that stress transmission in (b) must be dominated by minimum solid area (MSA) normal to the direction of the stress.

Figure 2-10 Schematic of the minimum solid area (MSA) mode concept (cross-hatched area = solid): (a) homogenous solid. (b) porous structure.

A Gibson-Ashby model [108,109] has been developed to predict the micro-properties from the viewpoint of micromechanics. A general open cell is idealized into an idealized unit cell as shown in Figure 2-11. In this model, it is considered that the deformation mechanism at the micro-level is generally bending of cell walls. On the scale of the dimension of the cells, a crack in the foam extends in a discrete way. Each time the row of cell walls along the crack front fractures, the crack advances by one cell width. The strength-porosity relationships reported by researches are shown in Table 2-13.

Figure 2-11 Schematic of the unit cell (a) and its deformation mechanism (b) [108].

Table 2-13 Strength-porosity equations for porous ceramics [110,111]

Author	Equations
Wang	$\sigma = \sigma_0 \exp(-b_1P - b_2P^2)$
Hasselman	$\sigma = \sigma_0 (1-P)(1+bP)$
Lam et al.	$\sigma = \sigma_0 (1-P/P_g)$
Rich [107]	$\sigma = \sigma_0 \exp(-bP)$
Gibson-Ashby [108,109]	$\sigma = \sigma_0 (1-bP)^{3/2}$

σ and P are strengths and porosity of porous ceramics, respectively. The subscripts 0 and g indicate the property of material without pore and green body, respectively. The value of b and b_1 are determined by fitting to the experimental results.

2.5.3 Fabrication of porous bioceramics

Gas foaming method

Gas bubbles can generate porosity in ceramic bodies. Some chemicals releasing gas during heating can be introduced to produce porous materials, for examples, CaCO_3 , NH_4NO_3 , $(\text{NH}_4)_2\text{CO}_3$, and H_2O_2 [112,113]. The chemicals are normally mixed with ceramic powders in a solid or solution form. Then, the samples are put in an oven to decompose the chemicals, releasing one or more gaseous components. As a result, a porous structure is obtained. However, porous ceramics made by this method have intrinsic shortcomings; it produces only “laminar porosity” and the obtained porosity is distributed randomly, i.e. not under control.

Coral replamineform method

In 1974, Roy and Linnehan [114] first used a hydrothermal method to form hydroxyapatite directly from corals. In 1996, M. Sivakumar *et al.* [115] developed the hydrothermal process to derive hydroxyapatite from Indian corals. The resulting HA was in the form of powder. In this method, porous HA was fabricated ceramics by duplicating

the macroporous microstructure of nature ocean coral. A remarkable similarity was noticed between the porous structures of certain coral species and those of human bones as shown in Figure 2-12. Although porous ceramics from this process have a high porosity and excellent macroporous structure, they are difficult to get widely clinical applications, because they are an expensive and more importantly, have insufficient mechanical strength for tissue engineering applications.

Figure 2-12 Comparison of porous structures between human bone (left) and coral-derived Hydroxyapatite (right).

Combustible pore former method

D. M. Liu [116,117] reported a method using polyvinyl butyral (PVB) particles as a pore former to prepare HA ceramics with controlled-porosity through both a solid process and a liquid process. In the solid method, PVB powders of certain particle sizes were homogeneously mixed with HA granules. The mixed powders were uniaxially die-pressed into compacts, followed by slowly heating to 500 °C to burn off the PVB particles and other organic binders. After densification sintering at 1200 °C, porous HA ceramics were produced with pores formerly occupied by PVB, as shown in Figure 2-13 [116].

Figure 2-13 Fractured surface of the porous HA sintered at 1200 °C for 30 h.

It turned out that the porosity of the HA ceramics could be easily controlled by the volume percentage and the particle size of PVB. Moreover, processing parameters such as die-pressing pressure and sintering temperature influenced the porous structure. One disadvantage of this method is that it can't obtain interconnected pore structure to suit bone ingrowth.

Beside PVA, some other organic materials such as polystyrene also can be used as the pore former. Figure 2-14 shows the segment of polystyrene. Expanded polystyrene (EPS) is one of important polystyrene products [118,119]. EPS is usually white and made of expanded polystyrene beads as shown in Figure 2-15. Properties of polystyrene and EPS are listed in Table 2-14.

Figure 2-14 Segment of polystyrene

Figure 2-15 Traded EPS beads [120]

Table 2-14 Properties of polystyrene and EPS [118,119,121,122]

	Polystyrene	EPS
Density (kg/m ³)	1050	25-200
Thermal conductivity (W/(m·K))	0.08	/
Young's modulus (MPa)	3000-3600	/
Tensile strength (MPa)	46-60	/
Elongation at break	3-4%	/
Melting point (°C)	240	240
Liner expansion coefficient (K ⁻¹)	80 x 10 ⁻⁶ -150 x 10 ⁻⁶	50-71 x 10 ⁻⁶

Foam relic process

Recently, a relic process for manufacturing porous scaffolds has been reported. In this technique, a foam or sponge is needed to serve as a pore template. The porous template is soaked in a slurry or sol. After full impregnation, the template is dried to remove the solvent, calcined to burn off the organic template and finally sintered to obtain a porous product. The resulting body will have an architecture that is analogous to that of the original template.

As the organic template is an important element in the relic process, a number of studies have been devoted to searching optimal templates, both natural [114,123] and synthesized [124, 125]. Recently, stereolithography (SL) technique has been introduced to manufacture porous templates. SL is a technique capable of taking the 3-D computer-scanning image or the computer design of an object and constructing a 3-D representation of the object from epoxy resin. It has versatility in making complicated-geometry objects, which is especially suitable for surgery [126]. One of the designed templates and its negative image are shown in Figure 2-16. The morphology of the obtained HA ceramic is shown in Figure 2-17.

Figure 2-16 3-D computer-designed epoxy molds (left: desired porous structure; right: negative image of design) [126].

Figure 2-17 Morphology of sintered HA implant from 3-D epoxy mold [126].

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Great advantages have been shown in this method. The method leads to a ceramic body having defined and controllable pore or channel size, pore or channel geometry, pore or channel interconnectivity, net shape architecture. However, further studies are still needed to get an optimal porous structure with proper structural and mechanical properties.

According the above review on the fabrication method of porous ceramics, it can be seen that these methods have their own limitations. The gas foaming is not controllable in pore shape and distribution. Coral replamineform is limited by the high cost of natural coral. Combustible pore former method can't obtain interconnected pore structure to suit bone ingrowth. The relic process is equipment dependent. Compared with the above method, the vacuum infiltration method is superior. The cost of this method is low due to the cheap EPS beads and no special equipment required. The pore size and porosity of the porous bodies can be tailored by choosing EPS beads with varied size and adjusting the packing condition of EPS beads template.

2.6 Bioactive coating on porous scaffolds

Ceramics such as alumina and zirconia and metallic biomaterials, such as titanium and its alloy, have been widely used in load bearing bone replacement due to their superior strength, stability and resistance to corrosion in physiological environment. However, they are all bioinert materials, leading to the formation of a non-adherent fibrous layer between the implants and the surrounding host tissue. Such implants tend to loosen, leading to clinical failures. To create a direct contact of the implant with the surrounding host tissue, surface modification is used to induce bioactivity to the implant, and promote rapid bone development between the implant and the host tissue. The most popular coating materials for the surface modification are HA and bioactive glasses.

2.6.1 Bioactive glass and glass-ceramic coatings

Bioactive glasses and glass-ceramics are excellent coating materials because of their controlled surface reactivity and good bone bonding ability [40]. They are able to strongly bond to the surrounding tissues by developing a chemical bonding. *In vitro* tests performed by P. Torricelli et al. [127] showed that bioactive glass (RKKP) coated Al_2O_3 and ZrO_2 elicited a significant increase in osteoblast proliferation. *In vivo* tests of a bioactive glass coated zirconia was carried out by V. Stanie et al. [128]. The implant showed very good contact at the material-bone interface after 30 days of implantation. The bone surrounding the implant showed regular trabecular architecture. This can be interpreted as evidence of good osteointegration.

Several methods have been developed for achieving glass and glass-ceramic coatings such as plasma spray [129,130], and laser deposition [131]. However, the two methods are not applicable for depositing coatings on porous structures. To apply a coating layer

on a porous scaffold, the techniques such as dip coating and sol-gel coating are widely accepted.

Dip coating

D. Shi et al. [132] reported his method to fabricate HA/bioactive glass composite coating on the porous alumina substrate. The method involved coating the alumina substrate with a suspension containing the HA/bioactive glass powder followed by sintering to densify the coating.

Sol-gel coating

Recently, sol-gel bioactive glasses processed at notably lower temperatures than for melt-derived bioactive glasses have been developed. These materials have an initial high specific surface area, and exhibit osteoconductive properties, both *in vitro* and *in vivo*. The use of sol-gel glasses coated on porous alumina could avoid aluminum release from alumina substrate due to the low temperature involved.

M. Hamadouche [133] synthesized bioactive glass coating using the sol-gel method. In this method, the substrate was immersed in a glass sol, followed by centrifugation to remove the excess sol, aging and drying. Finally, the material was fired at a relative low temperature to obtain the glass coating.

2.6.2 Hydroxyapatite coatings

HA has been widely used as a coating material on metal implants, such as hip joint prostheses. The HA coating not only provides stable fixation of the implant to bone and minimizes adverse reaction, but also decreases the release of metal ions from the implant to the body.

The plasma spraying technique is the most popular method to fabricate HA coatings on flat substrates. The coatings have been applied on various substrates, such as metal, carbon [134], sintered ceramics like alumina and zirconia, and polymers such as PMMA [135]. Dip coating [136] and sol-gel [137] coating methods are widely used for depositing HA coating on a porous structure.

More recently, A. L. Oliveiro et al. [138] reported a biomimetic method to develop a HCA coating on a porous scaffold. After only 6 hours of simulated body fluid immersion, the formation of an apatite-like layer was observed on the substrate. The layer could be observed inside the pores, clearly covering the pore walls. Thus this method is very promising for the development of the bone tissue engineering scaffolds.

In summary, Hydroxyapatite, bioactive glasses, and glass-ceramics are most widely used as bioactive coating materials to induce bioactivity on bioinert substrates. Dip coating and sol-gel coating are the popular methods to synthesize bioactive coatings on porous scaffolds. Biomimetic method can also impart more biocompatibility to the scaffolds.

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3.1 Introduction

The PhD project aimed at fabricating porous alumina scaffolds with suitable mechanical strength and superior bioactivity for bone tissue engineering. Therefore, experimental work on three areas had been conducted:

- Preparation and characterization of porous alumina ceramics.
- Preparation and characterization of sol-gel bioactive glasses.
- Preparation and characterization of bioactive glass coating on porous alumina ceramics.

Specifically, the sample preparation work included:

- Preparation of alumina/zirconia ceramics using the vacuum casting method.
- Preparation of porous alumina/zirconia ceramics using expanded polystyrene (EPS) beads as pore formers using the vacuum slurry infiltration method.
- Preparation of sol-gel bioactive glasses using the sol-gel method.
- Preparation of bioactive glass coatings on porous alumina ceramics by dip coating.

The sample characterization work comprised of:

- Characterization of microstructures, sintering behaviours and mechanical properties of alumina/zirconia composites.

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- Characterization of porous structures, microstructures, and mechanical properties of porous alumina/zirconia ceramics.
- Characterization of microstructures, mechanical properties and bioactivity of sol-gel bioactive glasses and bioactive glass coatings.

The flowchart of the experimental procedures and techniques are demonstrated in Figure 3-1.

Figure 3-1 Flowchart of experimental procedures and characterization techniques

3.2 Preparation of alumina/zirconia composite powders

3.2.1 Starting materials

In this study, the starting materials were alumina powder (AKP-30, 99.9 %, Sumitomo, Tokyo, Japan) with particle size of 0.31 μm (measured by a particle size analyser (Broikhaven BI-XDC) at 2000 rpm at room temperature) and a specific surface area of 7.96 m^2/g (measured by Micrometric ASAP2000 using nitrogen adsorption at 300 $^{\circ}\text{C}$), magnesium nitrate-6-hydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (99.8 %, BDH, Limited Poole, England), 3Y-TZP (3 mol% (mol percent) Y_2O_3 doped ZrO_2) (99.9%, Alderich Chemical Company, Inc.) with a particle size of 0.14 μm and a specific surface area of 8.72 m^2/g , ammonium polymethacrylic acid (PMAA) solution (DARVAN[®]C, R. T. Vanderbilt) and 5wt% polyvinyl alcohol (PVA) (DC Chemical Co., Ltd) solution.

For better sintering behavior, 0.5 wt% (weight percent) MgO was added into alumina powder by mixing the alumina powders with magnesium nitrate-6-hydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). The mixed powders were then heated to 900 $^{\circ}\text{C}$ at a heating rate of 5 $^{\circ}\text{C}/\text{min}$ and calcined for 1 hour, followed by wet planetary ball milling at 75 rpm for 2 hours using alumina balls. After drying and dry grinding using an alumina mortar and an alumina pestle, fine MgO-doped alumina powders were obtained. The obtained powders has a particle size of 0.26 μm and a specific surface area of 8.11 m^2/g . Compared with the pure alumina powders, MgO-doped alumina powders had smaller particle size. This was due to the ball milling process that made the ceramic particle finer.

All of alumina powders, zirconia powders and MgO-doped alumina powders were charactered by X-ray Diffraction (Lab XRD-6000 Shimadzu) using Cu-K_α radiation at 50 kV and 20 mA. To conduct XRD, about 10g of the powder was pressed tightly into a

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sample holder using a glass slide and made the sample surface flat. The morphologies of powders observed by field emission scanning electron microscope (FE-SEM, JSM-6340F) in bright field at 5 kV.

3.2.2 Preparation and characterization of composite powders

Different amounts of 3Y-TZP, i.e., 5 vol% (volume percent), 10 vol% and 20 vol% were then added into the MgO-doped alumina powder respectively. Both MgO-doped alumina powder and 3Y-TZP powder were suspended in distilled water one by one with continuous stirring. After that, the mixture was put into an alumina jar together with alumina balls as the media. In order to avoid leaching, a rubber washer was placed beneath the cover of the jar to prevent leakage. The jar were then fixed on a planetary ball milling machine and milled at 75 rpm for 2 hours to obtain a homogeneously mixed powder. The mixture was then dried in oven and ground into fine powders. The as-prepared alumina/zirconia composite powders were named Al, Al05Zr, Al10Zr, Al20Zr, corresponding with the different amount of 3Y-TZP addition (0, 5, 10, 20 vol%).

Table 3-1 The compositions of as prepared alumina/zirconia composite powders

Composite powder	Composition (vol%)	
	MgO-doped alumina	3Y-TZP
Al	100	0
Al05Zr	95	5
Al10Zr	90	10
Al20Zr	80	20

3.3 Slurry optimization and sample preparation and characterization

3.3.1 Preparation and characterization of ceramic slurries

Preparation of ceramic slurries

In the present work, ceramic powders were dispersed in distilled water with a 25 wt% ammonium polymethacrylic acid (PMAA) solution as the dispersant. A 5 wt% polyvinyl alcohol (PVA) solution was used as the binder. Then the suspensions were ball-milled for 2 hours on a rolling miller with alumina ball at a rolling speed of 50rpm to obtain ceramic slurries. After the milling, the slurries were put into a glass incubator connected with a pump to make the degasification for 5 minutes. Vacuum in the incubator created by the pump extracted gas bubbles from the slurries. pH values of the slurries were maintained at a basic range, e.g., pH 9-10.

Diluted alumina slurries with solid loading of 25 wt% were prepared for viscosity tests and settling experiments. Up to 1.2 wt% PMAA were added into the diluted ceramic suspensions. The solid loading, the dispersant content and the binder content can be expressed by equations 3-1, 3-2, 3-3 and 3-4.

$$\text{Solid loading of alumina slurries} = \frac{W_{\text{alu min a}}}{W_{\text{alu min a}} + W_{\text{water}}} \times 100\% \quad (3-1)$$

$$\text{Solid loading of alumina/zirconia slurries} = \frac{W_{\text{composite}}}{W_{\text{composite}} + W_{\text{water}}} \times 100\% \quad (3-2)$$

$$\text{Dispersant content} = \frac{W_{\text{PMAA}}}{W_{\text{alu min a}}} \times 100\% \quad (3-3)$$

$$\text{Binder content} = \frac{W_{\text{PVA}}}{W_{\text{alu min a}}} \times 100\% \quad (3-4)$$

where W is the weight of the components.

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Alumina slurries at varied solid loading, 25, 40, 60 wt%, with 0.5 wt% of dispersant addition were prepared for viscosity test. The concentrated Al, Al₁₀Zr and Al₂₀Zr slurries at solid loading of 60 wt% were also prepared with different PMAA content, up to 1.2 wt% for viscosity test.

Characterization of ceramic slurries

The viscosity as the function of PMAA content and solid loading of diluted alumina slurries and alumina slurries were measured by a viscosity analyzer (HAAKE Viscotester VT550) with a rotational speed of 200 rpm. The slurries were magnetic stirred on a hot plate for 15 minutes and ultrasonically dispersed for 30 minutes before testing.

A settling experiment as describe by Bertrand [139] was carried out: 10mL of each slurry was put in a graduated cylinder, followed by sealing with aluminum foil. Then they were allowed to settle for one week without disturbance. The sediment heights were measured and the relative sedimentation value RSH (The packed-powder height over suspension height) was determined. The sediment cakes were taken out and dried in air for 6 hours followed by oven drying at 80 °C for 2 hours. The particle packing of sediment cakes were observed under FESEM at 5kv.

3.3.2 Preparation and characterization of green compacts***Preparation of green compacts by vacuum slip casting***

Al, Al₀₅Zr, Al₁₀Zr and Al₂₀Zr green bodies of 15 mm in diameter and 3 mm in height were prepared by a vacuum slip casting method. The ceramic slurries used is at a solid loading of 60 wt% with PMAA content of 0.5 wt% and PVA content of 5 wt%, based on the slurry optimization results. The apparatus and the vacuum slip casting process are represented in Figure 3-2. The Gypsum plate with plaster of Paris powders/water weight

ratio of 1 was prepared and dried at 80 °C in oven for 2 hours. A volume graded plastic tube in diameter of 15mm was then attached to the Gypsum plate using silicone sealant to form a mold for the casting. After that, the Gypsum plate was put on a plastic disk with 6 holes of 3 mm in diameter. The connection sites between the gypsum plate, the plastic tube and the plastic support were sealed using the silicone sealant. Finally, the whole assembly was placed on a glass flask which was connected to a vacuum pump with pressure capacity of 2 MPa (Aspirator A-3S, Eyele, Japan) to facilitate the removal of water filtrate and the formation of the green compacts.

Figure 3-2 Schematic graph of the apparatus for vacuum casting process

To form the green compact, the alumina/zirconia slurry was added gradually into the plastic tube with the vacuum pump working continuously for several hours. Subsequently, the sample was allowed to dry in air for 12 hours followed by drying in oven of 80 °C for 6 hours. After that, the silicone sealant was split from the casting mold and the plastic tube was removed from the gypsum plate. Finally, green sample was removed from the plastic tube. The obtained green compact contains ceramics particles and some organic impurities of PMAA and PVA. In order to study the effect of vacuum on the casting time,

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15mL alumina slurries were added into the graded plastic tube with and without vacuum.

The drops of the slurry lever Δh within a casting time t were recorded.

Preparation of green compacts by vacuum infiltration

Porous alumina/zirconia ceramics were prepared using a vacuum infiltration method.

Optimized Al, Al_{0.5}Zr, Al_{1.0}Zr and Al_{2.0}Zr slurries were used based on previous characterizations. Ceramic slurries with a solid loading of 60 wt% were prepared by ball milling for 2 hours on a rolling miller with alumina balls at a rolling speed of 50 rpm followed by degassing. The vacuum infiltration apparatus used is shown in Figure 3-4.

The process of vacuum infiltration is illustrated in Figure 3-4.

Figure 3-3 Apparatus for vacuum infiltration

Figure 3-4 schematic of designed set-up for vacuum infiltration

Expanded polystyrene (EPS) beads with different size ranges, i.e., 2.36 mm-2.80 mm, 2.00 mm-2.36 mm, 1.70 mm-2.00 mm, 1.40 mm-1.70 mm and 1.0 mm-1.4 mm, were used to prepared porous alumina ceramics. The EPS beads were added into the casting vessel layer by layer. Depending on the EPS size, 3-5 layers of EPS beads were used to form an EPS compact of about 5 mm in height. A piece of thin cotton gauze with woven mesh of approximate 1 mm was used to cover the EPS beads compact to avoid extracting EPS from the holes in plastic cover and allow ceramic slurry pass through. After that, the EPS compact was pressed by the cover with 15 holes of 5 mm in diameter to allow the slurry to pass through. The plastic load plate was fastened by the screws and nuts to make the EPS beads deform and contact with each other. The deformation on the EPS beads was controlled by adjusting the screws. The deformation of the porous EPS bead template was represented by the strain of the EPS template, as shown in equation 3-5.

$$\varepsilon = \frac{\Delta h}{h_0} \times 100\% = \frac{h_0 - h_f}{h_0} \times 100\% \quad (3-5)$$

where h is the height of EPS bead template. Δh is the reduce in height under load. The subscripts 0 and f represented EPS bead template without load and under load.

During the vacuum infiltration process, the ceramic slurry was added gradually into the casting container and penetrated the porous EPS bead template. The water aspirator was run for several hours to facilitate the removal of the filtrate from the slurry. After drying in air for 12 hours and in oven for 6 hours, the green ceramic/EPS green compact was taken out of the container. The green compact had the composition of ceramic particles, EPS beads and impurities of PMAA and PVA.

Characterization of green compacts

The densities of the green compacts were measured by a geometry method. For cylinder green compacts without EPS beads, the weight and volume of the specimens were measured, and then the densities were obtained. For the rectangular green compacts with EPS beads, the densities were obtained by the following procedures:

- 1) Heat the specimens at 800 °C for 1 hour to burn out of the EPS beads.
- 2) Measure the weights (m_{green}) and the volumes of the specimens (V_{specimen}).
- 3) Calculate the volume of the burnt out EPS beads (V_{EPS}) using equation: $V = m/\rho$, where V is the volume of the burnt out EPS beads, m the weight of EPS beads in each specimen which was measured before vacuum infiltration, ρ the density of EPS beads which was already known from the product specification.
- 4) Calculate the density of the green body by the equation:

$$\rho = m_{\text{green}} / (V_{\text{specimen}} - V_{\text{EPS}}) \quad (3-6)$$

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The relative densities of the green bodies were calculated by dividing the measured bulk green density with their theoretical density. The theoretical density of the alumina/zirconia composite was calculated based on the volume percentage of each powder in the mixture using the following equation:

$$\rho_{\text{composite}} = \rho_{\text{alumina}} V_{\text{alumina}} + \rho_{\text{zirconia}} V_{\text{zirconia}} \quad (3-7)$$

where ρ_{alumina} and ρ_{zirconia} are the theoretical density of alumina and zirconia and equal to $3.98 \times 10^3 \text{ kg/m}^3$ and $6.01 \times 10^3 \text{ kg/m}^3$, V_{alumina} and V_{zirconia} the volume percentage of zirconia and alumina.

3.3.3 Sintering of green compacts and characterization of sintered samples

Sintering of green compacts without EPS beads and sample characterization

A furnace (Carbolite high-temperature furnace) with thermocouple was used to sinter samples. The green bodies were firstly heated to 700°C at a heating rate of 3°C/min followed by dwelling for 1 hour to burn out of the organic component in the green bodies. Then they were heated at a heating rate of 5°C/min to 1400°C , 1550°C and 1600°C and held for 2 hours. Finally, they were cooled to room temperature at the rate of 10°C/min . the obtained samples were labeled as Al1400, Al1550, Al1600, Al05Zr1400, Al05Zr1550, Al05Zr1600, Al10Zr1400, Al10Zr1550, Al10Zr1600, Al20Zr1400, Al20Zr1550, and Al20Zr1600, correspondingly. Here the numbers 1400, 1550 and 1600 stand for the sintering temperature of the ceramics, and the Al, Al05Zr, Al10Zr and Al20Zr represent the composition of the alumina/zirconia ceramics.

A dilatometer (Anter Unitherm 1161) was used to study the sintering shrinkage of Al, Al05Zr, Al10Zr and Al20Zr samples. Before tests, the diameters and the thickness of the

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disc samples were measured by an electronic caliper. The heating and the cooling rate were 5 °C/min. The samples were heated up to 1600 °C. The heating process was carried out in air.

The final densities of the sintered samples were measured by an electronic densimeter (MD 200S). Al, Al0.5Zr, Al10Zr and Al20Zr samples sintered at 1400 °C, 1550 °C and 1600 °C were ground and polished, followed by thermally etched at 1350 °C, 1500 °C and 1550 °C for 15 minutes to reveal the grain boundaries. The microstructures of the sintered samples were studied by SEM at a bright field at voltage of 20 kV. The average grain sizes of both zirconia and alumina were measured by UTHSCSA Image Tool 2.00. The phase compositions of the sintered bodies were identified by XRD. The fraction of monoclinic ZrO₂ was calculated using the following equation [140]:

$$X_m = \frac{I_m(111) + I_m(\bar{1}11)}{I_m(111) + I_m(\bar{1}11) + I_t(111)} \quad (3-8)$$

Hardness tests were carried out on polished (using 0.1 µm polishing paste) Al, Al0.5Zr, Al10Zr and Al20Zr samples sintered at 1400 °C, 1550 °C and 1600 °C by a Vickers hardness test (Shimadzu HSV20) with a constant load of 500 grams for 25 seconds according to technical manual. The indents were distributed with an interdistance of 5 mm to eliminate the influence of the stress field generated by other indents. After indentation, the diagonal lengths (2a) of the diamond-shaped impression and the resultant crack lengths (c) (as shown in Figure 3-5) were measured using the microscope attached to the hardness tester. The hardness values were automatically given by the instrument following the formula below:

$$H_v = 1.8544P/(2a)^2 \quad (3-9)$$

Figure 3-5 Schematic showing the indentation from the hardness test.

The fracture toughness K_{Ic} ($\text{MPa}\cdot\text{m}^{1/2}$) was calculated using the following equation [141]:

$$K_{Ic} = 0.015 \left(\frac{c-a}{a} \right) \left(\frac{E}{H} \right)^{2/3} \frac{P}{c^{3/2}} \quad (3-10)$$

Where c (μm) is the average crack length from the center of the indentation to the crack tip, a (μm) the half of the diagonal indentation, E (GPa) the Young's modulus, H (MPa) the hardness, P (N) the applied load. Young's moduli of 380 GPa, 372 GPa, 363 GPa and 346 GPa were used for Al, Al_{0.5}Zr, Al_{1.0}Zr and Al_{2.0}Zr samples, respectively. The Young's moduli of alumina/zirconia composites were calculated by the rule of mixture based on the volume percentage of alumina and zirconia in the composites using the equation 3-10.

$$E_{\text{composite}} = E_{\text{alumina}} V_{\text{alumina}} + E_{\text{zirconia}} V_{\text{zirconia}} \quad (3-11)$$

Where E_{alumina} and E_{zirconia} are the Young's modulus of alumina and zirconia and equal to 380 GPa and 210 GPa, V_{alumina} and V_{zirconia} the volume percentage of zirconia and alumina.

Sintering optimization, sintering of ceramic/EPS green compacts and sample characterization

Two main stages were involved in the sintering schedules of ceramic/EPS green compacts: burning out of the EPS beads at 500-600 °C and densifying the ceramic struts at sintering temperature. To optimize the burning out of the EPS beads, different heating rates, i.e., 1, 2, 5, 10 °C/min, were attempted to heat the green compact to 600 °C. The thermogravimetry analysis on the EPS beads was used to direct the removal of the pore former during the preparation of porous alumina/zirconia ceramics. The thermal stability of EPS beads was tested using a thermal gravimetric analyzer (TGA) by heating the EPS beads to 600°C at different heating rate, i.e., 1, 2, 5 and 10 °C/min. The weight loss during the heat treatment was recorded by the build-in software.

Al and Al₁₀Zr green compacts with EPS beads of different sizes were heated to 500 °C at a heating rate of 2 °C/min and held for 30 minutes to burn out of the EPS beads completely based on the optimized results, followed by sintering at 1550 °C (based on the optimized sintering results of dense alumina/zirconia ceramics) for 2 hours to obtain finally porous alumina ceramics. The heating rate and the cooling rate were 5 °C/min and 10 °C/min, respectively.

The morphology of the porous structures was characterized by a stereozoom microscope (Leica MZ6) and SEM at the voltage of 5-20 kV. The pore sizes of the porous structures were measured by UTHSCSA Image Tool 2.00.

The total porosity and the open porosity of the porous structure were measured by a geometric method with wax infiltration using the following procedures:

- 1) Measure the weight (m_p) and the bulk volume (V_T) of the porous structure, respectively.
- 2) Infiltrate melted wax into the porous structure. The wax candles were melted at 60 °C in an oven. In order to make sure of the thoroughly wax infiltration, the porous body were immersed in melted wax and put in a glass incubator which was connected to a pump to create vacuum in the incubator and remove the gas bubbles in the porous structure.
- 3) Measure the weight of the porous structure saturated with wax (m_{sat}).
- 4) Calculate the volume of the porous structure saturated with wax (V_{sat}).
- 5) Calculate the volume of the infiltrated wax (V_{wax}), which is equal to the volume of the open pores, using equation 3-11.
- 6) Calculate the total pore volume (V_p) using equation 3-12.
- 7) Calculate the total porosity, the open porosity and pore interconnectivity using equation 3-13, 3-14 and 3-15.

$$V_{wax} = (m_{sat} - m_p) / \rho_{wax} \quad (3-12)$$

$$V_p = V_{sat} - V_{solid} = V_{sat} - m_p / \rho_{solid} \quad (3-13)$$

$$\text{Total porosity} = V_p / V_T \quad (3-14)$$

$$\text{Open porosity} = V_{wax} / V_T \quad (3-15)$$

$$\text{Pore interconnectivity} = \text{Open porosity} / \text{Total porosity} \quad (3-16)$$

Where V_{solid} is the real volume of the dense ceramic, ρ_{solid} the theoretical density of the ceramic and the theoretical density of wax, i.e., 0.9 g/cm^3 , which is measured using a electronic densimeter MD 200S.

The compressive strength and compressive Young's modulus of the porous structures were studied by an instron tester (Model 5567). The crosshead speed was 0.5 mm/min . the compression strength of porous pure alumina, Al and Al10Zr ceramics sintered at 1550°C with various pore sizes were measured using cubic blocks with dimension of $1 \times 1 \times 1 \text{ cm}^3$. The Young's moduli for the porous ceramics were determined from the elastic stress-strain curves from the compression test. 7-10 identical samples were used for each sample type.

3.4 Preparation of sol-gel bioactive glasses and glass-ceramics

3.4.1 Starting materials

The starting materials used in this study were tetraethoxysilane (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$)(98.0%, Aldrich), triethylphosphate (TEP, $\text{OP}(\text{OC}_2\text{H}_5)_3$)(98.0%, Aldrich), nitrate tetra-hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$)(98.0%, Aldrich) and 1M HCl solution (Aldrich).

3.4.2 Preparation and characterization of sol-gel bioactive glass powders

The designed compositions of the sol-gel bioactive glasses are listed in Table 3-2. The bioactive glass sols were prepared through the hydrolysis and condensation of the mixed solutions of TEOS, TEP, and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ with HCl as a catalyst. Briefly, TEOS was gradually added into the mixture of distilled water and HCl ($\text{pH} = 4$) by magnetic stirring for 30min for the partial hydrolysis of TEOS [142]. Then TEP was added to the mixture

with 1 hour of stirring. For the complete hydrolysis of TEOS and TEP, the molar ratio of H_2O to (TEOS+TEP) was kept at 8. Calcium nitrate tetra-hydrate was then gradually added to the mixture. Finally, the mixture was stirred for 1 hour to obtain a homogenous and transparent solution.

Table 3-2 Compositions of sol-gel bioactive glasses

Composition code	Composition, wt%		
	SiO_2	CaO	P_2O_5
58S33C	58.0	33.0	9.0
68S23C	68.0	23.0	9.0
77S14C	77.0	14.0	9.0

For characterization of the sol gel bioactive glasses, fine bioactive glass powders were prepared. The as prepared bioactive glass sols were aged at 70 °C in oven for 2 hours to transform into gels, followed by drying at 180 °C in oven for 6 hours. Then the dried powders were heated to 700 °C at a heating rate of 5 °C/min and calcined for 1 hour, followed by planetary wet ball milling with alumina media at 75 rpm for 2 hours to obtain fine bioactive glass powders.

The obtained bioactive glass powders were examined using XRD with Cu-K_α radiation at 50 kV and 20 mA and observed under a transmission electron microscope (TEM, JEM 2010) in bright field at 200 kV. The specific surface areas of the bioactive glass powders were measured by Micrometric ASAP2000 using nitrogen adsorption at 300 °C

3.4.3 Crystallization of bioactive glasses

For the study on the microstructure evolutions of bioactive glasses and in vitro test, the obtained bioactive powders were uniaxially pressed into green compacts at 300MPa in a 13mm die using a Press machine (Enerpac, 15 Tons). Then, green compacts with 35-40 %

green density were obtained. To study the crystallization of bioactive glasses during heating, the green bodies were sintered at different temperatures, i.e., 800 °C, 1000 °C and 1200 °C, for 1 hour, separately. The heating rates during the sintering process were set as 5 °C/min and the cooling rates were 10 °C/min.

The crystallization process of bioactive glasses was studied using a differential scanning calorimetry (DSC) (NETZSCH) from room temperature to 1200 °C at a heating rate of 10 °C/min in air using alumina crucibles. The samples sintered at different temperatures were examined using XRD. The microstructures of the sintered samples were studied by SEM both at the bright field and at back scattered electron (BES). The apparent densities of the samples were measured using the electronic densimeter MD 200S.

3.4.4 In vitro SBF test

The *In vitro* bioactivity (or the ability of apatite layer formation) was conducted using the simulated body fluid (SBF) solution. The SBF solution was prepared using the method described by Kokubo et al [143]. Firstly, 50 ml 1M hydrochloric acid (half of the amount of HCl in the protocol) was added to 500 ml distilled water, then the reagent grade chemicals of NaCl, NaHCO₃, KCl, K₂HPO₄·3H₂O, MgCl·6H₂O and CaCl₂ (all Aldrich) were weighed according to the protocol and were added to the solution one by one with continuous magnetic stirring on a hot plate. Before each chemical adding, HCl were added to keep the pH value around 4 to avoid precipitation. After all the chemicals were added, the left HCl were added to the solution. Finally, the solution was heated to 37.5 °C and trishydroxymethyl-aminmethane (Aldrich) was added gradually to buffer the solution to 7.4. The ion concentrations of SBF were almost equal to those of the human blood plasma as shown in Table 3-3.

Table 3-3 Ion concentration of simulated body fluid (SBF) and human blood plasma [143]

	Ion concentration (mM)						
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	HPO ₄ ²⁻
SBF	142.0	5.0	1.5	2.5	148.8	4.2	1.0
Blood plasma	142.0	5.0	1.5	2.5	103.0	27.0	1.0

The sintered bioactive glass bodies were immersed into the SBF solution in glass vessels with the sample surface area to the SBF volume ratio kept at 0.1 cm⁻¹. The samples were then kept in the SBF for from 10 minutes to 4 weeks at 37 °C, separately. After each time period, the samples were taken out of the test solution and rinsed using ethanol and dried in air. The test solutions of the sintered bioactive glass bodies were collected to examine the concentration change of Ca²⁺ ion using inductively coupled plasma – mass spectrometry (ICP-MS) (Perkin Elmer, Optima 2000). The formation and morphology of apatite on the sample surface were observed using FESEM at 5 kV. The samples after SBF soaking were mounted in epoxy resin and cross-sectioned, followed by grinding and polishing. The cross-section was observed under SEM to observe the thickness of apatite layer.

3.5 Preparation of bioactive glass coatings on porous alumina/zirconia ceramics

3.5.1 Starting materials

In this study a dip coating method was used to prepare bioactive glass coatings on the porous alumina/zirconia ceramics. The starting materials used in this study were the as-prepared 58S33C bioactive glass powders, the as-prepared porous Al10Zr ceramics,

ammonium polymethacrylic acid (PMAA) solution and 5 wt% polyvinyl alcohol (PVA) solution.

3.5.2 Preparation and characterization of bioactive glass coatings

The bioactive glass slurries were prepared at a solid loading of 50wt% with 1wt% PMAA dispersant and 3 wt% PVA binder (based on optimization results). In brief, the bioactive glass powders were suspended into distilled water with adding the PMAA solution and the PVA solution, individually. The suspensions were then ball milled at a rolling speed of 50 rpm for 2 hours using a rolling ball mill. After milling, the slurries were degassed.

Dip coating was used to prepare the bioactive glass coating. Before coating, the porous Al₁₀Zr ceramics were ultrasonically cleaned in acetone for 10 minutes using an ultrasonic processor (Ultrasonic LC20H) and rinsed using distilled water.

The cleaned porous Al₁₀Zr ceramics was dipped into the bioactive glass slurry for 5 minutes. After taken out of the bioactive glass slurry, the sample was removed the extra suspension using a centrifuge (Tabletop Centrifuge 5420) at a speed of 1000 rpm for 30 seconds. Then the sample was dipped into the slurry again and the dipping-centrifuging process was repeated for three times to increase the thickness of the bioactive glass coatings. After drying at 80 °C in an oven for 6 hours and firing at 1200 °C at a heating rate of 10 °C/min for 1 hour, a bioactive glass coating was formed on the porous Al₁₀Zr ceramics.

The coated sample was observed under a stereozoom microscope. And the coated pore wall, cross-section surface and fracture surface of the coated samples were studied using SEM at 5-20 kV. The compression test was carried out on both the porous ceramics and

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coated porous ceramics at the crosshead speed of 0.5 mm/min. the samples used for compression test were cubic blocks with dimensions of 1 x 1 x 1 cm³. *In vitro* SBF test was also carried out on the coated porous ceramics. The bioactive glass coated samples were immersed into the SBF solution with the sample surface area to the SBF volume ratio kept at 0.1 cm⁻¹. The samples were then kept in the SBF for from 10 minutes to 4 weeks at 37 °C, separately. After each time period, the samples were taken out of the test solution and rinsed using ethanol and dried in air. The formation of apatite was observed under SEM at 5-20 kV.

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4.1 Introduction

In this project, one great contribution is that a novel method was developed to prepare porous ceramics with good pore structure and suitable mechanical properties for potential biomedical applications. The porous structures should have a pore size at least above 150 μm to allow bone tissue ingrowth. The pores should be connected to transport the blood and nutrition. The porous structure should have sufficient mechanical strength for load bearing applications. Moreover, too stiff a material is not suitable for bone implant. High stiffness would cause stress shielding to make the surrounding bone tissue resorbed. Therefore, a good pore structure should take a compromise between the porosity and the mechanical properties. The porous structure should have the appropriate porous structure to facilitate the bone ingrowth and have the mechanical properties comparable to those of host bone tissue.

Several methods, such as gas foaming, combustible pore former, coral replamineform and foam replica, have been used to prepare porous ceramics. However, they have their disadvantages which restrict their biomedical applications. In the first former two methods, the obtained porous ceramics showed porous structures with random pore distribution and irregular pore shape. The high cost and the shortage of supply of the natural corals also limited the clinical applications of the coral replamineform method. For the foam replica process, it relies on the organic templates. Compared with the foams, sponges and templates used in other studies, the EPS beads, a pore former used in the current study, have the advantages of low cost and ability to adjust the pore structure.

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Moreover, the vacuum infiltration method used in this study exhibits features of simple operation, low energy consumption and good control of the pore structure.

The process of vacuum infiltration involves three steps: (1) to form a porous EPS template by pressing a certain amount of EPS beads; (2) to prepare the alumina slurry; and (3) to infiltrate the EPS template with the slurry. During the infiltration, an aspirator is kept working to enhance the removal of the filtrate. In this chapter, the effects of the parameters involved in the vacuum infiltration method, such as viscosity of the ceramic slurry, characteristics of the EPS beads, load on the EPS template, and casting pressure or vacuum, were studied on the resulting porous structures. The pore structures and the microstructures of the porous pure alumina ceramics were characterized.

4.2 Ceramic slurry optimization

It is well known that a well-dispersed ceramic slurry is crucial to the casting process as well as the final sintered ceramics since it usually produces high average packing density compared with a strongly flocculated slurry. In the present preparation method, the alumina slurry is required to have a good flow ability to facilitate the vacuum infiltration process. The dispersion of the powder in a solvent can be achieved by the adjustment of the surface charge of the ceramic particles for electrostatic stabilization. When polymer molecules of a dispersant attach to the surface of the ceramic particles to prevent the close contact of the individual particles, steric stabilization and another dispersion mechanism is achieved.

In this section, the rheological properties of the slurries were discussed. The influence of the slurry concentration and the effect of the dispersant content on the viscosity and the stability of the slurries were examined. The effect of the stability of the slurries on the

green bodies was also studied. The optimal dispersant content was finally determined for the slurry.

4.2.1 Rheological properties of diluted suspensions

4.2.1.1 Effect of dispersant content on viscosity

Figure 4-1 shows the viscosities of the diluted alumina suspensions with a solid loading of 25 wt% and having different dispersant contents up to 1.2 wt%. The viscosity of the alumina slurry without the PMAA as the dispersant addition was as high as about 5 mPa·s. The viscosity of slurry dropped abruptly when PMAA was added. With a PMAA content of 0.5 wt%, a minimum viscosity about 1 mPa·s was reached. Further addition of the PMAA inversely increased the viscosity. The small amount of the PMAA addition (around 0.5 wt%) decreased the viscosity of alumina slurry, that is, improved the flow ability of the slurries, which would facilitate the casting process in the present study. The phenomenon indicated that the PMAA could well disperse the alumina slurries. However, too high addition of the dispersant inversely increased the viscosity of the alumina slurries due to the high viscosity of the PMAA itself.

Figure 4-1 Viscosity of 25wt% alumina suspensions as a function of dispersant content.

The effect of the dispersant could be attributed to both the electrostatic mechanism and the steric mechanism.

According to the DLVO theory (after the four scientists – Deryaguin, Landau, Verwey and Overbeek who were responsible for its development) [33, 34], a stable suspension can be obtained when there is a sufficient high surface charge density to generate a strongly repulsive force among particles. It is well known that an oxide powder dispersed in water can adsorb water molecules and form a hydration layer, especially the alumina powder used in this study was a nano-sized powder which can easily adsorb H^+ and OH^- ions on the powder surface for its huge specific surface area. The hydration reaction is shown in equations 4-1 and 4-2 depending on the pH in the suspension:

As Bertrand [139] reported, the isoelectric point (IEP), i.e. the pH value at the zeta potential is null, of alumina was reached at approximately pH 8.7. The pH values of slurries studied in the present work were about 9-10, which were close to the IEP of alumina particles. Therefore, in the alumina slurry without the PMAA addition, the alumina surface lacked charges and could not induce a sufficient repulsive force between the particles, leading to highly flocculated slurry. As a result, the alumina slurry without the PMAA addition exhibited a high viscosity.

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PMAA is an anionic polyelectrolyte. The dissociation reaction of PMAA creates free carboxylic acid groups (RCOO^-) which create negative charges. Its molecular formula as shown in Figure 4-2 and the dissociation reaction (equation 4-3) are shown as follows:

Figure 4-2 Molecular formula of the PMAA

The negatively charged carboxyl group dissociated from PMAA as shown in Figure 4-2 is very easily adsorbed to the particle surfaces and consequently the powder is negatively charged. With the increasing addition of PMAA (less than 0.5 wt%), the increased repulsive force between the negatively charged resulted in the dispersion of alumina particles and thus the decrease in the viscosity of the alumina slurry. However, when PMAA adsorption was full on the surface, further PMAA did not adsorb onto the particle surfaces, but resulted in the increase of the viscosity of the slurry due to its own high viscosity. Therefore, addition of PMAA much more than 0.6 wt% led to the increased viscosity of the alumina slurry.

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For the alumina slurry of pH 9-10, the PMAA added was negatively charged, whereas the zeta potential of the alumina particles (if no PMAA) is close to zero (IEP of alumina particle is pH 8.7). Thus, either binding with some Me-OH_2^+ groups or hydrogen interaction with Me-OH sites can contribute to the adsorption of the PMAA on the particle surface [144], although the Me-OH_2^+ sites and MeO^- sites should be balanced in the number of charges. The polyelectrolyte chains adsorb in a relatively flat conformation, covering a large surface of the particle with some tails still extended into solution, leading to a steric stabilisation of the suspension [145,146].

4.2.1.2 Effect of dispersant content on packing of alumina particles

For ceramic shape formation, the packing density of a green compact is important for the final quality. Therefore, it is important to study the packing efficiency of the slurries in the casting process.

Diluted alumina suspensions at the solid loading of 25 wt% with different dispersant contents ranging from 0.2-1.0 wt% were subjected to one week's settlement and the result is shown in Figure 4-3. Through observing the clarity of the supernatant liquids, it can be noted that at higher PMAA contents, the supernatant liquid were cloudy, indicating some particles stayed in the suspension. The relative sedimentation height (RSH) values are plotted as a function of the PMAA content as shown in Figure 4-4. It can be seen that the RSH value decreased sharply with the additions of PMAA. When the addition of PMAA increased up to 0.6 wt%, a plateau reached, i.e. no further decrease in the RSH with the increasing PMAA content. The decrease in RSH indicated more closed packing of alumina particles in the sediment cakes.

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The green densities of the sediment cakes are plotted as the function of PMAA content as shown in Figure 4-5. The green densities of sediment cakes were at the range of 42.7 % to 45.1 %. With the increasing PMAA content, the green density increased. However, with a large PMAA addition of 1 wt%, the green density of sediment cake decreased. It can be explained by the existence of excessive amount of PMAA, which occupied some volume in samples, resulting in reduced density of the samples.

Figure 4-6 shows the morphologies of the sediment cakes. One can note that the sediment cake from alumina slurry with the PMAA content of 0.6 wt% was denser and exhibited much more homogeneous particle packing than those from alumina slurries with the PMAA content of 0.2 and 1 wt%. The alumina slurry with PMAA content of 0.2 wt% was an insufficiently dispersed, the ones with PMAA contents of 0.4-0.6 wt% were well-dispersed and the one with PMAA content of 1 wt% was the slurry with extra amount of PMAA. It can be seen that a stable and well-dispersed slurry could lead to a higher green density of the cast samples.

Figure 4-3 Sediment heights of suspensions with different dispersant contents; (a) 0.2wt%, (b) 0.4 wt%, (c) 0.6wt% and (d) 1wt% (alumina solid loading being kept at 25wt%).

Figure 4-4 Relative Sedimentation Height (sediment cake height over the suspension height, RSH) versus PMAA content (slurries at a solid loading of 25 wt%).

Figure 4-5 Packing density versus PMAA content of the alumina slurries at a solid loading of 25 wt%.

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Figure 4-6 FESEM micrographs of the green compacts from the settlement experiment of slurries with different dispersant contents: (a): 0.2 wt%, (b): 0.6 wt and (c) 1 wt% (at a solid loading of 25 wt%).

Many studies [147,148] have been devoted to the packing mechanism of particles. The most famous one is the Furnas model [149]. The specific packing volume (packing volume/mass) is defined as the reciprocal of the packing efficiency (PE). According to the Furnas model, the theoretical maximum packing efficiency, PE_{max} of a mixture of coarse and fine particles is:

$$PE_{max} = PE_c + (1 - PE_c) PE_f \quad (4-4)$$

Or

$$PE_{max} = 1 - \Phi_c \Phi_f \quad (4-5)$$

where PE_c and PE_f are the packing efficiency of the coarse and fine particle fractions, respectively, and $\Phi = 1 - PE$, is the interstitial pore fraction of packed particles of a single size. Therefore, the packing mechanism of the Furnas model is such that smaller particles are introduced and distributed into the interstices of larger packed particles.

The Furnas model can well explain the packing volume and density as a function of the dispersant content. Without the dispersant or with a very low content of dispersant content, the suspension was agglomerated or not stable enough so that the agglomerates of particles settled immediately without smaller particles filling in the interstices. And the agglomerates themselves were loosely packed. As a consequence, the resultant packed body had a low density. With the increase of the dispersant content, the suspension became stable so that both large particles and small particles were dispersed and settled to form a densely packed body. However, with excess amount of dispersant, the polymeric component occupied a volume in samples, resulting in reduced density of the green samples.

4.2.2 Rheological properties of concentrated slurries

4.2.2.1 Effect of slurry concentration on viscosity

Figure 4-7 shows the shear stress-shear rate curves of alumina slurries at various solid loadings, 25 wt%, 40 wt% and 60 wt% at 0.5 wt% dispersant content. It can be seen that the shear stress increased with the increase of solid loading. The viscosity of slurries versus the shear rate is plotted in Figure 4-8. It can be seen that the slurries exhibited a decrease in viscosity with an increase in shear rate at a lower range of shear rate (up to 100 s^{-1}). It indicates that the slurries showed a shear-thinning behaviour, which is a

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well-known characteristic of colloiddally stable suspension [150]. The shear thinning could be attributed to the viscous forces affecting the suspension structure more than thermal motion. The rheological behaviour indicated that the slurries were pseudoplastic [151] and the viscosity increased with the increase of solid loading. At higher shear rates (up to 300 s⁻¹), a plateau appeared in viscosity as the result of dominated viscous forces.

Figure 4-7 Shear stress-shear rate curves of alumina suspensions with a certain dispersant content of 0.5 wt% at different solid loading: (■): 25 wt%, (○): 40 wt% and (▲):60 wt%.

Figure 4-8 Viscosity-shear rate curves of alumina suspensions with a certain dispersant content of 0.5 wt% at different solid loadings: (■): 25 wt%, (○): 40 wt% and (▲):60 wt%.

In ceramic slurries, the relationship between the shear rate (γ) and shear stress (τ) can be expressed as follows [152]:

$$\tau = k \gamma^m \tag{4-6}$$

where k is as constant related to viscosity. The m value indicates flux behaviour:

- $m < 1$ indicates pseudoplasty;
- $m = 1$ indicates Newtonian behaviour and
- $m > 1$ indicates dilatancy.

Thus, the behaviour of the ceramic slurry could be determined though plots of $\lg \tau$ versus $\lg \gamma$ as shown in Figure 4-9. Table 4-1 lists the calculated k and m values for three slurries.

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The m values of three slurries were all below 1, which indicates that the slurries were pseudoplastic. The result is in agreement with the report by Richard [151], which showed that the slurries used for casting were pseudoplastic.

Figure 4-9 $\lg \gamma - \lg \tau$ curves for alumina slurries with a certain dispersant content of 0.5 wt% at different solid loadings: (■): 25 wt%, (○): 40 wt% and (▲): 60 wt%.

Table 4-1 k and m values for alumina slurries with a certain dispersant content of 0.5 wt% at different solid loadings of 25 wt%, 40 wt% and 60 wt%

	25 wt%	40 wt%	60 wt%
m	0.103	0.098	0.063
k	10.423	11.350	14.859

4.2.2.2 Effect of PMAA content on the viscosity of concentrated slurries

Figure 4-10 shows the viscosity as a function of PMAA content in concentrated Al, Al10Zr and Al20Zr slurries with a solid loading of 60 wt% and pH value near 9. One can see that the effect of PMAA addition on the viscosity of the three slurries followed a similar trend which had been discussed on the diluted alumina suspensions. The viscosities of all three slurries dropped abruptly with the added PMAA. With the increase of the PMAA addition, the viscosity of slurries increased after reaching a minimum value.

The lowest viscosity of Al, Al10Zr and Al20Zr slurries shifted towards lower PMAA content of about 0.6 wt% for Al slurry, 0.3 wt% for Al10Zr slurry and 0.2 wt%. Moreover, lower viscosity was observed on the alumina/zirconia slurries. It was due to the lower IEP value of zirconia particles. Literature shows that the IEP values of alumina and zirconia are 8.7 [33] and 6 [34], respectively. At the slurry pH value near 9, the zirconia particles were more highly negatively charged than the alumina particles. The stronger repulsive force in the alumina/zirconia slurries could decrease the viscosities

Figure 4-10 Viscosity of 60wt%, Al, Al10Zr and Al20Zr slurries as a function of the dispersant content. (■): Al slurry; (○): Al10Zr slurry; and (▲): Al20Zr slurry

4.3 Effect of EPS beads on vacuum infiltration

In the present study, the EPS beads were packed to form a porous EPS template to be infiltrated by the alumina slurry. The geometry of the strut network of the porous alumina was determined by the shape, size, and size distribution of the EPS beads, as well as the surface morphology of the EPS beads. Figure 4-11 (a) shows that the EPS bead was in spherical shape and had a rather rough surface. Observed under a higher magnification (Figure 4-11(b)), the EPS bead showed a high porosity with micropores of 1-2 μm in size and macropores larger than 20 μm . A network of pore-free paths was also observed.

The formed porous EPS template is shown in Figure 4-12. The deformed EPS template under a load is schematically illustrated in Figure 4-13. When a load was applied on the EPS bead template, the EPS bead template was pressed in all the directions (both the load direction and side directions by the casting mould). The EPS beads shrunk and kept the spherical shape. Some necks were formed between the adjacent beads. With the increase of load, the dimension of EPS beads decreased, the contact areas of adjacent beads increased and the volume of interstices among the beads decreased.

Figure 4-14 shows the morphology of porous alumina ceramics prepared using EPS beads at the size range of 2.36-2.8 mm. The porous structure was composed of spherical macropores, open windows to interconnect the macropores and the slender ceramic struts. The porous structure was a negative replica of the porous EPS template: the interstices of the EPS template were occupied by ceramic particles to form ceramic struts or pore walls, whereas the space of the EPS beads were left as pores and the contact area between adjacent pores became pore windows. The rough surface of the pore walls resulted from

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the porous surface of the EPS beads. The pore size of the porous body was about 1.87 mm which was much smaller than the size range of the used EPS beads. It was because of the shrinkage of the EPS beads pressed to form a porous template. The shrinkage of the ceramic body during sintering was another reason for the smaller pore size. Moreover, the pore windows also could be generated by gas exudation during the pyrolysis of the EPS beads.

Figure 4-11 SEM micrographs showing: (a) the morphology of a single EPS bead and (b) the surface morphology of the EPS bead under a higher magnification.

Figure 4-12 Stereozoom micrograph of a porous EPS template.

Figure 4-13 Schematic of EPS bead template deformed under a load.

Figure 4-14 SEM micrograph showing the porous structure of the porous alumina.ceramics.

Figure 4-15 shows the curves of the weight loss of EPS beads versus the temperature, measured at different heating rates: 1, 2, 5, and 10 °C/min. It can be seen that the EPS beads could be completely burnt out below 500 °C. The majority of the weight loss occurred from 350 °C to 450 °C. It can also be seen that a lower heating rate corresponded to a lower temperature at which the EPS beads could be burnt out completely. To avoid contaminating the finally porous alumina ceramics, the pore former should be able to be removed completely. If firing is needed to remove the pore former, the pore former should be able to be burnt out at relative low temperature and not influence the densification of ceramics bodies. EPS bead was an ideal pore former. The EPS beads could be completely burnt out below 500 °C which was much lower than the sintering temperature of alumina ceramics and with no residua left. It can also be seen that a lower heating rate corresponded to a lower temperature at which the EPS beads could be burnt out completely. The effect of heating rate on the combustion of EPS bead was due to the extent of oxidation of the beads. During heating, EPS beads were oxidated into CO₂, CO, soot and unburned polycyclic aromatic hydrocarbon [153]. The latter two components were the products of insufficient oxidation. At a low heating rate, the EPS could be well oxidated or vaporized in to CO₂ and CO and reduce the amount of residual products.

Figure 4-16 is the derivative weight curves of EPS beads at different heating rates: 1, 2, 5, and 10 °C/min. The peak represented the maximum weight change rate during heating. It is clear that the maximum weight change peak shifted towards a lower temperature with the decreasing heating rate. It further confirmed a lower heating rate resulted in a lower temperature to burn out of the EPS beads.

Figure 4-15 TGA curves of the EPS beads measured at different heating rates: 1, 2, 5, and 10 °C/min.

Figure 4-16 Derivative weight loss versus temperature curves at different heating rates: 1, 2, 5, and 10 °C/min.

On the other hand, the porous samples sintered in a furnace at different rates, 1, 2, 5, and 10 °C/min to burn out of EPS beads were examined. It seemed that small heating rates,

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i.e., $< 2\text{ }^{\circ}\text{C/min}$, were required to keep the structural integrity. In the sintering process, burning out of the pore former was a key step. When the EPS beads were heated, the EPS beads melted and vaporized. Gases generated by EPS beads would be removed from the green bodies and disturb the network of the ceramic. With a slow heating rate, the rate of gas generation during the EPS vaporization was slow. Thus the generated gases had enough time to be released through the interstices between ceramic particles without breaking the compact. Therefore, to keep the structural integrity of a porous body, this step required a very low heating rate to slow the release of the gases and reduce the stress of disturbing the green compact. However, too low a heating rate would consume too long a time. In our study, the heating rate of $2\text{ }^{\circ}\text{C/min}$ was suitable to burn out of the EPS beads. At this rate, the samples maintained the pore structure well.

The low coefficient of thermal expansion (CTE) of EPS beads also contributed to the integrity of the ceramic compact. The EPS beads experienced thermal expansion with a thermal expansion coefficient of $35 \times 10^{-6}\text{ K}^{-1}$ (given by the manufacturer), in contrast to the value of $80\text{-}150 \times 10^{-6}\text{ K}^{-1}$ of unexpanded (or dense) polystyrene (PS) beads. Here, a quantitative analysis of thermal stress resulting from the expansion of EPS beads was conducted. During heating from room temperature to $500\text{ }^{\circ}\text{C}$, the EPS beads expanded while no volume change in alumina ceramic component due to the onset sintering temperature of $> 1000\text{ }^{\circ}\text{C}$ for alumina particles. Thus only the expansion of EPS beads resulted in the stress in the green compact. The tensile stress in the alumina green compact can be calculated using the following equation [154]:

$$\Sigma_{\text{compact}} = \frac{E\alpha}{1-\nu} \Delta T \quad (4-7)$$

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where E and ν are the Young's modulus (375GPa) and Poisson's ratio of alumina (0.232) [155], respectively, α the thermal expansion coefficient of the EPS bead, ΔT the change in temperature. Thus the stress can be calculated as 8.1 MPa. From literature [156], the green strength of alumina compact was 10-20 MPa. The alumina compact could bear the stress generated by the expansion of EPS beads. Moreover, a slow heating rate was desirable for avoiding the rapid thermal expansion of the EPS beads and removing the EPS beads through slow burning and thus could reduce the stress transmitted to the alumina network.

The original size and the expanded sizes of the EPS beads, the pore size of the green compact after removal of EPS beads and the pore size in sintered porous alumina are listed in Table 4-2. The original size of EPS beads was obtained by sieving. The expanded size of EPS beads was calculated using the thermal expansion coefficient (α) as follows:

$$\Delta D = \alpha \cdot \Delta T \cdot D \quad (4-8)$$

where D is the original diameter of an EPS bead, ΔT the temperature change from room temperature (25 °C) to 240 °C [157] (the melting temperature of polystyrene), ΔD the increase in the diameter of the EPS bead after expansion.

Due to no shrinkage of the green compact at 500 °C, the pores in the green compact after burning had the same size of the expanded EPS beads. The pore size of sintered alumina was calculated from SEM micrograph using UTHSCSA Image Tool 2.00. It can be seen that during burning of the EPS beads, the EPS bead expanded with an expansion of 0.020-0.021 mm which resulted in a larger pore size in green compact compared with the

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original size of EPS beads. After sintering, the pore size greatly decreased due to the shrinkage of the ceramic body.

Table 4-2 Size evolution in porous alumina ceramics

	Original EPS beads	EPS beads after expansion	Pores in green compact	Pores in sintered alumina
Size in diameter (mm)	2.63-2.8	2.653-2.821	2.653-2.821	1.87

4.4 Porous alumina ceramics prepared under various loads

In this project, the screws and nuts were used to fasten the load plate to apply a load on the porous EPS template. The load on the porous EPS template was represented by the deformation of the EPS template, as shown in Equation 4.9.

$$\varepsilon = \frac{\Delta h}{h_0} \times 100\% = \frac{h_0 - h_f}{h_0} \times 100\% \tag{4-9}$$

where ε is the strain of the EPS template, h_0 and h_f are the original height and the final height of EPS template, respectively. During the casting process, the load controlled the contact area between the EPS beads, which finally determined the pore structure of the porous alumina ceramics. The alumina slurry used was at the solid loading of 60 wt% and optimized with 0.5 wt% PMAA and pH near 9.

Figure 4-17 shows the porous structures of porous alumina ceramics prepared using different porous EPS templates. Figure 4-17 (a) shows the porous structure of a sample prepared using the porous EPS template without any deformation. One can see that most

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pores were closed ones, and the pores were distributed randomly. It was because the floating of the EPS beads during the slurry casting. Without pressing, the EPS beads were packed loosely. Due to the light weight of EPS beads, they tended to float in the slurry, which resulted in no contact between the beads and random distribution of EPS beads. Figure 4-17 (b) shows the porous alumina made from the EPS template with a strain of 10%. It can be seen that the pores were distributed uniformly and had an average pore size about 2.63mm. Some windows were open on the pore walls to connect the individual pores. The struts were strong enough to bear subsequent grinding and polishing. Unlike the EPS bead template with no deformation, the EPS beads in the deformed template were pressed by each other with similar packing as illustrated in Figure 4-13 and could not move during the casting process. Thus, the obtained porous body exhibited a uniform distribution of connected pores. The porous alumina ceramic from the EPS template with a strain of 20% is shown in Figure 4-17 (c). The porous alumina was constructed by ceramic struts as pore walls as shown in (a) and (b), and had the higher porosity and higher pore interconnectivity. The ceramic struts were 100-200 μm in thickness. The thin ceramic struts were formed by ceramic particles left in the narrow interstices between the deformed EPS beads as shown in Figure 4-13. With a higher deformation of the template, the interstices between EPS beads became smaller. Thus the prepared porous alumina exhibited thin ceramic struts.

Figure 4-17 Stereo-zoom optical micrographs showing the pore structures of porous alumina ceramics fabricated using different porous EPS templates with: (a) no deformation, (b) a strain of 10% and (c) a strain of 20%.

Figure 4-18 shows the influence of strain (degree of deformation) of the porous EPS template on the total porosity and the open porosity of the porous alumina ceramics prepared by using EPS bead templates with EPS bead size range of 2.36-2.80 mm. It can be seen that the total porosities were at the range of 65.3 %-67.1 % and did not significantly changed with the increasing strain of the porous EPS template. The open porosity was increased from 49.3 % to 59.4 % with the increasing strain of the porous EPS template. An explanation of the constant total porosity of the porous alumina prepared under varied strain is given here. As the space occupied by EPS beads became

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pores in the sintered porous samples, the total porosity (P) of a sample can be expressed as:

$$P = V_{\text{pores}}/V_{\text{sample}} = V_{\text{EPS}}/V_{\text{sample}} \quad (4-10)$$

where V_{pore} , V_{EPS} and V_{sample} are the volumes of pores, EPS beads and the bulk sample, respectively.

When the EPS bead template was subjected to a strain of ϵ , the volumes of both the EPS beads and the bulk sample shrunk. The shrunk volume of EPS beads and the bulk sample are, $V_{\text{EPS}}' = V_{\text{EPS}} (1 - \epsilon)$ and $V_{\text{sample}}' = V_{\text{sample}}(1 - \epsilon)$. The total porosity of the sample prepared using the deformed EPS bead template (P') is

$$P' = V_{\text{EPS}}'/V_{\text{sample}}' = V_{\text{EPS}} (1 - \epsilon)/V_{\text{sample}}(1 - \epsilon) = V_{\text{EPS}}/V_{\text{sample}} \quad (4-11)$$

Thus $P=P'$. It means that the strain of the EPS beads template did not affect the total porosity of the samples. The slight variance was due to the system error. The open porosity was increased from 49.3 % to 59.4 % with the increasing strain of the porous EPS bead template. It was because a higher strain caused more EPS beads in contact with the adjacent ones, resulting in more connected pores in the resulting porous ceramics.

Figure 4-18 Influence of the strain of the porous EPS template on the total porosity (a) and the open porosity (b) of the porous pure alumina ceramics prepared using EPS beads at the size range of 2.36-2.8 mm and sintered at 1550 °C for 2 hours.

The so-called pore interconnectivity is defined as the fraction of the open porosity in the total porosity, as shown in equation 4-12.

Pore interconnectivity = open porosity/total porosity (4-12)

The pore interconnectivities of the porous pure alumina ceramics prepared under different loads were calculated and plotted in Figure 4-19. It can be seen that the porous structure prepared in this study had a high pore interconnectivity of above 75.5%. With the increase of the load on the EPS template, the pore interconnectivity increased, indicating that the open pores took a higher fraction in the total pores. When the porous EPS template had a deformation of 25%, the pore interconnectivity reached 88.5%. From the

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image in Figure 4-17 (b), it can be seen that most of the spherical pores obtained in the porous bodies were connected to the rest of the neighbor pores by small throats. Nearly no isolated pores were observed. Well interconnected structures are indispensable in tissue engineering, as they allow the migration of cells into the scaffolds, and permit the good diffusion of nutriment and eventually signaling substances throughout the porous structures, which represents a basic requirement for tissue regeneration [9,11,15]

Figure 4-19 Influence of the strain of the porous EPS template on pore interconnectivity of the porous alumina ceramics prepared using EPS beads at the size range of 2.36-2.8 mm and sintered at 1550 °C for 2 hours.

In our vacuum infiltration process, the ceramic slurry penetrated into the pore spaces of the porous EPS template to form the ceramic network. The space occupied by the EPS beads would become the pores in the finally sintered samples. The contact areas would become the pore windows in the porous structure to connect the neighboring pores. Thus, the pore structures of the porous alumina ceramics could be effectively controlled by the packing conditions of the EPS beads. If no pressure was applied on the EPS bead template, the alumina slurry and the resultant alumina green compact tended to make the

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EPS beads isolated and result in a closed porosity. If too high a pressure was used, the pore spaces among the EPS bead template became too small for the slurry infiltration, which affected the infiltration efficiency and also resulted in a weak ceramic network with thin ceramic struts and low mechanical properties.

When the load was applied on the porous EPS template, the EPS beads were deformed and contacted with each other. With the increase of the load, the volume of the porous EPS template shrank and the contact area between the EPS beads increased, which resulted in larger and more pore windows in the finally sintered porous structures. Thus, the sintered porous structures prepared under a higher load showed a higher open porosity. While the total porosity of the finally sintered sample did not change significantly, the increase of the open porosity indicated a higher fraction of open porosity in the total porosity. Thus, the larger the load the higher the pore interconnectivity in the sintered porous structure.

Therefore, the optimal load in my current method should be synthetically determined by the pore interconnectivity, mechanical properties. In this case, when the EPS template with a strain of 10 % was used as the pore former, the obtained porous alumina ceramics showed a high pore interconnectivity of 82 %. The process showed relatively high efficiency meaning a short time period of infiltration.

4.5 Vacuum infiltration under different vacuum conditions

The vacuum was generated by an aspirator with a pressure capacity of 2 MPa in the present vacuum infiltration process. The curves of slurry volume drop versus the casting time under vacuum and without vacuum are shown in Figure 4-20. The two casting

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processes with and without vacuum started from the same initial slurry volume of 15 mL. It can be seen that the removed filtrate increased greatly under the vacuum. At the beginning of the casting process, the removed slurry volume increased from 0.2 mL without vacuum to 5 mL under vacuum. After twenty minutes of casting, no slurry was left in the sample under vacuum and a maximum removed slurry volume reached 9.5 mL, while the removed slurry of the sample without vacuum were just 1 mL. The slurry volume drops of pure alumina slurry, Al slurry and Al10Zr slurry under vacuum as a function of casting time are plotted in Figure 4-21. The curves show the same trend that a great slurry drop at the beginning of the casting, and the volume drop became slower with the increase of time, final a plateau reached, i.e. no further volume drop in the slurry with the increasing casting time. It also can be found that Al10Zr slurry showed higher volume drop than pure alumina slurry and Al slurry. It is because the lower viscosity of Al10Zr slurry, which is show in Figure 4-10. It means that the Al10Zr slurry had a higher flow ability, which facilitated the infiltration of Al10Zr slurry.

Figure 4-20 Slurry volume drop versus infiltration time with and without the vacuum (or a pressure).

Figure 4-21 Percentage of the slurry volume drop versus infiltration time for three slurries: pure alumina, Al and Al10Zr slurries with a vacuum (or a pressure).

The relative densities of the green struts in the porous pure alumina, Al and Al10Zr green samples prepared without vacuum and under vacuum are listed in Table 4-3. The relative densities of the green struts in the porous pure alumina, Al and Al10Zr green samples prepared without vacuum were 32%, 33% and 35%, respectively. The relative densities of the green struts of those green samples prepared under vacuum were 42%, 39% and 44%, respectively. It can be seen that the relative densities of the samples prepared under vacuum were higher than those of samples prepared without vacuum. The relative densities of the green struts were calculated using the weight and volume method. The apparent density (ρ^*) and the relative density (ρ) of the green struts in porous sample was determined in the following equation, respectively:

$$\rho^* = m_{\text{alumina}}/V_{\text{alumina}} = m_{\text{alumina}}/(V_{\text{bulk}} - V_{\text{EPS}}) \quad (4-13)$$

$$V_{\text{EPS}} = m_{\text{EPS}}/\rho_{\text{EPS}} \quad (4-14)$$

$$\rho = \rho^*/\rho_0 \times 100\% \quad (4-15)$$

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where m_{alumina} and m_{EPS} are the weights of the green sample after burning and the EPS beads used, which were measured using a balance, V_{alumina} , V_{bulk} and V_{EPS} are the volumes of the alumina struts, the bulk sample and the EPS beads, ρ_{EPS} the density of the EPS beads which is 89 kg/m^3 as given in the product specification. ρ_0 is the theoretical density of the ceramic involved.

Table 4-3 Relative densities of the three green samples prepared under and without the vacuum

	Pure alumina	Al	Al10Zr
No vacuum	32%	33%	35%
Under vacuum	42%	39%	44%

From the above results, it is obvious that when the vacuum was applied, the relative densities of the green compacts were increased. It is well known that during the casting process the green compact was formed by packing the ceramic particles and by the removal of the solvent (i.e., water). Uniformly dispersed slurry formed green compacts with homogeneous particle packing [158,159] resulting in a high green density. The casting time was related to the stability of the slurries. During a long time process, the ceramic slurry tended to become unstable and the ceramic particles in the slurry would agglomerate to form a heterogeneous particle packing. While applying vacuum, the casting time was greatly shortened. It doesn't mean that the vacuum broke up the soft agglomerates. When casting under vacuum, the casting time was shortened. The slurries could be kept in a well dispersed condition during the casting process. Thus the green compacts with uniform particle packing could be obtained.

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Comparing the relative green densities of the pure alumina, Al and Al10Zr samples, one notice that the relative densities of Al sample were close to those of pure alumina while the Al10Zr sample showed highest relative densities. It was due to the higher stability of alumina slurry added with zirconia. At pH about 9-10, zirconia particles were more highly negatively charged than alumina particles, because the IEP values of alumina and zirconia are 8.7 [33] and 6 [34], respectively. The stronger repulsive force in the Al10Zr slurry caused the better dispersion of the slurry.

4.6 Optimized process for vacuum infiltration

The optimized working condition of vacuum infiltration was finalized now. Briefly, alumina/zirconia slurries at the solid loading of 60 wt% with an optimal PMAA dispersant content of 0.5 wt% and a PVA binder content of 5 wt% (from literatures) were prepared for the casting (or infiltration) process. The EPS beads were weighed and added to the sample container, followed by adjusting the screws and nuts to press the EPS bead compact by a 10 % strain, with the EPS bead template being adjusted to the height of 5mm. Then, the aspirator was switched on and the ceramic slurry was poured gradually into the sample container. After 6 hours of infiltration, the aspirator was switched on and the sample was left dry in air for another 12 hours. After that, the sample together with the container was dried in oven at 70 °C for 6 hours and then the dried sample was taken out from the container. To remove the EPS beads, the sample was then heated up to 500 °C at the heating rate of 2 °C/min and held for 30 min.

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5.1 Introduction

To fabricate porous alumina ceramics with excellent mechanical properties, the mechanical properties of the struts of the porous ceramics must be improved by controlling the microstructure (such as composition and density) of the struts. It has been reported that the addition of ZrO_2 could reduce the sintering shrinkage of alumina by increasing the starting green density and suppress the grain growth of the matrix grains during sintering [160,161]. Thus, the objective of this study was to systematically investigate the influence of the zirconia content on the microstructure and the mechanical properties of alumina/zirconia ceramic composites.

Alumina/zirconia mixed powders with different zirconia contents were prepared using a wet ball milling method, followed by sintering at different temperatures, as described in the previous section. The as-prepared samples were characterized using XRD, SEM, FSEM, TEM and dilatometry. The optimal zirconia content of the alumina/zirconia composites was determined for optimal mechanical properties.

5.2 Characterization of starting ceramic powders

The XRD patterns of powders are shown in Figure 5-1. Pure Al_2O_3 powders and Al powders exhibited the alpha phase ($\alpha\text{-Al}_2\text{O}_3$). In the XRD pattern of 3Y-TZP powders, the major phase was the tetragonal phase ($t\text{-ZrO}_2$) and the mirror one was the monoclinic

phase (m-ZrO₂). Figure 5-2 shows the morphologies of powders observed by field emission scanning electron microscope (FE-SEM, JSM-6340F)

Figure 5-1 XRD patterns of the ceramic powders: (a) pure Al₂O₃ powder, (b) Al powder, and (c) pure 3Y-TZP powder

(a)

(b)

Figure 5-2 FESEM micrographs of ceramic powders: (a) pure Al₂O₃ and (b) pure 3Y-TZP

The mean particle sizes obtained from the three methods, i.e., SEM, BET, and particle size analyser, are listed in Table 5-1. It can be seen that the particle size obtained from the particle size analyser was higher than that from the BET method. For the testing of particle size analyser, a 10 wt% suspension was prepared with 1wt% PMAA as deflocculate. In the suspension, slight agglomeration would existed, which cause the higher data of particle sizes

Table 5-1 Particle sizes of ceramic powders measured using three methods

Methods	Particle size (μm)		
	Al ₂ O ₃	Y-TZP	Al
SME	0.2-0.4	0.1-0.2	0.2-0.4
BET	0.28	0.11	0.21
Particle size analyzer	0.31	0.14	0.26

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The particle size distributions of the pure Al_2O_3 , Al and pure Y-TZP powders are shown in Figure 5-3. It can be seen that all the powders had a narrow particle size distribution. The particle sizes of Al_2O_3 and Y-TZP were about $0.31\mu\text{m}$ and $0.14\mu\text{m}$, respectively. Compared with the pure Al_2O_3 , Al powder had smaller particle size. This was due to the ball milling process that made the ceramic particles finer.

Figure 5-3 Particle size distributions of ceramic powders: (a) pure Al_2O_3 , (b) Al, and (c) pure Y-TZP

5.3 Phase analysis of alumina/zirconia ceramics

The cross-sections of the sintered composite samples were characterized by x-ray diffraction (XRD). Figure 5-4 show the XRD patterns of the composite systems. After sintering at $1600\text{ }^\circ\text{C}$, the alumina/zirconia ceramics exhibited alpha alumina ($\alpha\text{-Al}_2\text{O}_3$) phase, tetragonal ZrO_2 (t- ZrO_2) phase, and minor monoclinic phase. The existence of the monoclinic phase was due to the phase transformation from the tetragonal phase to the monoclinic phase, which was caused by the high zirconia content and the inability of the alumina matrix to suppress the phase transformation, a typical phenomenon in tetragonal zirconia and its composites.

Figure 5-4 XRD patterns of (a)Al, (b)Al_{0.05}Zr, (c) Al_{0.10}Zr and (d)Al_{0.20}Zr samples sintered at 1600 °C for 2 hours (A: α -Al₂O₃ and t: tetragonal t-ZrO₂).

The peak positions (2θ) of Al₂O₃ were at 25.65° (122), 35.2° (104), 37.8° (110), 43.4° (113), 52.6° (024), 57.5° (116), 66.5° (214), and 68.2° (300), respectively. By comparing the accurate 2θ positions of the α -Al₂O₃ phase in the four XRD patterns, it can be seen that there no obvious shift of these peaks. The little or no shift of peak position was understandable as zirconia has a very low solubility (about 0.004-0.027 wt%) in alumina crystals, as reported by Matthew *et al.* [162].

According to the rule of mixtures [64], the relative densitie and Young's modulus of the alumina/zirconia composites could be calculated as follow:

$$\rho_{\text{composite}} = \rho_{\text{alumina}} V_{\text{alumina}} + \rho_{\text{zirconia}} V_{\text{zirconia}} + \rho_{\text{solution}} V_{\text{solution}} \quad (5-1)$$

$$E_{\text{composite}} = E_{\text{alumina}} V_{\text{alumina}} + E_{\text{zirconia}} V_{\text{zirconia}} + E_{\text{solution}} V_{\text{solution}} \quad (5-2)$$

where $\rho_{\text{composite}}$, ρ_{alumina} , ρ_{zirconia} and ρ_{solution} are the relative densities of the composite, alumina, zirconia and solid solution of alumina and zirconia, respectively. $E_{\text{composite}}$,

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E_{alumina} , E_{zirconia} and E_{solution} are the Young's modulus of the composite, alumina, zirconia and solid solution of alumina and zirconia, respectively. V_{alumina} , V_{zirconia} and V_{solution} are the volume fraction of alumina, zirconia and alumina/zirconia solid solution in the composite, respectively.

Due to the low solubility of zirconia in alumina crystals, $V_{\text{solution}} \ll V_{\text{alumina}}$ and V_{zirconia} , the values of $\rho_{\text{solution}}V_{\text{solution}}$ and $E_{\text{solution}}V_{\text{solution}}$ are neglectable. The relative density and the Young's modulus of the alumina/zirconia composites are finally calculated by the equation:

$$\rho_{\text{composite}} = \rho_{\text{alumina}}V_{\text{alumina}} + \rho_{\text{zirconia}}V_{\text{zirconia}} \quad (5-3)$$

$$E_{\text{composite}} = E_{\text{alumina}}V_{\text{alumina}} + E_{\text{zirconia}}V_{\text{zirconia}} \quad (5-4)$$

5.4 Sintering analysis by dilatometry

Figure 5-5 shows the sintering shrinkages ($\Delta L/L_0$) of alumina/zirconia samples with different zirconia contents and heated at a constant heating rate of 5 °C/min. It can be seen that there was no obvious sintering shrinkage at the temperatures below 1050 °C. At the beginning of densification, the shrinkage of the Al sample was higher than those of the zirconia containing samples. The addition of zirconia retarded the early stage sintering of the alumina-based samples. However, after 1465 °C for sample Al05Zr and 1505 °C for sample Al20Zr, the shrinkages of the zirconia containing samples were higher than that of the Al sample. At the end of the sintering, the shrinkages of Al05Zr and Al20Zr samples were 17.8 % and 18.5 %, respectively, higher than that of the Al sample (16.3 %). With the increase of the sintering temperature, a mutual solubility between alumina and zirconia should exist, but the XRD results suggested that the solubility should be very

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little. Nevertheless, the dilute solid solutions could enhance the sintering of the composites. On the other hand, with the increase of the zirconia content, the amount of the zirconia solid solution would increase due to the higher solubility of alumina in zirconia than that of zirconia in alumina [162]. As zirconia is normally easier to sinter than alumina, more zirconia solution than alumina solution in the composite should lead to a higher sinterability of the composite and also a higher sintering shrinkage.

Figure 5-5 Sintering shrinkage versus temperature for (a)Al, (b) Al_{0.5}Zr and (c)Al₂₀Zr samples tested at a heating rate of 5 °C/min.

The sintering behaviour of the samples can be also studied in terms of the sintering shrinkage rate ($d(\Delta L/L_0)/dT$). Figure 5-6 shows the sintering shrinkage rate as a function of the temperature for the alumina/zirconia samples. With the addition of zirconia, a step (flat line segment)) appeared at about 1300 °C, which indicated the retarded sintering of the composites. In present work, the zirconia contents in the composites were 5-20 wt%. Thus, zirconia particles would contact each other to form zirconia clusters. With the increase of the zirconia content, the amount and the size of the clusters would increase. The existence of clusters of an additive was previously reported by J. L. Shi et al. [163].

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During sintering, the zirconia clusters were densified prior to the sintering of the alumina matrix. The different sinterabilities of the zirconia clusters and the alumina matrix could be responsible for the retarded densification of the composites. It is known that the sintering temperature for Y-TZP zirconia is around 1300 °C, whereas that for alumina is around 1600 °C, depending on a few factors such as particle size and particle packing density. Therefore, when the temperature reached 1300 °C, the localized densification of the zirconia clusters did not contribute to the overall densification of the alumina-zirconia composites. Thus the sintering shrinkage rates of the composites did not increase at about 1300 °C. The phenomenon became more obvious with the increase in zirconia content. When the densification of the zirconia clusters was complete, and with the increase of the sintering temperature, the alumina matrix started to be densified, indicated by the increase of the sintering shrinkage rate as shown in Figure 5-6. A maximum shrinkage rate was reached at 1435 °C for Al sample, 1445 °C for Al5Zr sample and 1470 °C for Al20Zr sample. It can also be seen that with the addition of Y-TZP, the relevant samples showed higher maximum shrinkage rates than that of the Al sample. This was due to the formation of the solid solutions between Al_2O_3 and ZrO_2 but with very limited solubilities which could enhance the sintering of the composites, as discussed above.

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Figure 5-6 Shrinkage rate against temperature for (a) Al, (b) Al_{0.5}Zr and (c) Al₂₀Zr samples tested at the heating rate of 5°C /min.

Based on the isotropic shrinkage of the samples, the relative density as a function of temperature for alumina/zirconia ceramics can be calculated. Since the volume and the density of a sample is $V = \pi r^2 L$ and $\rho = m/V$, the time dependent relative density could be

$$\text{expressed as } \rho_t = \left(\frac{r_0}{r_t} \right)^2 \left(\frac{L_0}{L_t} \right) \rho_0. \quad (5-5)$$

where ρ_0, r_0 and L_0 are the initial density, diameter and height of the cylinder sample at time $t = 0$, respectively. ρ_t, r_t and L_t are the density, diameter and height of the cylinder sample at time t , respectively.

$$\text{or } \rho_t = \left(\frac{r_0}{r_0 + \Delta r} \right)^2 \left(\frac{L_0}{L_0 + \Delta L} \right) \rho_0$$

$$\text{or } \rho_t = \left(\frac{1}{1 + \frac{\Delta r}{r_0}} \right)^2 \left(\frac{1}{1 + \frac{\Delta L}{L_0}} \right) \rho_0, \text{ where}$$

$\frac{\Delta r}{r_0}$ and $\frac{\Delta L}{L_0}$ are the radial and longitudinal shrinkages of the cylindrical sample. Due to

the assumed isotropic shrinkage of the samples [164,165], thus $\frac{\Delta r}{r_0} = \frac{\Delta L}{L_0}$

$$\text{The } \rho_t = \left(\frac{L_0}{L_t} \right)^3 \rho_0 \quad (5-6)$$

The relative density as a function of the temperature for alumina/zirconia samples is shown in Figure 5-7. It can be seen that the samples began to densify at about 1120 °C.

When the sintering temperature was slightly higher than 1120 °C, the relative densities of the alumina/zirconia samples were lower than that of Al. At the temperatures above 1465

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°C for Al_{0.5}Zr and 1505 °C for Al_{2.0}Zr, the alumina/zirconia samples had higher relative densities than Al. At the temperature of 1600°C, the relative density was increased to 94 % for Al_{0.5}Zr and 96% for Al_{2.0}Zr, compared to 89.2% for Al.

Figure 5-7 Relative density versus temperature for (a)Al, (b)Al_{0.5}Zr and (c)Al_{2.0}Zr samples tested at the heating rate of 5 °C/min.

Based on the above dilatometry results and other density measurements, the onset sintering temperatures, the maximum shrinkage temperatures, the relative densities at the maximum experimental temperature (1600 °C) of the alumina/zirconia bioceramics are compared in Table 5-2.

Table 5-2 Dilatometry results comparison of the alumina/zirconia bioceramics

	Al	Al _{0.5} Zr	Al _{2.0} Zr
Onset sintering temperature, °C	1120	1085	1063
Maximum shrinkage temperature, °C	1435	1445	1470
Relative density at 1600 °C, %	89.2	94	96

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It can be seen that the onset sintering temperatures of the samples were slightly decreased while the maximum shrinkage temperatures increased with the addition of zirconia. Compared with Al, both Al_{0.5}Zr and Al₂₀Zr achieved rather higher relative densities at the maximum experimental temperature (1600 °C). Al₂₀Zr showed a higher relative density than Al_{0.5}Zr, which is because more solid solutions existed in Al₂₀Zr, which could enhance the sintering of the composites.

The dilatometry results obtained above were used to optimise the isothermal sintering process of the ceramics in an electric furnace. Thus, other samples used for the project were optimally sintered at 1550 °C for 2 hours with the heating rate being 5 °C/min for dense samples and the cooling rate being 5 °C/min.

5.5 Morphological observation of the isothermally sintered alumina/zirconia ceramics

The SEM micrographs in Figure 5-8, Figure 5-9, Figure 5-10 and Figure 5-11 were obtained on the polished and thermally etched surfaces of alumina/zirconia ceramics sintered at different temperature, i.e., 1400 °C, 1550 °C and 1600 °C for 2 hours.

Figure 5-8 shows the effect of sintering temperature on the densification of Al sample without zirconia addition. It can be seen that with the increase of the temperature, the sample was densified and the ceramic grains grew. At the relatively low temperature of 1400 °C as shown in Figure 5-8(a), the microstructure was still porous and composed of fine grains. It was because that the densification was dominated by pore elimination and slow grain growth. This result was in agreement of the dilatometry study in which the maximum shrinkage rate temperatures of the Al sample was 1435 °C. At a higher sintering temperature of 1550 °C, the alumina/zirconia ceramics (Figure 5-8(b)), were

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well densified and the alumina grains did not grow significantly. With further increase of the sintering temperature up to 1600 °C (Figure 5-8(c)), obvious grain growth took place with a grain size of about 3 μm . It is well known that grain growth and densification occur simultaneously as intergranular pores are removed through grain boundary diffusion. With further sintering at a higher temperature, grains would rapidly grow by the coalescence of neighboring grains through grain boundary migration. Moreover, elongated grains larger than 5 μm and faceted with several fine grains were observed in the microstructure. These elongated grains were the result of abnormal grain growth [166]. As the literature [166,167] revealed, on sintering, a few grains would start to grow extremely large by consuming small matrix grains. The phenomenon of abnormal grain growth would adversely affect the further densification of the sample, because the majority of pores are trapped within or between the abnormally grown large grains. Therefore, prevention of abnormal grain growth in the final stage of densification is utmost important to obtain high-density alumina ceramics. In the present work, zirconia additive was used to control the grain growth of alumina ceramics.

Figure 5-9, Figure 5-10 and Figure 5-11 show the microstructural evolutions of alumina/zirconia composites at different sintering temperatures. The light grains in the composites were zirconia and the dark ones were alumina matrix. It is obvious that the microstructures were composed of finer and more homogeneous grains in most regions compared with the Al sample (without zirconia addition) and the zirconia grains were distributed at the grain junctions in the alumina matrix. Additionally, one can notice that some voids were left on the surfaces of the zirconia containing samples due to the peeling of grains occurring during grinding and polishing of the surfaces. It was because the T to M transformation induced residual stresses and microcracking during the grinding and polishing process [61,63].

Compared with the Al sample without zirconia addition (in Figure 5-8), samples with a zirconia content of 5 vol% and sintered at 1400 °C (as showed in Figure 5-9) were much more porous, indicating that the presence of the zirconia phase delayed the initiation of densification. At a higher sintering temperature of 1550 °C, the zirconia/alumina samples exhibited a finer alumina grain size. Thus the zirconia phase hindered both the grain growth of alumina at a high temperature but also retarded the densification of the composite at a low temperature. With further increase of the sintering temperature up to 1600 °C, significant inhibition of the abnormal grain growth was achieved. It can be seen that the addition of zirconia was very effective in inhibiting the grain growth during densification. These results were in agreement with the dilatometer results. In earlier studies, Lange *et al.* [168] and Zhao [167,169] reported the grain-growth hindrance of alumina ceramics by zirconia phase. This particular fact at grain-growth hindrance can be explained by a second-phase pinning effect [170]. In the current study, the alumina/zirconia composites exhibited fine particles (zirconia) in the microstructure. Thus, the zirconia grains functioned as second phase to retard the movement of grain boundaries of the alumina matrix and finally retard the densification of alumina/zirconia composites.

In the zirconia/alumina composite with the 5 vol% zirconia content, zirconia particles were dispersed in four-grain junctions in the alumina matrix and they didn't grow up during sintering due to the suppression of the alumina matrix. On sintering, densification occurred by pore coalescence through grain boundary movement. Since the zirconia phase moved with the alumina four-grain junctions, it exerted a dragging force on the alumina grains and pinned the grain boundary movement, which resulted in the hindrance of the grain growth of the alumina matrix and prevented exaggerated grain growth. With

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the slow down of the grain boundary movement, the rate of the intergranular pore elimination decreased, which caused the delay of the initiation of densification.

With increasing zirconia content, as shown in Figure 5-10 and Figure 5-11, the zirconia particles were less isolated and more continuous and interconnected. These zirconia particles eventually coalesced with each other to form large zirconia agglomerates. It can be seen that the zirconia agglomerates also inhibited the grain growth of alumina matrix. French et al. [171] observed a similar behavior in ZTA (zirconia-toughened alumina) containing a high volume fraction of cubic zirconia and associated it with a grain boundary pinning effect. In the microstructures of the composites with 10-20 vol% zirconia contents, the zirconia agglomerates were located at grain junctions. Thus, the agglomerates resulted in the difficulty in mass transfer throughout the matrix, mainly because of the limited solid solubility between alumina and zirconia, and the long diffusion distance. It was reported that the second phase particle (agglomerate) dragging was more effective than the grain boundary pinning effect on the suppression of grain growth [57-59].

Figure 5-8 SEM micrographs of the Al samples sintered at (a) 1400 °C, (b) 1550 °C and (c) 1600 °C for 2 hours.

Figure 5-9 SEM micrographs of the Al_{0.5}Zr samples sintered at (a) 1400 °C, (b) 1550 °C and (c) 1600 °C for 2 hours.

Figure 5-10 SEM micrographs of the Al10Zr samples sintered at (a) 1400 °C, (b) 1550 °C and (c) 1600 °C for 2 hours.

Figure 5-11 SEM micrographs of the Al₂O₃/ZrO₂ samples sintered at (a) 1400 °C, (b) 1550 °C and (c) 1600 °C for 2 hours.

5.6 Density analysis of alumina/zirconia ceramics

Figure 5-12 shows the densities of alumina/zirconia ceramics as a function of the zirconia content. At the relatively low temperature of 1400 °C, the densities of the samples were decreased at 5 vol% ZrO₂, but increased at higher ZrO₂ contents. For the other two high sintering temperatures, i.e., 1550 °C and 1600°C, the densities of the samples tended to increase with the increasing Y-TZP content. The theoretical densities of the composites can be calculated as follows:

$$\rho_s = \rho_A V_A + \rho_Z V_Z \quad (5-7)$$

$$V_A + V_Z = 1 \quad (5-8)$$

where ρ_s , ρ_A and ρ_Z are the theoretical densities of the composite sample, the pure alumina and the pure zirconia, respectively, and V_A and V_Z are the volume fractions of the pure Al₂O₃ and the pure zirconia, respectively. Here, the theoretical densities of zirconia and alumina are 6.08 x10³ kg/m³ and 3.98 x10³ kg/m³, respectively. Since the solubility is low between alumina and zirconia, thus the theoretical densities of pure alumina and zirconia are used here.

The relative density (ρ^*) for each composite was calculated by the equation 5-9:

$$\rho^* = \rho/\rho_s \quad (5-9)$$

where ρ and ρ_s are the measured densities and the theoretical densities of the composite samples. The effect of zirconia content and sintering temperature on the relative density is shown in Figure 5-12. It can be seen that at the low temperature of 1400 °C, the zirconia - addition decreased the relative density of the samples. The result is in coherence with the

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dilatometry analysis and the microstructural observation. At the first sintering stage, the presence of zirconia phase delayed the densification of samples by inhibiting the grain boundary migration. However at the higher temperatures, i.e., 1550 °C and 1600 °C, the zirconia added ceramics had higher relative densities. HoZhao and Harmer [167] also reported such a result and attributed this beneficial sintering effect to the smaller grain size and associated faster kinetics. It can be explained by the grain growth hindrance of zirconia phase and intergranular pore elimination. The densification of the samples was done by removing the intergranular pores through grain boundary migration. In the final sintering stage, when the mobility of grain boundary is high enough, a few grains may grow by swallowing adjacent fine grains as well as intergranular pores to trap pores. With the grain growth control by zirconia, the abnormal grain growth can be effectively inhibited. Therefore, the samples with zirconia addition exhibited higher relative densities.

Figure 5-12 Dependence of the relative density on the zirconia content of the samples sintered at different temperatures, i.e. 1400 °C, 1550 °C and 1600 °C for 2 hours in air.

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Figure 5-13 shows the influence of zirconia content on the alumina grain size of the alumina/zirconia ceramics sintered at different temperatures of 1400 °C, 1550 °C and 1600 °C. At 1400 °C, the Al sample exhibited a grain size of 0.65 μm , compared to the original particle size of the Al powder (0.2-0.4 μm). With the zirconia addition, there was no obvious grain growth in the samples at 1400 °C. As the dilatometry results showed, Al sample started sintering at 1120 °C and reached a maximum shrinkage rate at 1435 °C. Thus, when sintered at 1400 °C for 2 hours the Al sample was densified and exhibited grain growth. With zirconia addition, the zirconia phase delayed the densification of alumina matrix at the first sintering stage by dragging the alumina grain boundary migration, which caused the finer alumina grain size and higher porosity in the Al0.5Zr, Al1.0Zr and Al2.0Zr compared with those in Al sample. The samples sintered at 1550 °C showed more noticeable grain growth. It can be seen that with increasing zirconia content, the grain sizes of samples did not increase significantly. Zirconia additive showed the effective pinning effect on the grain growth of alumina ceramics. At the temperature of 1600 °C, the additive showed a significant effect in limiting the grain growth. In fact, the grains of Al sample grew to 3.85 μm , and after adding zirconia, the sample exhibited grain sizes of less than 1.5 μm .

Figure 5-13 Dependence of the alumina grain size on the zirconian content in the samples sintered at different temperatures, i.e. 1400 °C, 1550 °C and 1600 °C for 2 hours.

5.7 Mechanical properties of alumina/zirconia ceramics

Figure 5-14 shows the Vickers hardness of the Al, Al05Zr, Al10Zr and Al20Zr samples sintered at 1600 °C for 2 hours. It can be seen that with 5 vol% zirconia addition, the hardness increased. With 5 vol% zirconia, the density of the composite increased from 97.1 % to 99 %. The increase in density would increase the hardness of the composite. On the other hand, due to the lower hardness of zirconia compared (12 GPa) with alumina (about 24 GPa) [172],the hardness of the composite would decrease with zirconia addition. In the composite with 5 vol% zirconia, the effect of density on the hardness was dominated, thus an increase in hardness occurred. However, further addition of zirconia decreased the hardness of the samples. Since the zirconia containing samples at 1600 °C were nearly fully densified (99.0%-99.4%), thus the effect of density could be small. The effect of intrinsic low hardness of zirconia became dominated. Therefore, a high amount of zirconia addition tended to decrease the hardness.

Figure 5-14 Effect of zirconia content on the hardness of alumina/zirconia ceramics sintered at 1600 °C for 2 hours.

Figure 5-15 shows the fracture toughness of the alumina/zirconia ceramics sintered at 1600 °C for 2 hours. It can be seen that with the addition of zirconia, the fracture toughness of the composites increased. For the 5-20 vol% zirconia containing samples, they had densities higher than 99%. Thus the effect of density could not be used to explain the increase of the fracture toughness. The increase of K_{Ic} was thus considered as a result of the well-known transformation toughening effect of the zirconia phase. It is known that the metastable tetragonal zirconia additives which are dispersed in a ceramic matrix will transform to monoclinic form on application of an external tensile stress around a crack tip [53,173]. Such a $t \rightarrow m$ phase transformation, which is accompanied by a volume expansion (about 4 %) and shear strain (about 6 %), will provide a compressive stress which acts to reduce and eventually stop the propagation of the crack. The extent of transformation toughening can be evaluated by the fraction of transformed monoclinic zirconia phase in the alumina/zirconia composites.

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Figure 5-15 Effect of zirconia content on the fracture toughness (K_{Ic}) of the alumina/zirconia composite samples sintered at 1600 °C for 2 hours.

The monoclinic ZrO_2 fractions in alumina/zirconia samples can be calculated using the following equations according to the XRD patterns in Figure 5-4 and listed in Table 5-3.

$$X_m = \frac{I_m(111) + I_m(\bar{1}11)}{I_m(111) + I_m(\bar{1}11) + I_t(111)} \quad (5-10)$$

$$F_m = X_m F_{zirconia} \quad (5-11)$$

where X_m is the monoclinic phase fraction in zirconia, $F_{zirconia}$ and F_m are zirconia fraction and monoclinic phase fraction in the composite sample, respectively. I_m and I_t are the intensity of the monoclinic phase and the tetragonal phase, respectively.

Table 5-3 Monoclinic ZrO_2 fraction in alumina/zirconia samples

Sample	Sintering temperature (°C)	Mono. ZrO_2 (%) (ground and polished)	
		in zirconia (X_m)	in composite (F_m)
Al05Zr	1600	27.5	1.375
Al10Zr		22.5	2.25
Al20Zr		21.9	4.38

Data listed in Table 5-3 indicate that large amounts of tetragonal ZrO_2 (21.9 % -27.5 %) were transformable. It was therefore concluded that transformation toughening mechanism played an important role in the toughening of the composites. An important phenomenon could be observed that the fraction of monoclinic zirconia phase to total zirconia decreased from 27.5 % in Al05Zr to 21.9 % in Al20Zr when the volume fraction of zirconia increased in the composites. The trend is in agreement with that reported by

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Huang et al [55]. It can be explained as the addition of zirconia increased the relative density of the composite. Higher degree of densification is beneficial to retain tetragonal ZrO_2 at room temperature. However, with increasing zirconia content, the fraction of monoclinic zirconia phase in composite samples increased from 1.375 % in Al05Zr to 4.38 % in Al20Zr. The higher fraction of monoclinic zirconia phase indicates that the composite was toughened to a higher extent. Therefore, the increase of fracture toughness of the composites was accompanied by the increasing zirconia content.

After fully densified at 1550 °C for 2 hours, the alumina/zirconia composite ceramics could reach their own optimal microstructure and mechanical properties. According to the results from the microstructural observation and the mechanical testing, the microstructure and the mechanical properties of alumina/zirconia composite ceramics are summarized in Table 5-4.

Table 5-4 Microstructure and mechanical properties of alumina/zirconia composites sintered at 1550 °C for 2 hours.

Samples	Al	Al05Zr	Al10Zr	Al20Zr
Grain size, μm (alumina grains)	0.93	0.75	0.62	0.6
Relative density, %	97.1	99	98.5	99.3
Hardness, GPa	22.12	22.65	21.89	20.63
Fracture toughness, $\text{MPam}^{1/2}$	4.32	4.63	4.77	4.88

One can find that with the addition of zirconia, the alumina/zirconia ceramics exhibited finer grain and improved mechanical properties.

The addition of zirconia improved the microstructure of alumina/zirconia composites such as grain size and grain size distribution, and subsequently caused the improvement

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in relative density and mechanical properties. Compared with Al, zirconia containing samples exhibited higher relative density and higher fracture toughness. The hardness of the alumina/zirconia composites increased at a low zirconia content (<5 vol%) due to the improvement of microstructure. With the addition of more zirconia, the mechanical properties of zirconia itself would affect those of the composites. Due to the low hardness of zirconia i.e. 12.2 GPa [46], at a higher zirconia content (>5 vol%), the hardness of the composites decreased with increasing zirconia content.

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6.1 Introduction

It is known that for bone ingrowth and new bone formation in porous structures, interconnected pores with a pore diameter bigger than 150 μm is required [13,15]. The mechanical properties of the porous structures are also important and are affected by the pore characteristics such as pore size, pore shape and porosity. In this chapter, a vacuum infiltration method which was optimized in chapter 4 was used to fabricate the porous ceramic structures. Spherical expanded polystyrene (EPS) beads were used as a pore former to control the pore size and the porosity of the porous structure. Uniform porous structures with various pore sizes and porosities were developed. The pore structures and the microstructures of the porous Al and Al10Zr ceramics were studied. The effects of the pore size on the mechanical properties were also discussed.

6.2 Structural observation of the porous alumina/zirconia ceramics

In the present forming technique, the pore size of the porous Al ceramics was controlled by the size of the EPS beads used. Figure 6-1 shows the porous structures of the porous Al ceramics with average pore sizes from 1.21 mm to 2.09 mm. The different pore sizes were obtained using EPS beads of different size ranges, that is, 1.40 mm-1.70 mm, 1.70 mm-2.00 mm, 2.00 mm-2.36 mm, and 2.36 mm-2.80 mm. The spherical macropores were basically interconnected by much smaller pore windows. However, the morphology of the porous structure with the pore size of 1.21 mm (Figure 6-1 (d)) exhibited non-uniform pore and pore window distributions compared with other porous structures. This resulted

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from the packing of the EPS beads. Due to the light weight of the EPS beads, the smaller the EPS beads, the more static-electronic effect existed. During the fabrication process, the EPS beads with a smaller size tended to pack in a random pattern and part of the EPS beads did not contact other beads, resulting ununiformly distributed pores and isolated pores.

Figure 6-1 Stereo-zoom optical micrographs showing the porous Al ceramics sintered at 1550 °C for 2 hours using different EPS bead sizes: (a) 2.36 mm-2.80 mm, (b) 2.00 mm-2.36 mm, (c) 1.70 mm-2.00 mm, and (d) 1.40 mm-1.70 mm.

In the fabrication process, the porous structures were fabricated by slurry infiltration through deformed EPS bead templates with a strain of 10 %, followed by burning off the EPS beads, and final sintering. It was inevitable that the pore sizes of the sintered bodies

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were not exactly the same as the original EPS bead sizes. Here, three types of pore sizes, that is, initial EPS bead size in the green compact of the EPS beads and the ceramic particles, the pore size in the porous green compact but after burning off the EPS beads and the sintered pore size in the finally sintered body, were considered.

For EPS beads deformed at a strain of 10 % (assuming isotropic shrinkage,) to form a porous EPS template, the initial pore size (D_{initial}) or the deformed EPS bead size can be calculated as follows:

$$D_{\text{initial}} = D_{\text{EPS}} (1 - \varepsilon) \quad (6-1)$$

where D_{EPS} is the EPS bead size and ε (=10 %), is the strain of the deformed EPS template.

The EPS beads were burnt out by heating the samples to 500 °C in air. During heating, EPS beads would expand initially and possibly only slightly, as the EPS beads were porous already. However, the glass transition temperature of the EPS polymer is typically around 240 °C, thus EPS beads started to collapse above the T_g and formed a viscous residual. Slight expansion may occur in the viscous residual due to the evaporation of the residual pentane. Subsequent increase of the temperature led to decomposition or burning of the polymer. The expanded size of the EPS beads can be calculated using the thermal expansion coefficient (α). The pore size of the porous compact after burning is assumed to be similar to the expanded size of the EPS beads and can be calculated by the following equations:

$$\Delta D = \alpha \cdot \Delta T \cdot D_{\text{initial}} \quad (6-2)$$

$$D_{\text{green compact}} = D_{\text{initial}} + \Delta D \quad (6-3)$$

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where ΔT is the temperature change from room temperature (25 °C) to 240 °C, ΔD is the increase in the diameter of the EPS bead after expansion, α is the thermal expansion coefficient of the EPS bead equals to $35 \times 10^{-6} \text{ K}^{-1}$ as given by the manufacturer.

The calculated initial pore size or the deformed EPS bead size, the pore size in the porous green compact after burning and the pore size after sintering are listed in Table 6-1. It can be seen that the average macropore sizes of the sintered bodies were smaller than those of the green compacts with and without burning. Thus the final pore size of the sintered bodies became smaller with the shrinkage of the ceramic networks. The pore size shrinkage of the porous Al samples during sintering was calculated and plotted in Figure 6-2. The pore size shrinkages range between 12.5 % to 14.8 %, which were comparable with the shrinkage of the whole samples of 15.8 %. However, as mentioned in Chapter 5, the size shrinkage of the dense Al bodies after sintering at 1550 °C for 2 hours was about 18.3 %. The lower sintering shrinkage of the porous bodies suggested that the existence of the macropores somehow limited the densification of ceramic networks. The same phenomenon was observed by Bose [106]. The macropores in the porous structures resulted in a low overall density (for the whole porous structure, not the struts) and with the presence of the macropores, the sintering shrinkage of the struts could also be restricted by the neighbouring struts.

Table 6-1 Data of different ‘pore’ sizes for the porous Al samples

Samples	EPS bead used (mm)	Initial pore size (mm)	Burned out pore size (mm)	Sintered pore size (mm)
a	2.63-2.80	2.12-2.52	2.14-2.54	2.09
b	2.00-2.63	1.80-2.12	1.81-2.14	1.68
c	1.70-2.00	1.53-1.80	1.54-1.81	1.47
d	1.40-1.70	1.26-1.53	1.26-1.54	1.21

Figure 6-2 Pore size shrinkages of the porous Al samples with EPS beads of different size ranges after sintering at 1550 °C for 2 h. EPS size ranges: (a) 2.63 mm-2.80 mm, (b) 2.00 mm-2.63 mm, (c) 1.70 mm-2.00 mm, and (d) 1.40 mm-1.70mm.

Figure 6-3 shows the SEM micrograph of the porous structure of the porous pure alumina ceramic. The porous structure was composed of spherical macropores, open windows to interconnect the macropores and slender ceramic struts. The pore windows were about 250-300 μm in diameter. The surfaces of the macropore walls were rather rough, due to the coarse surfaces of the EPS beads.

Figure 6-3 SEM micrograph showing the porous structure of the porous Al ceramics prepared using the EPS beads with a size range of 2.00-2.63 mm being sintered at 1550 °C for 2 h.

In our study, zirconia was also added to the alumina ceramics to inhibit grain growth of the alumina matrix. Figure 6-4 shows the thermally etched surfaces of the struts in the porous Al and the porous Al10Zr samples. Figure 6-4 (a) shows the microstructure of the Al struts. The grain size was about 3-4 μm . Some large elongated grains existed indicating the abnormal grain growth. And a large amount of microspores can be observed on the grain boundaries and in the interior of the grains. Figure 6-4 (b) shows the struts of the porous Al10Zr sample. With the addition of the zirconia, the alumina grain size was reduced greatly to about 1-2 μm . No abnormal grain growth was observed. The porosity in the microstructure was also reduced.

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(a)

(b)

Figure 6-4 SEM micrographs of the struts of the porous structures: (a) Al sample and (b) Al10Zr sample.

Figure 6-5 shows the microstructure of the pore walls in the porous structures with different additives. As shown in the low magnification micrographs in Figure 6-5 ((a) and (c)), the surfaces of the pore walls were very rough. Under a higher magnification shown in Figure 6-5 (b) and (d)), the pore walls revealed the grains that were packed together and formed the coarse surfaces in a microscale. In the porous alumina ceramics, the

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addition of zirconia hindered the grain growth of the alumina grains and improved the final densification of the struts, which is in agreement of the results shown in Chapter 5. However, due to the low green density of the green struts compared with that of the green compact without EPS beads, it was difficult to obtain fully densified struts even with the zirconia addition. With the zirconia addition, the microstructure of the ceramic struts was improved. Moreover, the ceramic struts would be toughened by the zirconia additive through a transformation toughening mechanism. Thus, an improvement in mechanical strength of the struts would be expected which would result in a higher mechanical strength of porous bodies. The mechanical properties of porous structures will be further discussed in the following sections.

Figure 6-5 SEM micrographs of the pore walls of the porous structures with different compositions: (a) and (b) Al; (c) and (d) Al₁₀Zr.

6.3 Porosity analysis of porous alumina/zirconia ceramics

Porosity is one of the most important porous parameters used to characterize the porous materials. For porous bioceramics, the total porosity and the open porosity are of great interest. The total porosity describes the total pore volume fraction in a porous structure, whereas the open porosity indicates the open pore volume fraction in a porous structure. A porous scaffold with a high open porosity is required for bone ingrowth, although a high total porosity decreases the mechanical properties of the porous scaffold. In the fabrication process, the packing method of the EPS beads, the EPS size, and the applied load to deform the EPS beads could all affect the total porosity and the open porosity of the porous scaffolds.

Figure 6-6 shows the total porosities and the open porosities of porous Al ceramics with different average pore sizes. These samples were prepared under the same deformation strain of the porous EPS templates, i.e., 10% and were sintered at 1550 °C for 2 hours. It can be seen that with the increase of the pore size, the total porosity did not change significantly and varied from 61.89 % to 64.82 % and the open porosity of the porous structures increased from 48.32 % to 52.33 %.

Figure 6-6 Relationship between the average pore size and the total porosity (a) and the open porosity (b) of the porous Al ceramics prepared using the porous EPS templates deformed at a strain of 10 % with different EPS bead sizes of 1.40 mm-1.70 mm, 1.70 mm-2.00 mm, 2.00 mm-2.36 mm, and 2.36 mm-2.80 mm. Samples were sintered at 1550 °C for 2 hours.

The unchanged total porosity can also be explained by EPS stacking. In our study, EPS beads were packed to form the closest array. A face centered cubic unit cell can be the basis of the three dimensional EPS bead array as shown in Figure 6-7. The unit cell has 4 EPS beads (1/8 EPS bead at each corner and 1/2 EPS bead on each face). In the face centered cubic unit cell, EPS beads touch across the face diagonal as shown in Figure 6-8.

Figure 6-7 Schematic of the close packing of the EPS beads in a two-dimensional view (a) and a three-dimensional view (b).

Figure 6-8 Face centered cubic with the face diagonal being equal to $4r$, where r is the radius of EPS bead.

Thus, the volumes of the unit cell, V_{cell} , the EPS bead, V_{EPS} , and the volume fraction of the EPS beads in the unit cell can be calculated as follows:

$$a = \frac{\sqrt{2}}{2} \times \text{length of diagonal} = \frac{\sqrt{2}}{2} \times 4r = 2\sqrt{2}r \quad (6-4)$$

$$V_{\text{cell}} = a^3 = 16\sqrt{2}r^3 \quad (6-5)$$

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$$V_{EPS} = 4 \times \frac{4}{3} \pi r^3 = \frac{16}{3} \pi r^3 \quad (6-6)$$

$$\text{Volume fraction of the EPS beads} = \frac{V_{EPS}}{V_{cell}} \times 100\% = 74\% \quad (6-7)$$

With the increasing size of the EPS beads, the dimensions of the cell unit increase. However, the volume fraction of the EPS beads is not related to the dimensions of the cell unit and the radius of EPS beads. Therefore, the total porosity of the porous ceramics is constant. In actual porous structures, the total porosities were 61.89 % to 64.82 %, which were smaller than the theoretical one, 74 %. This is because part of EPS beads did not pack in the closet pattern due to the static electronic forces between EPS beads and other factors.

Figure 6-9 shows the calculated pore interconnectivities of the porous structures with different average pore sizes. The porous structures had high pore interconnectivities ranging from 78.07 % to 84.60 %. It can be seen that the pore interconnectivity of the porous structures increased slightly with the increase of the average pore size. In an ideal condition, in which EPS beads are uniformly packed and contact each other and the ceramic particles fill the interstices of the EPS bead template fully, the pores in the obtained porous body should be totally open ones and the pore interconnectivity should be nearly 100%. However, due to the existence of static electronic forces between EPS beads, the ideally packed EPS bead template is impossible to achieve. Some EPS beads did not contact other beads and finally resulted in closed pores. With the increase of the EPS bead size, the effect of the static electronic force became smaller. Thus, the EPS beads could be packed more uniformly and the resultant porous structures could have less isolated pores and higher pore interconnectivity. Moreover, with the decrease of the EPS bead size, the pathway for the ceramic slurry to infiltrate became narrower and the

difficulty in slurry infiltration increased. The isolated voids due to incomplete infiltration could also decrease the pore interconnectivity of the porous structures.

Figure 6-9 Relationship between the average pore size and the pore interconnectivity of the porous alumina ceramics prepared at 10 % of the strain of the porous EPS templates with different bead sizes of 1.40 mm-1.70 mm, 1.70 mm-2.00 mm, 2.00 mm-2.36 mm, and 2.36 mm-2.80 mm. The samples were sintered at 1550 °C for 2 hours.

6.4 Mechanical properties of the porous alumina/zirconia ceramics

Figure 6-10 and Figure 6-11 show the compressive strength and the compressive modulus of the Al and Al10Zr samples as a function of the average pore size, respectively. For the porous alumina ceramics and the porous composites with the porosities from 61.89 % to 65.93 %, and the pore sizes from 1.21mm to 2.63mm, the porous Al ceramics had 7.92 MPa to 5.33 MPa in compressive strength and the Al10Zr composites had 8.12 MPa to 5.73 MPa. In addition, the compressive modulus varied from 1.7 GPa to 1.5 GPa for the porous Al ceramics and 1.82 GPa to 1.58 GPa for the porous Al10Zr composites. It can be seen that for all the porous structures the compressive strength and the compressive

modulus decreased with the increase of the average pore size. The compressive strengths were comparable to those of cancellous bones, ranging from 2 to 12 MPa [1,7].

Figure 6-10 Dependence of the compressive strength on the average pore size of the porous Al ceramics and the porous Al10Zr ceramic composites prepared using the EPS beads of different sizes of 1.40 mm-1.70 mm, 1.70 mm-2.00 mm, 2.00 mm-2.36 mm, and 2.36 mm-2.80 mm. The samples were sintered at 1550 °C for 2 hours.

Figure 6-11 Dependence of the compressive modulus on the average pore size of the porous Al ceramics and the porous Al10Zr ceramic composites prepared using the EPS beads of different sizes of 1.40 mm-1.70 mm, 1.70 mm-2.00 mm, 2.00 mm-2.36 mm, and 2.36 mm-2.80 mm. The samples were sintered at 1550 °C for 2 hours.

6.4.1 Effect of zirconia addition on the mechanical properties

It can be observed that with the addition of zirconia, the mechanical strength of the porous composite scaffolds increased. The effect of zirconia addition on the mechanical strength can be attributed to these two mechanisms. Firstly, the addition of zirconia inhibited the grain growth of the alumina matrix and enhanced the density of the composite. Thus the flaws which caused the failure of the materials were reduced. Secondly, zirconia additive could toughen the alumina matrix through the transformation toughening mechanism. According to the Gibson-Ashby model [108], the bending fracture of the struts causes the failure of a porous structure. Therefore, reinforcing the ceramic struts can enhance the mechanical strength of the porous structure. The Griffith's fracture theory [174] describes the fracture of a brittle material as the result of the propagation of a crack. The fracture strength could be expressed as:

$$\sigma_f = \frac{K_{Ic}}{y\sqrt{\pi a}} \quad (6-8)$$

where K_{Ic} is the fracture toughness which is a constant for a certain material, y is a geometrical constant, and a is the crack size or flaw size.

With the addition of zirconia, the microstructure of the ceramic struts was featured with smaller grain size and less porosity compared with those of the Al sample as shown in

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Figure 6-4. Since the micropores in the struts were the defects and the origins of failure, it is obvious that the less and smaller the micropores, the higher the mechanical strength. Therefore, in current study, zirconia additive improved the microstructure of the ceramic struts and enhanced their mechanical strength, and finally resulted in a strengthened porous structure.

Moreover, the ZrO_2 additive had a significant T-M transformation toughening on the alumina matrix as discussed in Chapter 5. When the metastable tetragonal zirconia additives which are dispersed in a alumina matrix transform to their thermodynamically stable monoclinic form, a volume expansion of 4 % occurs [176]. The phase transformation will provide a compressive stress which acts to reduce and eventually stop the crack propagation.

6.4.2 Effect of porosity on the mechanical properties

Figure 6-12 and Figure 6-13 show the effects of porosity on the compressive strength and compressive Young's modulus of the porous alumina/zirconia ceramics. One can see that for the porous Al ceramics with porosity from 61% to 65%, the compressive strength varied from 7.92 MPa to 5.33 MPa and the compressive Young's modulus varied from 1.7 GPa to 1.5 GPa. For the porous Al10Zr ceramics with porosity from 61% to 65%, the compressive strength varied from 8.12 MPa to 5.73 MPa and the compressive Young's modulus varied from 1.82 GPa to 1.58 GPa. These mechanical properties data were significantly lower than those of the dense Al and Al10Zr (4000 MPa and 400 GPa for dense alumina and 3800 MPa and 375 GPa for dense Al10Zr, respectively). It can be seen that porosities greatly reduced the mechanical properties of alumina/zirconia ceramics. Similar results were also reported by other researchers [100, 102]. Moreover, the compressive strength and the compressive Young's modulus decreased with the increase

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of the porosity. The low mechanical properties of the porous alumina/zirconia ceramics are important for bone implantation applications. The mechanical properties of the dense alumina ceramics (4000 MPa for compressive strength and 400 GPa for compressive Young's modulus) are much higher than those of the cancellous bones (1-100 MPa for compressive strength and 1-2 GPa for compressive Young's modulus, as presented in Table 2-1). Therefore, the dense alumina implant would cause stress shielding in the host bone and make the bone less dense and weaker. In this study, the mechanical properties of these porous Al and Al10Zr ceramics were comparable to those of the cancellous bones. It provides the potential for the porous alumina/zirconia ceramics to serve as bone implants.

Figure 6-12 Compressive strength versus porosity for porous Al and Al10Zr samples sintered at 1550 °C for 2 hours

Figure 6-13 Compressive Young's modulus versus porosity for porous Al and Al10Zr samples sintered at 1550 °C for 2 hours

The strength-porosity dependence is expressed by Rice [107] using the following equation:

$$\sigma = \sigma_0 \exp(-bP) \tag{6-9}$$

where σ is the mechanical strength at the porosity P ; σ_0 is the mechanical strength of dense struts, and b is related to the pore characteristics, such as pore shape and pore size. A fitting of compressive strength of porous Al and Al10Zr samples versus porosity to Rice's equation (6-9) is shown in Figure 6-14. Table 6-2 lists the parameters for the curve fitting of Al and Al10Zr samples. The corresponding correlation factor r^2 is also presented in the table.

Figure 6-14 Rice’s model fitting of the porosity-strength dependence for porous Al and Al10Zr samples sintered at 1550 °C for 2 hours

Table 6-2 Parameters (σ_0 and b) determined for equation 6-9 to fit the compressive strength-porosity relationship of Al and Al10Zr ceramics

	σ_0 (MPa)	b	r^2
Al	3560	0.10	0.87
Al10Zr	3655	0.13	0.79

The relationship between compressive Young’s modulus and porosity is described as follows:

$E = E_0 \exp(-b'P)$ (6-10)

where E is the compressive Young’s modulus at the porosity P ; E_0 is the compressive Young’s modulus of the dense struts, and b' is related to the pore characteristics, such as pore shape and pore size. Figure 6-15 shows the fitting curve of the Young’s modulus of porous Al and Al10Zr samples versus porosity. Table 6-3 lists the parameters for the curve fittings.

Figure 6-15 Rice's model fitting of the porosity- compressive Young's modulus dependence for porous Al and Al10Zr samples sintered at 1550 °C for 2 hours

Table 6-3 Parameters (E_0 and b') determined for equation 6-10 to fit the compressive Young's modulus-porosity relationship of Al and Al10Zr ceramics

	E_0 (GPa)	b'	r^2
Al	181	0.04083	0.01077
Al10Zr	222	0.04572	0.05930

The predicated theoretical compressive strengths and compressive Young's modulus of the struts for the curve fitting were lower than reported values of, 4000 MPa and 400 GPa for dense alumina (as presented in Table 2-3) [39, 46] and 3800 MPa and 375 GPa for dense Al10Zr (calculated using the rule of mixture), respectively. In Rice's model, the struts in the sample are fully sintered and defects free. During the current fabrication of porous bodies, the presence of defects in the struts might result in the lower values obtained for the compressive strength and the compressive Young's modulus. Liu [117] also reported low compressive strengths and flexural strength fitted using Rice's model for macroporous HA ceramics.

6.4.3 Effect of pore size on the mechanical properties

In this study, with the change of the size of the EPS beads, the pore size of the porous structures changed, while the total porosity of the porous structure did not change significantly. Thus, only the effect of the pore size on the mechanical properties of the porous alumina/zirconia ceramics is discussed here.

From the results of the compressive strength and the compressive modulus in Figure 6-10 and Figure 6-11, it can be found that the compressive strengths and the compressive modulus decreased with the increasing pore size of the porous structures. Liu [175] reported a similar compressive strength-pore size relationship in porous hydroxyapatite (HA). Gibson and Ashby [108,109] built a model to evaluate the porosity dependence of mechanical properties using a ideal cell unit. The break-down of the porous structure is attributed to the bending of the cell walls. Although the pore structures prepared in this study were different from foams in the Gibson-Ashby model, a similar model can be built to discuss the pore size effect. The pore structure can be idealized as stacked porous cubic cells with spherical pores as shown in Figure 6-16. The cell edges in this study were not as uniform as those in the Gibson-Ashby model. The porous structure failure means that the fracture begins at the most slender part of the cell edges as shown in Figure 6-17.

Figure 6-16 Schematic of a unit cubic cell (a) and an assembly of stacked porous cubic cells (b).

When the force, F , is applied on the porous structure, the dense strut transfers the load. Thus, a single unit cell will experience the compressive force at the centre of the cell edge. The cell edge is subjected to a tensile stress in the pore surface. The stress concentrated at the crack tip (as shown in Figure 6-17) of the pore surface results in the failure of the unit cell.

Figure 6-17 Tensile stress concentration mechanism for a porous structure under a compressive load in a unit cell of the porous structure (2D)

For the porous structures with the same porosity, when the pore size increased due to larger EPS beads used, the dimension of the struts also changed. As shown in Figure 6-13, when the pore size was larger, the cell edges (struts) became slender and longer and thus could be bended to fracture more easily. Thus, the increase of the pore size weakened the porous structure and resulted in the decrease of the compressive strength as well as the compressive modulus.

6.4.4 Failure analysis based on the MSA model

A minimum solid area (MSA) model reported by Rice [107] can be used to describe the properties of porous materials. In this model, porous structures may be idealized as a regular stacking of cells having regular shapes such as cubes or spheres. The minimum solid areas are the bond area between the idealized stacked particles in the model, and correspond to the solid cell walls/edges in actual materials as shown in Figure 6-18. Obviously, the minimum solid area is the controlling factor of the properties of porous materials because these areas dominate the transmission of stress throughout the body.

Figure 6-18 Schematic illustration of the minimum solid area (MSA) for stress (P) transmission in a porous structure.

Based on the MSA model, the failures of porous structures are controlled by the minimum solid areas corresponding to the ceramic struts. Figure 6-19 shows an ideal cross-section in the porous structure under compression. The porous structure failure means that the fracture begins at the most slender part of the struts. When the force, F , is applied on the porous structure, the dense struts transfer the load. In the struts, two kinds of load conditions take place as shown in Figure 6-19 (a) and (b). The struts in the oblique direction are the type (a) and experienced the bending action. The failure of the bended struts (due to tensile stresses) will result in the failure of the porous structure. The struts in the normal direction (type (b)) experience the compressive force, which causes densification or packing of the porous body during the collapse of the struts. When the pore size increased, the struts would become slender, as discussed above. Clearly, a slender strut could bear lower load than a thicker one. Thus the mechanical properties of the porous alumina ceramics with a larger pore size decreased.

Figure 6-19 Failure mechanism for a porous structure under compressive load. An ideal cross-section in the porous structure.

Figure 6-20 shows the compression curves of the porous pure alumina samples with different average pore sizes of 2.09 mm, 1.68 mm and 1.21 mm. It can be seen that all the curves exhibited two major stages: (I) At the beginning of the compression, a linear elastic behavior was observed. This linear elastic curve was used to determine the compressive modulus of the porous alumina (Note: you need to use stress and strain). (II)

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After the maximum load or the point of fracture, a zig-zag fluctuation occurred. The zig-zag fluctuations of the three samples were slightly different. The porous structures with larger pore sizes (such as 2.09 mm) showed great fluctuation, which is because they had much weaker struts. The curves of the porous structures with smaller pore sizes (such as 1.68 mm and 1.21 mm), had slight fluctuation.

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Figure 6-20 Load-displacement compression curves of the porous pure alumina samples with different average pore sizes of (a) 2.09 mm, (b) 1.68 mm and (c) 1.21 mm.

The MSA failure mechanism is also used to explain the zig-zag fluctuation in the compression curves of porous pure alumina ceramics. In the compression test, the initial stage of the curve was associated with the misalignment of the sample and the gap between the cross-head and the sample. It was followed by a linear elastic region which was due to the deformation of the struts. When the stress in the struts exceeded a critical point, the porous ceramic structure broke and the stress fell suddenly. After that, the opposing pore walls would touch each other and further strain made the fractured solids compressed, leading to the final increase of the load due to compaction. When the load reached to a certain level, the porous structure would collapse again and again. Thus the zigzag fluctuation took place.

Chapter 7 Sol-gel Bioactive Glasses and Their Coating on Porous Alumina/Zirconia Ceramics

7.1 Introduction

Bioactive glass coatings have widely been applied to alumina [176], zirconia or their composite substrates [177,178]. The bioactivity of bioactive glasses is also superior to that of HA. Melt-derived bioglass® 45S5 (45 wt% SiO₂, 24.5 wt% Na₂O, 24.5 wt% CaO and 6 wt% P₂O₅) has been well studied [179,180]. Recently, a group of glasses with the components of SiO₂-CaO- P₂O₅ has been developed using a sol-gel technique [181]. These glasses exhibit high specific surface areas and excellent bioactivity. Compared with the melt-derived 45S5 bioactive glass, the sol-gel bioactive glasses have the advantages of low synthesis temperature and high compositional homogeneity.

In our project, a series of sol-gel bioactive glasses was prepared for use as coating materials to increase the surface bioactivity of the porous alumina/zirconia ceramics. The study was focused on synthesis, microstructural evolution and bioactivity of the sol-gel bioactive glasses. Finally, the bioactive glass-coated porous alumina/zirconia ceramics were also studied.

7.2 Characterization of sol-gel bioactive glasses

The XRD patterns of three powders are shown in Figure 7-1. No diffraction peak was observed and only a broad band between 20° and 40° was detected. It indicates the amorphous nature of the sol-gel bioactive glass powders. The particle morphologies of

the as prepared 58S33C sol-gel bioactive glass powders were shown Figure 7-2. The bioactive glass powder contained small particles of 50-100nm in size. The glass powder had a high level of agglomeration.

The characteristics of the powders are summarized in Table 7-1. It shows that the sol-gel bioactive glass powders had a porous structure and with a large surface area. The three glasses showed a pore size in the mesopore range (2-50 nm). The average pore size decreased from 8 nm to 2 nm as the silica content increased from 58 % to 77 %. Also the BET surface area increased with the increase of the silica content. This porous nature of the sol-gel powder was not owned by the melt-derived bioactive glass powders.

Figure 7-1 XRD patterns of the sol-gel bioactive glass powders with different compositions calcined at 700 °C.

Figure 7-2 TEM micrographs showing the morphologies of the 58S33C sol-gel bioactive glass powders calcined at 700 °C.

Table 7-1 Characteristics of the sol-gel bioactive glass powders calcined at 700 °C

Characteristics	Glasses		
	58S33C	68S23C	77S14C
Surface area (m ² /g)	164	191	545
Pore volume (cm ³ /g)	0.33	0.32	0.31
Average pore size (nm)	8.143	6.762	2.472

7.3 Crystallization of sol-gel bioactive glasses

Figure 7-3 shows the DSC curves of the sol-gel bioactive glass powders with different compositions in the temperature range from the room temperature to 1200 °C using a heating rate of 10 °C/min. All the curves exhibited an exothermal peak indicating the crystallization. The crystallization occurred at the temperatures of 935 °C, 951 °C and 977 °C for the 58S33C, 68S23C and 77S14C samples, respectively. It can be seen that the

crystallization temperature of the bioactive glasses was dependent on the composition, and increased with the decrease of the calcium content.

Figure 7-3 Differential scanning calorimetry (DSC) curves of the three bioactive glass powders calcined at 700°C.

Here the sol-gel derived 58S33C bioactive glass was used as an example to study the crystallization. Figure 7-4 shows the XRD patterns of the 58S33C sol-gel derived bioactive glass powder and the samples sintered at different temperatures, i.e., 800 °C, 1000 °C, and 1200 °C. The sol-gel derived 58S33C bioactive glass powder was amorphous in nature. The sample sintered at 800°C was still in the amorphous state. This result was in agreement with the DSC result shown in Figure 7-3. The crystallization of 58S33C bioactive glass occurred in the temperature range of 910-960 °C. After the samples were sintered at higher temperatures, i.e. 1000 °C and 1200 °C, there existed the crystalline phase, i.e. wollastonite (JCPDS card: No. 43-1460). With increasing

temperature, the peaks became sharper (based on the half height width of each peak), indicating a higher level of crystallization

Figure 7-4 XRD patterns of the 58S33C sol-gel bioactive glass sintered at different temperatures: (a) as-calcined glass powder, (b) 800 °C, (c) 1000 °C, and (d) 1200 °C (W: wollastonite).

Figure 7-5 shows the back scattered electron (BSE) micrographs of the 58S33C samples sintered at 1200 °C for 1 hour and for 2 hours. Two phases existed in the micrographs. The grey phase was the glass phase and the bright one was the crystalline phase. It can be seen that the crystalline phase grew within the glass matrix into dendrites. The area ratio of the glass phase to the crystalline phase from the micrographs in Figure 7-5 (a) and (c) was used to evaluate the crystallization degree of the 58S33C bioactive glass. There was about 65 % crystalline phase in the sample sintered at 1200 °C for 1 hour, and there was more than 85% crystalline phase in the sample sintered at 1200 °C for 2 hours. It can be concluded that higher sintering temperature and longer sintering time resulted in higher degree of crystallization in the 58S33C bioactive glasses. Because the glass phase was less corrosion resistant than the crystalline phase [182], the glass phase tended to be

etched when soaked in the HCl solution. From Figure 7-5 (b) and (d), it can be seen that some porosity was left in the crystalline phase due to the removal of the glass phase.

Figure 7-5 BSE micrographs of the 58Si33C samples: (a) sintered at 1200 °C for 1 hour, (b) sintered at 1200 °C for 1 hour and etched in 1N HCl for 5 minutes, (c) sintered at 1200 °C for 2 hours, and (d) sintered at 1200 °C for 2 hours and etched in 1N HCl for 5 minutes.

Figure 7-6 shows the FESEM micrograph of the 58S33C bioactive glass sample sintered at 1200 °C for 1 hour. It can be seen that a high level of porosity was present and could be due to the melting and penetration of the glassy phase. Figure 7-7 shows that at temperatures below 1000 °C, the bulk density of the samples increased with the increase of temperature. However, higher sintering temperatures resulted in the decrease of the

bulk density of the samples. It is known that the crystallization temperature of the 58S33C was about 935°C. Thus, during the heating process and at the temperatures below this crystallization temperature, the samples were densified via the viscous sintering of the glass phase. The viscous sintering of glass was reported by other researchers [183,184]. Thus the density of the samples increased with the increase of the sintering temperature. However, at the sintering temperature of 1200 °C, crystallization took place before full densification. The residual glass phase became a viscous liquid and tended to be redistributed among the crystalline phase. The small amount of the viscous flow did not fill the available pores or spaces among the formed crystals. Thus, the bioactive glass sample showed a high level of residual porosity and a low bulk density as shown in Figure 7-6. To get a dense glass-ceramic, one needs to control the densification and the crystallization processes during the sintering. The samples should be densified at the temperatures lower than the crystallization temperature, followed by heating to a higher temperature to allow the crystallization.

Figure 7-6 FESEM micrograph of the 58S33C bioactive glass sample sintered at 1200 °C for 1 hour.

Figure 7-7 Influence of the sintering temperature on the density of the 58Si33C bioactive glass samples.

7.4 Effect of composition on the bioactivity of the sol-gel bioactive glasses

7.4.1 Surface microstructural evolution of the sol-gel bioactive glasses due to SBF immersion

Figure 7-8 shows the morphologies of the apatite layers on the 58S33C green pellets(or calcined powder but without sintering). Figure 7-8 (a) shows the morphology of the bioactive glass green pellet before soaking in SBF. After 0.5 hour of soaking (Figure 7-8 (b)), there was still no apatite layer formation on the surface of the sample. However, it can be seen that the soaked surface was rich in the Si content due to the leaching of the Ca ions. With the increase of the soaking time, the newly formed Si-rich layer was covered with an apatite layer (as shown in Figure 7-8 (c) and (d)). Figure 7-8 (e) reveals the formation of a fairly dense apatite layer after 1 week of soaking.

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Figure 7-8 SEM micrographs and EDS spectra of the surfaces of the green compact of the as-calcined 58S33C powder (a) before soaking, and after soaking in SBF for different times: (b) 0.5 hour, (c) 1 hour, (d) 1 day, and (e) 1 week.

Figure 7-9 shows a cross-section of the apatite layer on the 58S33C green pellet. It can be seen that after soaking in the SBF for 21 days the apatite layer grew to about 4-8 μm in thickness. Zhong et al. [185] and Jallot et al. [186] reported the apatite layers formed on their bioactive glasses were 1-2 μm and 3-4 μm in thickness, respectively. Thus the excellent bioactivity of the 58S33C glass sample was confirmed.

Figure 7-9 SEM micrograph showing the cross section of the apatite layer on the 58S33C green pellet after soaking in the SBF for 21 days (arrows indicating the apatite layer).

Figure 7-10 and Figure 7-11 show the apatite layers formed on the 58S33C and the 77S14C green pellets after soaking in the SBF for 14 days. The apatite layer formed on the 58S33C was fairly dense (shown in Figure 7-10 (a)). Under a high magnification as shown in Figure 7-10 (b), the apatite layer consisted of spherical particles with particle sizes below 1 μm . The same spherical apatite particles were reported by other researchers [188-190]. On the other hand, from Figure 7-11, it can be seen that the apatite was made of needle-like crystals with an axial length below 1 μm . Furthermore, the apatite layer formed on the 58S33C bioactive glass was much denser than that on the 77S14C bioactive glass.

Figure 7-10 FESEM micrographs showing the apatite layer formed on the 58S33C green pellet after soaking in the SBF for 14 days: (a) at a low magnification; (b) at a high magnification.

Figure 7-11 SEM micrographs showing the apatite layer formed on the 77S14C green pellet after soaking in the SBF for 14 days: (a) at a low magnification; (b) at a high magnification.

7.4.2 Surface phase analysis for the sol-gel bioactive glasses subject to SBF tests

The XRD patterns of the three sol-gel bioactive glasses before and after SBF immersion are plotted in Figure 7-12. As literature shown [187], well crystalline hydroxyl carbonate apatite (HCAp) layer was formed on the bioactive materials surface after SBF soaking.

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The reaction stages begin with exchange of alkali ions such as Ca^{2+} , K^{+} and Na^{+} from the glass with H_3O^{+} from the SBF and network dissolution through attack of the silica structure by hydroxyl ion. This produces a layer of silanols (Si-OH) on the bioglass surface through which Ca^{2+} and PO_4^{3-} migrate from surrounding fluids and form an amorphous $\text{CaO-P}_2\text{O}_5$ -rich film which finally crystallizes to HCAp by incorporation of OH^{-} and CO_3^{2-} from the SBF.

One can see that the glasses with higher Ca concentrations, i.e. 58S33C and 68S23C glasses, showed the formation of calcite during the early 2 hour soaking while the 77S14C glass had no obvious change. After immersion for 2 hours, the apatite peaks could be found in the XRD pattern of the 77S14C glass. For the 58S33C and 68S23C glasses, the calcite was the dominant substance formed on the sample surfaces. For a longer immersion period, i.e. 1-2 weeks, the HCAp layers were formed on all the sample surfaces. It also can be noted that with increasing silicon content, the calcite peak of bioglass samples became broader, which shows the lower crystallization degree of the HCAp. The results proved that the high silicon content decreased the bioactivity of bioglasses which is in agreement with the microstructure results.

Figure 7-12 XRD patterns of (a) 58S33C, (b) 68S23C and (c) 77S14C green pellets before and after soaking in SBF for 0.5 hour, and 2 hours, and 2, 5, 7, 14 days. (A = apatite, C = calcite).

7.4.3 Inductively coupled plasma (ICP) analysis

Figure 7-13 shows the change of the Ca^{2+} ion concentration in the SBF for the three bioactive glasses with the immersion times. It can be seen that the Ca^{2+} concentration increased greatly with the immersion time and reached a maximum value after 24 hours for 58S33C, 48 hours for 68S23C and for 77S14C, respectively. After that the Ca^{2+} ion concentration decreased. During the early soaking period, there existed exchange between Ca^{2+} ions in the bioactive glass and H_3O^+ ions in the SBF, which would increase the concentration of Ca^{2+} ions in the SBF. The higher the Ca^{2+} concentration in the bioactive glass, the greater increase of the Ca^{2+} concentration in the SBF. The later decrease in the Ca^{2+} concentration in the SBF was attributed to the apatite nucleation and grain growth, involving the consumption of the calcium and phosphate ions from the surrounding fluid. It can be seen that the 77S14C glass showed a slower decrease of the Ca^{2+} concentration compared with the 58S33C and the 68S23C glasses. This fact was due to the formation of calcite on the surfaces of the 58S33C and the 68S23C glasses (as shown in Figure 7-12). Within the early soaking period, the formation of the calcite hindered the apatite formation on the 58S33C and the 68S23C glasses. However, during the later immersion period, the calcite crystals modified the formation of the apatite by serving as the nuclei, leading to small and spherical HCAp crystals.

Figure 7-13 Time dependence of the concentration of the Ca^{2+} ions in the SBF after immersing the bioactive glass pellets.

From above microstructural study and SBF tests, one can see that with increasing silicon content, the bioactivity of sol-gel bioactive glasses decreased. The apatite formation on the bioactive glasses soaked in the SBF is based on the following mechanism: the bioactive glass releases calcium ions to the fluid and this is followed by ionic exchange with the protons in the solution, resulting in the increase of Si-OH groups on the glass surface. The Si-OH groups then incorporate the soluble calcium and phosphate ions from the SBF to form apatite nuclei. The apatite nuclei then grow spontaneously by consuming the calcium and phosphate ions from the surrounding fluid or solution. Although silicon plays an important role in the apatite formation, it doesn't mean the higher the silicon content the higher the bioactivity. For some compositions of glass-ceramics containing SiO_2 , Na_2O , CaO and P_2O_5 , the limit of SiO_2 content for bioactivity in melt-derived glasses was about 60 mol% [39,40]. For sol-gel bioglass, the expansion of the bioactive

composition is expanded up to 90 mol% SiO₂ due to the larger porosity and the higher concentration of silanols on the surface and the higher surface area than those of melt-derived glasses [73,74,180,188]. Concerning the kinetics of formation of the apatite phase, the important calcium release allowed the formation of numerous nucleation sites for the apatite phase [179]. For the low calcium containing bioactive glasses, i.e., the 77S14C, the soaking process during the first 24 hours resulted in a lower amount of calcium release and a lower amount of Si-OH groups was formed after the release of calcium ions to the SBF. Therefore, the 77S14C glass had a slow rate of heterogeneous nucleation of apatite compared to the 58S33C glass which had higher calcium content.

In addition, once the apatite nuclei were formed, they grew by incorporating calcium and phosphate ions from the SBF. The ion transfer or exchange occurred near the glass surface. The 77S14C bioactive glass had a higher surface area and a higher surface porosity which may cause less nucleation sites in unit surface area and a lower apatite growth rate. M. Mami, et al [189] reported the growth of apatite. Small spherical crystallites of the apatite phase were formed and grew with the immersion time up to a limited size, always under 1 μm . New particles were continuously formed simultaneously to the growth of the initial ones. Because the 77S14C showed lower apatite nucleation and growth rates, the apatite on the 77S14C could only grow into fine needle-like crystals, instead of large spherical particles of the apatite layer on the 58S33C bioactive glass surface.

7.5 Effect of crystallization on the bioactivity of crystallized sol-gel bioactive glasses

Figure 7-14, Figure 7-15 and Figure 7-16 show the formation of apatite layers on the 58S33C bioactive glass samples sintered at 800 °C, 1000 °C and 1200 °C for 1 hour and immersed in the SBF solution for different time periods. From Figure 7-14, it can be seen that the 58S33C bioactive glass sintered at 800 °C showed a high degree of bioactivity similar to that of the green pellets of the calcined powders. After only 1 hour of immersion, apatite particles could be observed on the sample surface. After 1 day of immersion, a fairly dense apatite layer was formed. The thickness of the apatite layer increased with the increasing time period of immersion. Moreover, the crystallized glass samples showed a very different behaviour as shown in Figure 7-15 and Figure 7-16. For short time periods of immersion, such as 1 and 24 hours, no apatite was formed on the crystallized samples. This fact indicated that the crystallization of the bioactive glass decreased the bioactivity. However, after immersion in the SBF for more than 3 days, an apatite layer was formed.

Figure 7-14 SEM micrographs of the 58S33C bioactive glass samples sintered at 800 °C and immersed in the SBF for (a) 1 hour, (b) 24 hours, and (c) 7 days.

Figure 7-15 SEM micrographs of the 58S33C bioactive glass sintered at 1000 °C and immersed in the SBF for (a) 1 hour, (b) 24 hours, (c) 3 days, and (d) 7 days.

Figure 7-16 SEM micrographs of the 58Si33C bioactive glass sintered at 1200 °C and immersed in the SBF for (a) 1 hour, (b) 24 hours, (c) 3 days, and (d) 7 days.

The apatite layers were observed under a higher magnification as shown in Figure 7-17. The apatite layer formed on the sample sintered at 800 °C was fairly dense and made of spherical particles with a particle size of about 1 μm. However, a porous apatite layer was formed on the bioactive glass sample sintered at 1200 °C. This could be due to the crystalline phase, CaSiO_3 , which decreased the apatite nucleation and growth rates on the sample surface. The crystalline phase CaSiO_3 was difficult to react with the SBF compared to the glass phase and the release of calcium ions during the soaking process was greatly slowed down [190]. Therefore, the apatite nuclei were difficult to form on the

surface of the crystallized sample. This could lead to the porous structure of the apatite layer on the crystallized sample.

Figure 7-17 FESEM micrographs showing the apatite layers formed on the 58S33C bioactive glass samples sintered at (a) 800 °C and (b) 1200 °C after immersion in the SBF for 7 days.

From above results, it can be seen the crystallization reduced the bioactivity of sintered bioactive glasses. During heat treatment, part of glass phases was crystallized as wollastonite phase. The wollastonite phase was not dissolvable to SBF solution. Thus, the crystallized bioactive glasses resulted in a lower amount of calcium release and a lower amount of Si-OH groups, which slow down the apatite formation.

7.6 Bioactive glass-coated porous alumina/zirconia ceramics

7.6.1 Microstructure of the bioactive glass-coated porous alumina/zirconia ceramics

Figure 7-18 is an optical micrograph of the 58S33C bioactive glass-coated porous Al₁₀Zr. After being coated with the bioactive glass layer, the porous structure still had a good

pore interconnectivity as the pore windows were not blocked. And the bioactive glass coating made the pore walls glazed. The glazed pore walls had less microcracks and micropores than the un-coated ones, which resulted in the improvement of the mechanical properties of the porous structures. This will be further discussed in the next section.

Figure 7-18 Stereo-zoom optical micrograph showing the dip-coated 58S33C bioactive glass layer on a porous Al₁₀Zr ceramic sintered at 1200°C.

Figure 7-19 shows the micrograph of the cross-section of the 58S33C-coated porous Al₁₀Zr ceramic. The 58S33C glass coating was homogeneously attached to the surface of the pore walls in the porous structure. The coating was about 15-20 μm in thickness. No microcrack existed on the interface. EDS technique was used to identify the coating near the interface. From the EDS pattern, one can see that a small amount of Al was detected in the coating, which was due to the alumina contamination from the ball milling.

Figure 7-19 SEM micrograph with EDS patterns showing the 58S33C bioactive glass coating on the porous Al/10Zr ceramic. The coating was sintered at 1200°C.

Figure 7-20 compares the morphologies of the pore walls with and with the bioactive glass coating. Before coating, the pore walls were rough due to the coarse surfaces of the

EPS beads and the as sintered grain boundaries. After coating, the coating covered the surfaces of the pore walls and made them smooth. Crystals were observed in the coating due to the high process temperature (1200 °C), which caused the crystallization of the bioactive glass layer.

Figure 7-20 SEM micrographs showing the morphologies of the pore walls in the porous alumina ceramic (a) before coating and (b) after coating of the bioactive glass layer.

7.6.2 Mechanical properties of the bioactive glass-coated porous alumina/zirconia ceramics

Figure 7-21 compares the compressive strengths of the porous Al₁₀Zr ceramics before and after the bioactive glass coating. It can be seen that the mechanical strengths of the porous ceramics were slightly increased by the coating process. The mechanical strength of the coated porous ceramics could be affected by the differential thermal expansions between the coating and the substrate.

Figure 7-21 Effect of the average pore size on the compressive strength of the porous Al10Zr ceramics before and after the 58S33C bioactive glass coating.

Generally speaking, it is difficult to obtain a very thick coating due to the difference in the coefficients of thermal expansion (CTE) between the coating and the substrate. Residual thermal stresses could be generated at the interface between the substrate and the coating due to cooling down and different thermal expansions. Lee et al. [191], estimated the residual thermal stress, σ , using the following equation:

$$\sigma = \frac{E}{1 - \nu} \Delta\alpha\Delta T \tag{7-1}$$

where E and ν are the Young's modulus and the Piosson's ratio of the coating, respectively, $\Delta\alpha$ is the difference of thermal expansion coefficients between the substrate and the coating, and ΔT is the temperature drop during cooling. In this study, the Young's modulus of 58S33C bioglass was 63 GPa and the Piosson's ratio was 0.2. The CTEs of 58S33C bioglass and alumina were measured as $0.73 \times 10^{-6} \text{ K}^{-1}$ and $9.47 \times 10^{-6} \text{ K}^{-1}$. The calculated residual thermal stress was 600 MPa. The residual thermal stress is much

smaller than that of diamond coated titanium, of the order of 3-7 GPa, reported by Y. Fu et al.[192]. Due to the smaller CTE of the bioactive glass (or smaller dimensional shrinkage), the stresses in the coating could be compressive in nature as schematically shown in Figure 7-22. As a result, the 58S33C bioactive glass would not crack when coated onto the alumina substrate. It also can be used to explain the good interface bonding in the cross-section image in Figure 7-19.

Figure 7-22 Schematic illustration of the residual thermal stresses in bioactive glass coating during cooling.

Moreover, although the CTEs of the bioglass and the substrate is different, the resultant thermal stress could be relaxed due to the softening of the glass ($T > T_g$). The actual thermal stress should be much smaller than the calculated one.

7.7 Bioactivity evaluation of bioactive glass coatings

At the treatment temperature (1200 °C), the bioactive glass coating would inevitably react with the alumina substrate. This reaction would reduce the bioactivity of the bioactive

glass coating. Therefore, it was necessary to confirm the bioactivity of the coating. Figure 7-23 shows the SEM micrographs of the pore walls in the bioactive glass coated porous ceramics after immersion in the SBF solution for 24 hours and 2 weeks, respectively. It can be seen that a layer of apatite was formed on the pore walls after 24 hours immersion. Observed under a higher magnification, apatite spheres were formed but not a thin apatite layer. Only after long time immersion, a relative thicker apatite layer developed and covered the pore wall surface. The crack visible is resulted from the SBF solution penetration into the apatite layer. Compared with the apatite formation on the bioactive glass sample in Figure 7-8, this dip coated bioactive glass coating showed a lower formation rate. Above results suggest that the bioactive glass coating prepared by the dip coating process had some bioactivity but much lower than the original bioactive glass powder or bulk sample. The reduction of the bioactivity was the result of the reaction between the bioactive glass coating and the substrate. Reports [193,194] showed that the Al ions could react with the bioactive glass at a high temperature and reduced its bioactivity. Two aspects should be considered in dealing the reaction between the bioactive glass coating and the substrate. To reduce the firing temperature is a effective way. The firing process aims at obtaining well bonded coating layers. The firing temperature should be as low as possible to reduce the reaction. Recently, the sol-gel coating method was developed to fabrication coating at very low temperatures (400 °C -700 °C).

Figure 7-23 SEM micrographs shows the 58S33C bioactive glass coated porous Al10Zr ceramics after immersion in the SBF solution for 24 hours (a)(b) and 2 weeks(c)(d), respectively.

Chapter 8 Conclusions

In the present work, porous alumina ceramics coated with bioactive glass coatings were developed for potential orthopedic and dental applications. A method of vacuum infiltration was developed and optimized to prepare the porous alumina ceramics. Alumina/zirconia composites were also studied to find a superior substrate material. Several sol-gel bioactive glasses were prepared and characterized to serve as coating materials. Finally, the bioactive glass-coated porous alumina ceramics were studied. Based on the experimental data and analysis, the following conclusions were drawn:

1. A novel vacuum infiltration method was developed for preparing porous alumina ceramics. In this method, the pore formers were porous templates made by pressing expanded polystyrene (EPS) beads. The porous alumina ceramics were formed by infiltrating alumina slurries through the porous templates under the vacuum produced by a water aspirator, followed by drying and sintering. After optimization, the process parameters were established. During the vacuum infiltration, a load was applied to deform the EPS beads with a strain of 10 %. After 6 hours of infiltration, the sample was air dried for 12 hours followed by drying in an oven at 70 °C for 6 hours to obtain the green compact. The green compact was then heated to 500 °C at a heating rate of 2 °C/min and held for 30 min to burn out of the EPS beads completely, and then heated to 1550 °C at the heating rate of 5 °C/min and held for 2 hours. After cooling, porous alumina samples were obtained,
2. The prepared porous alumina ceramics were featured by the uniformly distributed pores, high total porosities above 61.9 %, high open porosities above 48.3 % and excellent pore interconnectivity. The compressive strength and the compressive

modulus of the porous alumina ceramics decreased with the increasing pore sizes. When the pore sizes of the porous alumina ceramics increased from 1.21 mm to 2.63 mm, the compressive strength decreased from 7.52 MPa to 5.42 MPa and the compressive modulus decreased from 1.64 GPa to 1.17 GPa.

3. In the present work, 3Y-TZP was added into the alumina ceramics to obtain well densified alumina/zirconia composites with enhanced mechanical properties. The introduction of zirconia to the alumina matrix would retard the densification process at low sintering temperatures ($<1500\text{ }^{\circ}\text{C}$) through the second-phase pinning effect. However, at higher sintering temperatures ($>1500\text{ }^{\circ}\text{C}$), the zirconia compound increased the sintering rate due to their lower sintering temperature than alumina. All the alumina/zirconia samples sintered at 1600°C had the relative density over 94%, which indicated a very high level of densification.
4. The addition of ZrO_2 in the alumina matrix hindered the abnormal grain growth of the alumina grains and improved the microstructure of the ceramic struts. The grain sizes reduced from $3.85\text{ }\mu\text{m}$ of the Al sample sintered at the temperature of $1600\text{ }^{\circ}\text{C}$ to less than $1.5\text{ }\mu\text{m}$ of zirconia contained composites sintered at the same temperature. The ZrO_2 additive had the significant effect on the toughening of the alumina matrix. With a small zirconia content (5 vol%), the hardness of the composite was increased. However, further addition of zirconia decreased the hardness of the samples. The fracture toughness of the composites increased with the increasing zirconia content.
5. The sol-gel bioactive glasses were amorphous in nature and CaSiO_3 (wollastonite) phase was formed after crystallization. The bioactive glass powder were particles with the particle size of 50-100 nm, in a porous structure and with a large surface

area. The pore size of the glasses was in the mesoporous range (2-50 nm). The average pore size decreased with the increasing silica content. The sol-gel bioactive glass showed excellent bioactivity. The 58S33C and the 68S23C glasses showed the formation of an apatite layer during the early 2 hours of soaking in SBF while the 77S14C glass showed the apatite peak only after immersion of more than 2 hours. It was shown that with the increasing silica content, the bioactivity of the sol gel bioactive glasses was reduced.

6. The sol-gel 58S33C bioactive glasses were coated on the porous Al10Zr ceramics through a dip coating method followed by heating up to 1200 °C at a heat rate of 5 °C/min and holding for 1 hour. The bioactive glass coating could be bonded to the alumina substrate well and improved compressive strengths were obtained from the coated porous Al10Zr ceramics. The bioactivity of the sol gel bioactive glass coatings was significantly reduced compared with that of the original bioactive glass samples. It was due to the reaction between the bioactive glass coating and the alumina substrate.
7. In the current study, the prepared porous alumina ceramics with bioactive glass coatings showed the pore sizes ranging from 1.2 mm to 2.6 mm, porosities ranging from 60.84 % to 65.93 %, high pore interconnectivity above 78.07 % and excellent surface bioactivity imparted by the bioactive glass coatings. Such porous structures could satisfy the requirements for the porous scaffolds for biomedical applications. In the porous structure, the macropores could provide sufficient space for tissue ingrowth, the high pore interconnectivity could allow the development of a vascular system to maintain the supply of blood and nutrition and the bioactive surface could facilitate the cell adherence and ingrowth of the surrounding tissue. Moreover, the

Chapter 8 Conclusions

mechanical properties of the porous ceramics were comparable to those of the nature bones. The results of the porous structures and the mechanical properties suggested that the prepared porous alumina ceramics could be suitable for biomedical applications. However, further *in vitro* and *in vivo* studies are needed to justify the potential of the porous materials developed.

Chapter 9 Recommendations

Some studies on the preparation and characterization of the porous alumina/zirconia ceramics with bioactive glass coatings were done for the PhD project. Further research can be carried out in the processing routes and characterization methods.

In the present work, the porous structures had pore sizes at the range of 1.21-2.09 mm. The large pore sizes allowed further processing such as coating with multiple coat layers and filling with bone cement. Further studies are required to pursue better porous structures with excellent mechanical properties and biological response.

With the enhanced requirements for life quality of human being, and the great development in materials science and biological techniques, tissue engineering evokes more and more attentions and has wide applications not only in hard tissue (mentioned in the thesis) engineering but also soft tissue (skin, organ) engineering. The materials involve ceramics, polymers, metals and various composites. In the aspect of material study, 3-dimensional porous scaffolds are the important component of tissue engineering. How to mimic the human tissues in the composition, the structure and the function is a key issue in design and fabrication of 3-dimensional porous scaffolds. It is well accepted that no single material and single structural configure could fulfill the requirements for the porous scaffolds in tissue engineering. Some work could be attempted on two kinds of 3-dimensional porous scaffolds:

1. Composition graded 3-dimensional porous scaffolds

Human tissue has complex composition and architecture. To mimic the nature tissue, one can fabricate the porous scaffolds using a series of composites. The advantage of such scaffolds is that they could exhibit graded mechanical properties and biological properties to work in complex stress environments and play the biological functions. The study in this project utilized the alumina/zirconia composites and bioactive glasses as the material system and fabricated a graded porous scaffold with the alumina matrix and the bioactive glass coating. A further study can be conducted to prepare multilayer coatings using a series of bioactive glasses with varied compositions. Other material systems can also be considered, such as HA, HFA, TCP, and bone cement. One possible design can be illustrated in Figure 9-1. In this structure, graded mechanical and biological properties exist, that is, mechanical property: alumina/zirconia > 77S14C > 68S23C > 58S33C and bioactivity: alumina/zirconia < 77S14C < 68S23C < 58S33C. The implant from such a scaffold can well transmit stresses between the implant and host tissue to avoid stress shielding and also exhibit excellent surface bioactivity.

Figure 9-1 Schematic illustration of porous alumina/zirconia scaffold with graded bioglass coating layers.

2. Porosity graded 3-dimensional porous scaffolds

To mimic the whole bone cross-section with the compact bone and the cancellous bone, porosity graded 3-dimensional porous scaffolds are reasonable. The porous scaffolds with a graded pore configuration have other advantages. For example, the mechanical strength or the load bearing capability can be increased due to the porous part with a low porosity or a small pore size and bone ingrowth can be enhanced in the porous part with a high porosity. The graded porous implants would exhibit strong bone bonding due to the mechanical interlocking, matched Young's moduli and increased surface contact area to the surrounding host tissue. To prepare the porous scaffolds with a graded pore configuration, EPS beads with varied bead sizes are stacked layer by layer to form the porous EPS template. The porous structure with graded pore configuration is shown in Figure 9-2.

Figure 9-2 schematic diagram showing the arrangement of graded porous scaffold.

Due to the limit of fund and time, *in vitro* cell response study and *in vivo* animal test are not involved in the thesis. However, cell study and in vivo animal test are important parts of the project and valuable to conduct in the future.

1. Cell culture assays

The cytotoxicity of the scaffold should be evaluated to determine whether it kills cells directly or indirectly through the inhibition of cell metabolic pathway. The cell culture assays are standardized by ASTM, ISO and BSI. A direct contact method can be used. Firstly, a near confluent layer of fibroblasts are prepared in a culture plate followed by removing the old culture media and adding fresh one. Then, the scaffold being tested is placed onto the cultures, which are incubated for 24 hours at 37.5 °C. After that, the scaffold and the culture media are removed. The remaining cell are fixed and stained, dead cells are lost during fixation and only the live cells are stained. The cytotoxicity of the scaffold is indicated by the absence of stained cell around the materials. The morphology of the cells adhered to the scaffold can be observed using SEM.

2. *In vivo* test

The animal test is used to evaluate the bone implant interactions. Implant should have an appropriate size for the species chosen and for the bone implantation site. The ISO recommends the dimensions of the implants for *in vivo* studies. Common mechanical testing used on tissue harvested from *in vivo* studies includes torque removal tests (screw-type implants), pull-out test and push out tests (screw, cylindrical implants). These tests are used to evaluate the strength of the interaction between the bones and implant surface.

Appendix: Publications and Presentations

Publications

1. J. Liu, X. Miao, "Sol-gel derived bioglass as a coating material for porous alumina scaffolds", *Ceramics International*, 30(7), 2004, 1781-1785.
2. J. Liu, X. Miao, "Porous alumina ceramics prepared by slurry infiltration of expanded polystyrene beads", *J. Mater. Sci.*, 40(23), 2005, 6145-6150.
3. J. Liu, Z. Dong, X. Miao. "Porous Alumina/Zirconia Composite Scaffold with Bioactive Glass 58S33C Coating", *J. Biomim. Biomat. Tissue Eng.*, accepted.
4. X. Miao, Y. Hu, J. Liu and A. P. Wong, "Porous calcium phosphate ceramics prepared by coating polyurethane foams with calcium phosphate cements", *Materials Letters*, Volume 58, Issues 3-4, January 2004, 397-402.
5. X. Miao, D. Sun, P. W. Hoo, J. Liu, Y. Hu, Y. Chen, "Effect of titania addition on yttria-stabilised tetragonal zirconia ceramics sintered at high temperatures", *Ceramics International*, 30(6), 2004, 1041-1047.
6. X. Miao, Y. Hu, J. Liu, B. Tio, P. Cheang, K.A. Khor, "Highly interconnected and functionally graded porous bioceramics", *Key Engineering Materials*, Volume 240-242, 2003, 595-598.
7. J. Liu, Y. Hu, P. Cheang, W. Dietmar, W. Hutmacher, X. Miao, "Characteristics of porous alumina prepared by three different pore formers", In: *1st International Conference on Materials Processing for Properties and Performance [MP3]*, edited by H. A. Hhor, S. Y. Zhang, P. Hing, F. Boey, Institute of Materials [East Asia], Singapore, 222-229.

Presentations

8. J. Liu, M.Y. Ng, K. H. Loh, Y. Hu, X. Miao, "Porous Bioinert Alumina Prepared by Vacuum Infiltration", In *1st International Bioengineering Conference*, September, 2004
9. J. Liu, Y. Hu, X. Miao, "Porous alumina bioceramic modified with bioglass coating", *7th World Biomaterials Congress*, May. 2004,
10. Y. Hu, J. Liu, M. Khor, P. Cheang, X. Miao, "Graded porous 3Y-TZP ceramics prepared by pressure filtration", In: *1st International Conference on Materials Processing for Properties and Performance [MP3]*, edited by H. A. Hhor, S. Y. Zhang, P. Hing, F. Boey, Institute of Materials [East Asia], Singapore, 2002, Pages 230-238.
11. Y. Hu, J. Liu, X. Miao, "Graded porous zirconia as a preform for bioceramic composites", *7th World Biomaterials Congress Managers*, May. 2004.
12. X. Miao, Y. Hu, J. Liu, Y. Chen, "Interpenetrating biomaterial composites with calcium phosphate cement as a filter", *7th World Biomaterials Congress Managers*, May. 2004.

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