Dense/porous bioceramic composites

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Dense/Porous Bioceramic Composites

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ABSTRACT

This thesis reports the preparation and characterization of porous yttria-stabilized-tetragonal zirconia polycrystals (TZP) and porous TZP/alumina composites featuring a uniformly porous structure, a graded porous structure and/or a porous/dense non-uniform structure. These new types of porous materials were prepared for bone replacement and reconstruction. The pores were designed for bone ingrowth, whereas the graded pores and the dense cores were introduced for load bearing capability. For bone ingrowth, the porous structures must have a high porosity, a high interconnectivity, and a suitable pore size.

The processing method was based on vacuum casting, in which a dispersed ceramic suspension was allowed to impregnate the pores or channels of a specially arranged expanded polystyrene (EPS) bead compact used as a pore former. TZP and TZP/20wt% alumina slurries for vacuum casting were prepared with a solids loading of 50wt% and 0.5 wt% and 0.7wt% of ammonium polyacrylate (PMAA) as a dispersant, respectively. The resulting ceramic particle compacts together with the pore formers were fired to burn off the EPS and yield sintered porous ceramics.

The microstructures of the porous bioceramics were fully characterized by microscopy and X-ray diffraction and the most important mechanical properties measured. The TZP ceramics were 50% to 70% porous, with highly interconnected pore windows suitable for bone ingrowth, and pore sizes from 0.98mm to 2.22mm. The addition of alumina into zirconia retarded the densification of the TZP substrates, but resulted in desirable reduction of sintering shrinkage. In spite of the large open macropores limited by the available EPS sizes, high compressive and diametral strengths and low Young's moduli were obtained ranging from 3.3 to 36.8MPa, 1.5 to 17.6MPa and 0.24 to 2.25GPa, respectively, depending on the pore size and porosity.

The mechanical properties of the porous ceramics were comparable to those of cancellous bones.

To take advantage of the good mechanical properties of the porous structures based on zirconia and alumina, a coating layer of hydroxyapatite (HA)/borosilicate glass composite was used to make the pore walls of the porous ceramic structures bioactive and favorable for bone ingrowth. Sintering the HA/borosilicate glass-coated porous structures at 1200°C resulted in an HA-rich porous outer layer, whereas the borosilicate glass phase flowed into the interior of coating layer, forming a graded bioactive coating on the porous ceramic structures. Good interfacial bonding between the coating layer (about 50µm thick) and the TZP substrate was confirmed by indentation with Vickers hardness testing.

Publications – PhD Student Hu Yifei

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(Chapter 7, Section 7.4)
2. **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.
(Chapter 6, Section 6.3 ~ 6.5)
3. **Y. Hu**, J. Liu, X. Miao, "Graded Porous Zirconia as a Preform for Bioceramic Composites", Transactions 7th World Biomaterials Congress, 17-21 May 2004, Sydney, Australia, p. 1299.
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TABLE OF CONTENT

ABSTRACTi

Publications – PhD Student Hu Yifeiiiii

ACKNOWLEDGEMENTS.....iv

TABLE OF CONTENTv

Chapter 1 Introduction1

1.1 Background.....1...

1.2 Objectives.....4...

1.3 Scope5...

Chapter 2 Literature Review6

2.1 Structure and mechanical properties of bone6.

 2.1.1 Composition of bones6

 2.1.2 Architecture of bone7.

 2.1.3 Mechanical properties of bone8.

2.2 Overview of biomaterials9.

 2.2.1 Metallic implant materials.....9.

 2.2.2 Polymeric implant materials.....10

 2.2.3 Ceramic implant materials.....11

 2.2.4 Bioceramic composites.....17

2.3 Review of porous bioceramics20

 2.3.1 Structure and mechanical properties of porous ceramics20

 2.3.2 Sintering behavior of porous ceramics25

 2.3.3 Fabrication of porous bioceramics26

 2.3.4 Bone ingrowth of porous ceramics30

2.4 Graded porous bioceramics31

2.5 Review of bioactive coatings on bioinert substrates34

 2.5.1 Materials and methods used for bioactive coatings35

 2.5.2 Bioactive coatings in porous structures37

Chapter 3 Experimental Procedure38

3.1 Starting materials38

 3.1.1 Zirconia powder.....38

 3.1.2 Alumina powder39

 3.1.3 Borosilicate glass powder.....39

 3.1.4 Hydroxyapatite powder39

 3.1.5 Dispersant.....40

 3.1.6 Preforms.....41

3.2 Slurry optimization and particle consolidation.....42

 3.2.1 Ceramic slurry preparation and characterization.....42

 3.2.2 Preparation and characterization of the green compacts43

3.3 Sintering of zirconia and zirconia/alumina green compacts without EPS beads ..45

3.4 Structures and properties of uniformly porous TZP and ZA20 ceramics47

 3.4.1 Preparation of uniform pore sized porous structures47

 3.4.2 Characterization of the porous structures49

3.5 Structures and properties of non-uniformly porous TZP ceramics51

 3.5.1 Preparation of graded porous and porous/dense TZP ceramics.....51

 3.5.2 Characterization of the non-uniformly porous TZP ceramics53

 3.5.3 Preparation of HA/glass coatings on dense and porous TZP substrates. 53

 3.5.4 Characterization of HA/glass coatings on dense and porous TZP
substrates54..

Chapter 4 Optimization of Ceramic Slurry for Vacuum-Casting55

4.1 Introduction55..

4.2 Zeta potential for dilute suspensions56

4.2.1 Effect of pH on zeta potential56

4.2.2 Effect of PMAA content on zeta potential58

4.3 Effect of PMAA content on the viscosity of concentrated slurries62

4.4 Green density vs. viscosity in slip casting63

4.5 Kinetics of vacuum casting66

4.6 Summary68.

Chapter 5 Dense Zirconia Ceramics and Zirconia/Alumina Composites69

5.1 Introduction69.

5.2 Effect of alumina addition on the densification of zirconia70

5.2.1 Densification during heating70

5.2.2 Densification due to sintering at high temperatures74

5.3 Effect of alumina addition on the grain growth of zirconia.....80

5.4 Hardness and fracture toughness of zirconia/alumina ceramics86

5.5 Summary89.

Chapter 6 Structures and Properties of Uniformly Porous TZP and ZA20 Ceramics90

6.1 Introduction90

6.2 Sintering behavior of the uniformly porous TZP ceramics90

6.3 Morphology of the uniformly porous TZP structures93

6.3.1 Vanations in pore size93

6.3.2 Vanations in porosity94

6.4 Porosity control of uniformly porous structures96

6.5 Mechanical properties versus porous structures98

6.5.1 Effect of pore size on mechanical properties98

6.5.2 Effect of porosity on mechanical properties102

6.5.3 Effect of both pore size and porosity on compressive strength 106

6.6 Summary.....112

Chapter 7 Structures and Properties of Non-Uniformly Porous TZP Ceramics113

7.1 Introduction113

7.2 Porous TZP ceramics with graded pore size.....113

 7.2.1 Morphology113

 7.2.2 Compressive strength for porous TZP structures with two porous layers
.....115

 7.2.3 Compressive strengths for porous TZP structures with five porous layers
and different porosities117

7.3 Porous/dense TZP structures121

 7.3.1 Morphology of porous/dense TZP structures121

 7.3.2 Internal stresses from drying, sintering, and cooling.....124

7.4 Porous TZP with HA/borosilicate glass coating.....131

 7.4.1 Microstructure of the HA/glass composite coating132

 7.4.2 HA/glass coating on flat, dense TZP substrate134

7.5 Summary.....137

Chapter 8 Conclusions and Future Work138

8.1 Conclusions138

8.2 Future work.....141

References144

Chapter 1

Introduction

1.1 Background

Bone performs several integral functions in the maintenance of body systems, such as the protection of vital organs, providing support and a site of muscle attachment for locomotion, and retaining reserve stores of calcium, phosphate, and other important ions[1,2]. Therefore, pathologies of bone can be very serious, affecting a wide range of bodily functions [3]. Although minor injuries are repaired by natural bone healing and remodeling processes, severe damage requires surgical intervention. There are five methods of bone treatment: autografting (using the patient's own bone), allografting (using donor bone), xenografting (using animal bone), biocompatible synthetic materials (biomaterials), and tissue engineering (biomaterials and cells). The first three methods are standard treatments, but all have shortcomings. For example, in large defects, the grafts can be resorbed by the body before osteogenesis is complete [4,5]. Not only is the operating time for harvesting auto-grafts expensive, but often donor tissue is scarce, and there can be significant donor site morbidity associated with infection, pain, and hematoma [6, 7 , 8, 9, 10]. Allografting and xenografting introduce the risk of disease or infection; they may cause a reduction or complete loss of the bone inductive factors [11,12]. As a result, biomaterials and tissue engineering scaffolds which can be synthesized and fabricated in a wide variety of shapes and forms have become more important in bone treatments. Over the past 15–20 years, a wide range of new and exciting biomaterials have emerged, and the number of professionals working in the field has grown enormously [13]. Metallic

implant materials of pure titanium and its alloys, cobalt-based alloys, stainless steel and Ni-Ti alloys, are widely used as load bearing replacements in medical applications. Polymeric implant materials such as PEEK (poly (etheretherketone)), PE (polyethylene), PLC (poly (DL-lactide-co-caprolactone)), PLGA (poly (lactic-co-glycolic acid)), and PGA (polyglycolide), were developed for drug delivery and gene therapy. Ceramic implant materials such as zirconia, alumina, hydroxyapatite, tricalcium phosphate and bioglass, have been used as bone replacements and dental implants.

Bioceramics can be classified as bioinert, bioactive and bioresorbable. The bioinert materials include alumina, zirconia and their composites. Alumina and zirconia exhibit high mechanical properties (For example, 4100 and 2000 MPa for compression strength for alumina and TZP, respectively.) and can be used as load-bearing implants. However, their Young's moduli are very high, leading to stress shielding which prevents bone from being loaded and loosening of the implants. Bioactive ceramic materials such as hydroxyapatite and bioglass have proved to be biocompatible, bone-bonding and osteoconductive. However, the mechanical strengths of these materials are poor. The most widely used biodegradable ceramic materials are tricalcium phosphates that are similar to bioactive materials. They are biocompatible and osteoconductive. But their mechanical behaviors are also poor.

In recent years, particular attention has been paid to the fabrication of bioceramics with porous configurations. The Young's modulus of a porous ceramic can be lowered substantially to prevent the stress-shielding problem. The porous network also allows bone tissue ingrowth which enhances implant-tissue attachment. The porous ceramics can be colonized by bone tissues with the same characteristics as implanted tissues when pores of suitable architecture are used. For instance, the minimum pore size for bone ingrowth is about 100 microns and 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

pore size gradient, time of implantation, materials' biocompatibility, depth of porosity into the implant, implant stiffness, and the amount of micromotion between the implant and adjacent bone.

Although porous bioceramics provide obvious advantages of tissue ingrowth, they frequently have poor mechanical properties that restrict them to low or non-load-bearing applications. Therefore, it is important to design a porous structure with both a suitable porosity and reliable mechanical properties. In this regard, porous bioceramics with a graded pore configuration have several advantages. For example, the mechanical strength or the load bearing capability can be increased by the combination of low porosity or small pore size components. Graded porous implants would exhibit strong bone bonding due to mechanical interlocking, matched Young's moduli and increased surface contact area. Graded porosity also mimics the whole bone cross-section from a cancellous bone and a cortical bone. However studies on the fabrication and the characterization of graded porous bioceramics are limited.

To produce porous ceramics, various methods based mainly on mixing of sacrificial foreign combustible organic material that after sintering, leaves free spaces or pores in the resultant body have been used. The organic powders (e.g., polyvinyl butyral) in the production of macroporous bioceramics were selected to have low burn-out temperatures. These methods, however, are unsatisfactory as they did not ensure the interconnectivity of pores in the porous ceramic bodies. Thus, new methods are needed to control the nature of the porous structures.

Furthermore, the assumption of bone ingrowth into porous bioinert ceramics is not always true. Additional bioactivity could be advantageous for a bioinert material, since it can enhance osseointegration and provide direct bone bonding. To encourage bone ingrowth, the pore wall surfaces should be bioactive. Thus, it is important to apply a bioactive coating to bioinert ceramics, so that both mechanical properties and bone ingrowth ability can be achieved.

1.2 Objectives

The overall objective of this project was to design and fabricate bioceramics with appropriate porous structures and mechanical properties. Critical parameters include a uniform pore size and porosity, graded pore sizes, porous/dense layers, a porous outer layer-dense core design, and conversely a dense outer layer-porous core configuration. In all cases, the pore surfaces of the bioinert ceramics must be rendered bioactive.

The specific objectives of this project were:

1. To develop methods to produce uniformly porous structures, pore size graded structures, and porous/dense non-uniform structures. The porous structures should have a sufficient porosity, an adequate pore size (>100 microns) and a high interconnectivity to promote bone ingrowth.
2. To study the effects of processing parameters on the morphology, pore size and porosity of the final structures.
3. To determine mechanical properties such as compressive strength, diametral strength and Young's modulus of the structures.
4. To correlate mechanical properties with characteristics such as pore size and porosity.
5. To coat the bioinert porous substrates with a bioactive layer.

1.3 Scope

In this thesis, gypsum molds made from plaster of Paris powder were used to fabricate porous structures through a vacuum casting method. The rheological properties of zirconia and zirconia/alumina slurries and sintering behavior of the resultant ceramic bodies were studied. Bioinert porous structures based on tetragonal zirconia ceramics and zirconia/alumina composites were prepared. Porosity was created by burning out the expanded polystyrene (EPS) beads. The pore size was controlled by the EPS bead size and the porosity by the deformation of the EPS. Uniformly porous, graded porous and porous/dense non-uniform structures were prepared. The mechanical properties (compressive strength, diametral strength and Young's modulus) of the porous structures were measured. The porous structural characteristics were correlated to the measured mechanical parameters. In order to introduce bioactivity into the porous zirconia and the zirconia/alumina substrates, a bioactive coating layer (hydroxyapatite/borosilicate glass) was coated on the pore surfaces of the bioinert porous substrates.

Chapter 2

Literature Review

2.1 Structure and mechanical properties of bone

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

2.1.1 Composition of bones

Bone has two major load bearing components: polymer and ceramic. The polymer is collagen, a protein which is the most abundant structural material in the bodies of mammals. There are actually more than a dozen different kinds of collagen determined by the particular sequence of amino acids in its molecules. Bone matrix also contains a small amount of other proteins and molecules. The ceramic component of bone is composed of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$). However, there are many substitutions in hydroxyapatite: K^+ , Mg^{2+} and Na^+ for Ca^{2+} ; carbonate (CO_3^{2-}) for phosphate (PO_4^{3-}), and fluorine (F^-) for OH (OH^-). Some of these substitutions are thought to play significant roles in the structure and mechanical properties of bone [14].

2.1.2 Architecture of bone

Bone contains a mineralized collagenous framework for skeletal support of the body, that is either cancellous (also called spongy, Fig.2-1) or cortical (also called compact, Fig.2-1) in structure. Both cortical and cancellous bone have high pore interconnectivity. Cortical bone has a porosity from 5% to 30% and the cancellous bone from 30% to 90%. Non-uniform porosity is also present in bone at the microscopic level, where the canaliculi and small vasculature channels are in the 1~5 μm range. Osteocyte lacunae and Volkmann's canals are typically 5~15 μm in diameter, whereas the larger Haversian canals are from 50 to 100 μm in diameter. The above pore sizes are associated with the pores in cortical bone and in the trabeculae of cancellous bone, respectively. For cancellous bone, the spaces between the trabeculae are large pores (from less than 1 mm to 5mm) and filled with soft red marrow. Thus the range of pore size in normal bone is approximately from 1-5,000 μm [15].

Fig.2-1 Optical photograph of a bone cross-section showing the cortical and the cancellous bone [16]

2.1.3 Mechanical properties of bone

The organic components of bone (mainly collagen) behave as a compliant material with high toughness, low modulus and other properties characteristic of polymers. The inorganic components, i.e., hydroxyapatite (HA) crystals, provide stiffness to the bone. As a ceramic-organic composite, bone exhibits high toughness and relatively high modulus. The high toughness of bone is related not only to the presence of collagen, but also to its complicated fibrous microstructure. The mechanical properties of cortical and cancellous human bones are summarized in Table 2-1. While the apatite (HA) content and the collagen fiber orientation are important factors controlling the mechanical properties of bone, hierarchical pore ordering is also important, such as pore size and porosity. The lower mechanical strengths of the cancellous bone are obviously due to the larger pore size and high porosity.

Table 2-1 Mechanical properties of cortical and cancellous bones [17,18]

Properties		Cortical bone	Cancellous bone
Compressive strength, MPa		100-200	2-12
Flexural strength, MPa		50-150	10-20
Strain to failure, %		1-3	5-7
Young's modulus, GPa	Compression	15.1-19.7	0.1-3
	Tension	11.4-19.1	0.2-5
Fracture toughness, MPa.		2-12	Not available

In summary, the non-uniformly porous structure and the mechanical properties of bone can be used as criteria to guide the design and the fabrication of biomaterials for bone replacement and regeneration.

2.2 Overview of biomaterials

The main clinical reasons to develop bone replacement alternatives arise from the need for better filler materials. The reconstruction of large orthopaedic defects requires implants mechanically suitable to their biological environments. The traditional biological methods of bone-defect management include autografting (tissue from another location of the same body) and allografting (tissue from a different individual of the same species), but both have negative impacts on human body including risks of disease or infection, unpredictable bone resorption, the need of additional surgery and the rejection by patient's body. Biomaterials, however, offer the possibility for replacement and regeneration of the damaged bones. The following sections will review dense metallic, polymeric, ceramic and composite biomaterials.

2.2.1 Metallic implant materials

Metals presently account for a substantial percentage of clinically used materials and for many applications represent the benchmark for success. Metals have the attributes of strength, stiffness, toughness and impact resistance, properties that are particularly important for load-bearing applications such as total joint replacement.

The principle metals used in medical and dental applications today include: pure titanium and its alloys (largely the $\alpha+\beta$ alloys), cobalt-based alloys (primarily cast Co-Cr-Mo, wrought Co-Ni-Cr-Mo, and wrought Co-Cr-W-Ni), stainless steel (primarily type 316L), Ni-Ti alloys, Au-based materials and dental amalgam (Ag-Sn alloys) [19]. These materials do not show any toxicity, but some dissolved metal ions, corrosion products and wear debris can show toxicity when they combine with biomolecules and cells [20]. The corrosion of metals in aqueous solutions takes place via an electrochemical mechanism with different metals having different intrinsic aptitudes to corrode. The more noble the metal, the less its susceptibility to corrode.

Reactions taking place on metal surfaces in specific environments may cause radical changes in the theoretical nobility. After implantation, the metal is surrounded by serum ions, proteins and cell that may all modify the effect on local corrosion reactions. The corrosion behavior of a metal in non-physiological *in vitro* studies, physiological *in vitro* and *in vivo* studies may vary dramatically. Due to the fact that every metal implant corrodes inside the human body, the applications of metallic biomaterials demand surface modification such as ion-beam-assisted deposition of hydroxyapatite as a coating layer on metal-based substrates [21].

2.2.2 Polymeric implant materials

The use of polymers in medicine dates back almost to the birth of the field of polymer science. Nylon sutures were reported in the early 1940s and review articles on the use in surgery of polymers such as nylon, poly (methylmethacrylate) (PMMA), Dacron[®] polyester and polyvinyl chloride began appearing in prominent medical journals in the mid 1940s [22]. These original materials have been joined by additional bulk commodity polymers (Teflon, high-density polypropylene, polyurethane) likewise adapted for use in surgery after their initial uses for other purposes. These polymers remain important in clinical medicine as essential components of permanent prosthetic devices including hip implants, artificial lenses, large diameter vascular grafts and catheters.

Polymeric implant materials used in medical area can be divided into bioinert, bioactive and biodegradable, depending on the tissue-implant interactions. Bioinert polymeric implants include HDPE (high-density polyethylene), UHMWPE (ultra high molecular weight polyethylene), PE (polyethylene) and PEEK (poly(etheretherketone)). Bioactive polymeric implants include PLC (poly(DL-lactide-co-caprolactone)), PA (polyactive) and PEGIPBT (poly(ethylene glycol)/poly(butylenes)). Biodegradable polymeric materials include polyesters (PLA (poly-lactic acid), PGA (polyglycolide),

PCL(poly-carpolactone) and their copolymers), poly(orthoesters), poly(anhydride), and pseudo-poly(amino acids).

While the original use of polymers in surgery centered primarily on replacement of connective tissues, a host of new applications are emerging as a result of major advances in the sciences of molecular cell biology and developmental biology. Arrays of new protein and nucleic acid-based drugs, which cannot be taken in classical pill form, are providing the impetus for the development of new implantable polymers for controlled drug delivery and gene therapy. Applications in the relatively new field of tissue engineering, where polymers are used to assist regeneration of three-dimensional tissue and organ structures, are nascent and more integrated with biological demands.

2.2.3 Ceramic implant materials

Historically, ceramics have been an essential part of the medical industry with containers, chemical ware and thermometers. However, the potential applications of ceramics to new areas of medicine and dentistry have recently expanded. Ceramics have high strengths, which make them useful orthopedic and dental implants [23]. The types of ceramic materials for musculoskeletal prostheses are also divided into three classes according to their chemical reactivity with the biological environment: (1) nearly inert, (2) bioactive, and (3) completely resorbable.

Nearly Inert Crystalline Bioceramics

1. Alumina

Alumina (α -Al₂O₃) with high-density (98% of theoretical density or higher) and high-purity (>99.5%) was the first bioceramic widely used clinically. Since alumina has excellent corrosion resistance, high wear resistance and strength as well as good biocompatibility, it is used in load-bearing hip prostheses and dental implants [24]. Although some dental implants are single-crystal sapphire [25], most alumina devices

are very-fine-grained polycrystalline α -Al₂O₃ in which, a small amount of magnesia (<0.5 wt%) is used as sintering aid and grain growth inhibitor.

Strength, fatigue resistance and fracture toughness of polycrystalline α -Al₂O₃ ceramics are functions of grain size and amount of sintering aid. Alumina with an average grain size of < 4 μ m and purity > 99.7% exhibits good flexural strength and excellent compressive strength. Extensive testing has shown that alumina implants which meet or exceed ISO standards have excellent resistance to dynamic and impact fatigue and also resist subcritical crack growth [26].

Alumina noncemented cups for the acetabulum (socket) of the hip are widely used due to their low wear rates [27]. The cups are stabilized by bone growth into grooves or around pegs of the cups. The mating femoral ball surface is also made of alumina that is bonded to a metallic stem. Long-term results in general are excellent, especially for younger patients. However, Christel *et al.* [28] cautioned that stress shielding of the bone could occur. This can be explained by the high Young's modulus of alumina, which prevents the bone from being loaded, a requirement for bone to remain healthy and strong. The Young's modulus of cortical bone ranges from 7 to 25GPa, which is 10 to 50 times lower than that of alumina. Other clinical applications of alumina implants include knee prostheses, bone screws, alveolar ridge (jaw bone) and maxillofacial reconstructions, ossicular (middle ear) bone substitutes, blade, screw or pot-type dental implants.

2. Zirconia

In the late sixties of last century, zirconia began to be used as a ceramic biomaterial due to its good chemical and dimensional stability, mechanical strength and toughness. Several solid solutions (ZrO₂-MgO, ZrO₂-CaO and ZrO₂-Y₂O₃) were tested for biomedical applications in the early stage of development, but research focused on tetragonal zirconia polycrystalline (TZP) material, which was characterized by fine-grained microstructures [29,30].

I. Stabilization of zirconia phases

Zirconia occurs in three forms: monoclinic (M), cubic (C) and tetragonal (T). Pure zirconia is monoclinic at room temperature. This phase is stable up to 1170°C, above which it transforms into a tetragonal and finally a cubic phase at 2370 °C. During cooling, the T→M phase transformation takes place with a volume expansion of approximately 3~4%. Stresses generated by the volume expansion cause cracks in pure zirconia ceramics. The addition of various metal oxides can remove this disruptive transformation by partially or fully stabilizing the cubic or the tetragonal phase at low temperatures. By adjusting the amount of the additional metal oxides (CaO, MgO, CeO₂ or Y₂O₃), it is possible to control the content of the cubic, monoclinic and tetragonal phases in zirconia [31].

The yttria-zirconia system has been extensively studied. The phase diagram of the Y₂O₃-ZrO₂ system is shown in Fig.2-2. TZP containing approximately 2~3 mol% Y₂O₃ have sub-micron tetragonal grains sizes. Retention of the tetragonal phase at room temperature is an important factor in the transformation-toughening phenomenon, although it is metastable by nature. A critical grain size exists (Fig.2-3), depending on the yttria concentration, above which, a spontaneous T-M transformation takes place. However, this transformation is inhibited in fine-grained structures [32,33].

Fig.2-2 Yttria-zirconia phase diagram (PSZ: partially stabilized zirconia, with the tetragonal phase among the cubic phase; TZP: tetragonal zirconia polycrystalline; m_{ss}: monoclinic phase system; t_{ss}: tetragonal phase system; c_{ss}: cubic phase system)[32]

Fig.2-3 Retention of tetragonal phase. Critical grain size against yttria content in tetragonal zirconia [32]

II. Mechanical properties of the TZP

TZP ceramics are the materials of choice by almost all manufacturers of zirconia ball heads. Table 2-2 lists the mechanical properties of TZP comparing with alumina. One can see that TZP has higher bending strength and fracture toughness than alumina, while its compressive strength, Young's modulus and hardness are lower. As mentioned earlier, a low Young's modulus is preferred to prevent the stress-shielding problem [34].

Table 2-2 Mechanical properties of alumina and TZP [35]

Property	Units	Alumina	TZP
Chemical composition		99.9% Al ₂ O ₃ + MgO	ZrO ₂ + 3 mol% Y ₂ O ₃
Density	g cm ⁻³	≥3.97	> 6
Porosity	%	<0.1	<0.1
Bending strength	MPa	>500	900-1200
Compression strength	MPa	4100	2000
Young modulus	GPa	380	210
Fracture toughness K _{IC}	MPa.m ^{-1/2}	4	7-10
Thermal expansion coefficient	K ⁻¹	8x10 ⁻⁶	11x10 ⁻⁶
Thermal conductivity	WmK ⁻¹	30	2
Hardness	HV 0.1	2200	1200

Bioactive ceramic materials

1. Hydroxyapatite

Hydroxyapatite (HA, chemical formula Ca₁₀(PO₄)₆(OH)₂) is the main mineral constituent of teeth and bones. It exhibits no cytotoxic effects and shows excellent biocompatibility with hard and soft tissue including skin and muscle [36,37]. Moreover, HA can directly bond to bone and seems to be an ideal material for bone replacement. However, HA has its limitations including poor mechanical reliability, especially in wet environments [38] and cannot be used for heavy load-bearing applications. Nevertheless, numerous studies have been undertaken to fabricate more mechanically reliable bioactive HA [39]. One of the most important clinical applications of HA is as a coating on metal implants, such as hip joint prostheses. This

concept combines the mechanical advantages of metal alloys with the excellent biocompatibility and bioactivity of HA with the coating most often applied by plasma spraying.

2. Bioactive Glasses and Glass-Ceramics

Bioactive glasses are silicates containing sodium, calcium and phosphate as their main components. They bond to bone by a surface layer of hydroxyapatite that forms through chemical reaction with the glass, which has been confirmed by several investigators [40,41].

Bioactive glasses can be distinguished from the traditional soda-lime-silica glasses by three key compositional features: (1) $<60\text{mol\%SiO}_2$, (2) high Na_2O and CaO content, and (3) high $\text{CaO/P}_2\text{O}_5$ ratio. This makes the surface highly reactive when exposed to an aqueous medium. One example is Bioglass (45S5) that contains 45wt% SiO_2 , 24.5wt% Na_2O , 24.5wt% CaO , 6wt% P_2O_5 , MgO and K_2O [42].

Bioglass can be used as an implant itself to fill orbital floor fractures [43] or replace ossicular bone in middle ear [44]. However, the use of bioactive glasses for orthopedic applications has been somewhat limited because of the poor mechanical properties. One method to improve the strength is to heat-treat the glass to form a glass-ceramic. Japanese researchers have used a calcium-phosphate-silicate formulation to create high-strength, bioactive apatite and wollastonite glass-ceramic system [45]. These materials have been shown to bond with bone, yielding failure loads comparable to those for dense hydroxyapatite [46]. The bioactive glass-ceramics have a number of clinical applications in orthopedics, including vertebral spacers and structural prostheses used to fill the iliac crest following the harvesting of autogenous bone [47].

Biodegradable Ceramic Materials

The most widely used biodegradable ceramic materials are calcium phosphates, which

show a range of solubility. Resorbable calcium phosphates include alpha and beta tricalcium phosphates [48]. Listed in Table 2-3 are some biodegradable calcium phosphate compounds. While the forming method and exact stoichiometry will have an effect on solubility, the generally accepted order of solubility is [24]:

$$ACP > DCP > TTCP > \alpha\text{-TCP} > \beta\text{-TCP} \gg HA$$

The Ca/P ratio is important in determining the solubility and tendency for resorption in body. The presence of micropores in sintered materials can increase the solubility of these phases.

Table 2-3 Some calcium phosphate compounds [48]

Chemical name	Abbr.	Chemical formula	Phase	Ca/P
Amorphous calcium phosphate	ACP	-	-	-
Dicalcium phosphate	DCP	CaHPO ₄	Monetite	1.00
Tricalcium phosphate	α -TCP	Ca ₃ (PO ₄) ₂		1.50
Tricalcium phosphate	β -TCP	Ca ₃ (PO ₄) ₂	Whitlockite	1.50
Pentacalcium hydroxylapatite	HA	Ca ₁₀ (PO ₄) ₆ (OH) ₂	Hydroxyapatite	1.67
Tetracalcium phosphate monoxide	TTCP	Ca ₄ O(PO ₄) ₂	Hilgenstockite	2.00

2.2.4 Bioceramic composites

In the past twenty years, ceramic composites have been widely studied and developed. The mechanical and biological properties of the composites can be tailored. The bioceramic composites can also be divided into bioinert, bioactive and biodegradable.

Bioinert ceramic composites

Zirconia and alumina are widely used bioinert ceramics. However, many reports have shown that zirconia/alumina composites exhibit higher performance than single-phase ceramics [49]. For alumina matrix based composites, the main toughening and strengthening mechanisms are zirconia phase transformations and microcracking [49]. Casellas *et al.* [50] reported the effect of zirconia particle size on the phase

transformation in zirconia-toughened alumina (ZTA), while Kaya *et al.* [51] developed high strength and ZTA with a helical spring shape from a sol-derived paste. Huang *et al.* [52] reported the influence of zirconia content and sintering temperature on the microstructure and the mechanical properties of ZTA. Another composite is TZP based. It also shows higher toughness and strength than single phase TZP ceramics. The increased toughness is due to the microstress-induced strengthening [53]. In this regard, Shi *et al.* [54] studied nano Y-TZP/ Al_2O_3 composites and Travitzky *et al.* [53] fabricated Y-TZP/20wt% Al_2O_3 composites using direct microwave sintering, which resulted in nearly full densification in spite of the relatively high alumina content in the composites. Pabst *et al.* [55] prepared alumina-toughened zirconia (ATZ, 20wt% alumina, 80wt% zirconia containing 3mol% yttria) using a commercial ATZ powder and a liquid binder for paste extrusion at the room temperature.

Bioactive ceramic composites

HA based bioactive ceramic composites have been widely developed to increase the mechanical properties of HA. In recent years, many reinforcements, including polymer [56], partially stabilized zirconia [57], aluminium oxide [58] and metal dispersoids [59] (e.g. Ti, Ti-6Al-4V) have been used in HA ceramics to improve the toughness and strength. However, the introduction of foreign materials into the HA matrices may reduce biocompatibility and promote the decomposition of HA into TCP. The presence of TCP increases biodegradability [60] and slow crack growth susceptibility. It also negatively influences the densification of the composite and decrease the strength.

Bioactive glasses are also used to prepare HA-based composites. The combination of bioactive glasses with HA results in bioceramics with improved mechanical properties but no less of biocompatibility and/or bioactivity. HA/bioactive glass composites can be prepared by sintering of appropriate powder mixtures [61]. If sintering is carried below 1000°C , HA does not react significantly with bioactive glass. The product is

also dependent on glass composition. Other constituents' of bioglass based composites include stainless steel/Bioglass[®], Poly-(D, L-lactide) (PDLLA)/Bioglass[®], caprolactone-lactide copolymer (P (CL/DL-LA))/bioglass and Si₃N₂/bioglass.

Biodegradable ceramic composites

Biodegradable ceramic composites include TCP/PLA, TCP/PLGC (poly (L-lactide-*co*-glycolide-*co*- ϵ -caprolactone)), TCP/PHB, TCP/PLCL (poly (L-lactide-*co*- ϵ -caprolactone)), and HA nanocrystal and chitosan incorporated composite bone pastes.

In summary, metallic biomaterials have been widely used due to their excellent mechanical properties. Stainless steel, Co-based alloys, Ti and its alloys are the most popular metal implants now being employed for hard tissue replacement. However an evident disadvantage for metallic biomaterials is the release of metal ions (i.e. corrosion) into surrounding tissue with possible toxic side effects. Polymeric materials have a wide variety of applications for implantation since they can be easily fabricated into many forms: fibers, textiles, films, rods and viscous liquids. Polymeric materials possess the desired toughness, however, their biocompatibility remains to be optimized. Ceramic materials have been extensively studied as implant materials since they possess certain highly desirable characteristics including inertness to body fluids, high compressive strength and good aesthetic appearance, but conversely are susceptible to brittle fracture. Since no single-phase material can satisfy these stringent mechanical and biological requirements, composites and coatings have been studied to integrate in a single product the necessary features of a product for particular applications.

2.3 Review of porous bioceramics

For all the dense biomaterials mentioned above, there are porous counterparts. Early biomedical applications of porous ceramics were osteointegration of dental implants [62], fillers of osseous cavities, implants of improved biocompatibility [63], and long-term fixation and stress transfer for the cementless skeletal fixation by bone ingrowth [64]. Porous ceramics are recently used as matrices for tissue engineering [65] to carry cells and tissues [66]. They can offer two significant advantages over their nonporous counterparts [67], i) a porous structure has interconnected macropores (bigger than $100\mu\text{m}$) suitable for cell penetration, tissue ingrowth and vascularisation; and ii) by tailoring pore size and porosity, the material can provide mechanical properties sufficient for some applications involving load bearing. The mechanical strength and the preparation of porous ceramics are reviewed in the following sections.

2.3.1 Structure and mechanical properties of porous ceramics

Structure of porous ceramics

Porosity is the singularly important structural parameter of porous ceramics. Pores can be isolated (closed) or connected (open). The definitions of various porosities are listed in Table 2-4. Pore size and its distribution are also important. Studies show that a minimum pore size of $100\mu\text{m}$ is necessary for bone ingrowth [68]. Pores bigger than $100\mu\text{m}$ were considered macropores in this thesis, and originated from burning off polymer pore preform. Pores rising from incomplete sintering due to powder agglomeration were considered micropores. Both pore shape and internal surface morphology are important. Open pores need not be of uniform dimensions along the pore channel, alternating between narrow (throat) and wide (stomach) portions. If the throat is too narrow, cells and/or tissues may not be able to migrate or grow into the pores. For open porous ceramics, the volume that is not occupied by the open macropores is filled by webs, networks or struts.

Table 2-4 Definitions of porous parameters

Parameter	Definition
Total porosity	Total pore volume/bulk volume
Open porosity	Open pore volume/bulk volume
Closed porosity	Closed pore volume/bulk volume

Mechanical properties of porous ceramics

The basic mechanical properties of porous ceramics include Young's modulus, hardness, strength and fracture toughness. Their importance lies in the fact that a bone replacement requires a certain level of robustness. Compared with dense counterparts, porous ceramics exhibit much poorer mechanical reliabilities. However, the open porosity is necessary for body fluid circulation, cell attachment and tissue ingrowth. Thus it is a practical issue to achieve an optimal balance between porosity and the mechanical properties. So it is critical to understand the mechanisms of failure and the relationship between mechanical parameters and pore configuration.

Various methods have been used to mechanically test porous ceramics. Luo and Stevens [69] measured the elastic modulus by the ultrasonic velocity method and Vickers hardness of porous yttria-stabilized zirconia (3Y-TZP) ceramics. Barinov [70] performed fracture experiments with notched and un-notched three-point bending specimens of porous zirconia ceramics. Callcut and Knowles [71] studied the compressive strength of a reticulated glass-reinforced hydroxyapatite foam. Aue and Hosson [72] measured the acoustic emission (AE) from highly porous ceramics subjected to the Brazilian (loading in the radial direction of a disk specimen) test or dimetral test. Panakkal [73] used longitudinal ultrasonic velocity to calculate the Young's modulus of porous ceramics. Latella *et al.* [74] observed the surface and subsurface damage patterns in porous ceramics using a bonded-interface sectioning technique.

While the mechanical properties are dependent on the porous structural parameters such as porosity, pore size and pore shape, the relationships between them are

complex. However for well-specified systems, rigorous modeling is possible.

Gibson and Ashby [75] developed a model (GA model) capable of explaining the mechanical behavior of brittle cellular materials. The GA model assumes that the unit cell for open-cell materials is represented as a cubic array of square struts of cross section t and length L (Fig.2-4). Adjoining cells are staggered so that their members meet at their midpoints. The relative density of the cell is given as:

$$\frac{\rho_{cf}}{\rho_s} \propto \left(\frac{t}{L}\right)^2 \quad (2.1)$$

where ρ_{cf} is the bulk density of the ceramic foam and ρ_s the density of the solid struts.

Fig.2-4 Unit cell in open-cell material [75]

The GA model suggests that the mechanics of a unit cell can be applied to describe the overall deformation behavior of the foams. The dependence of compressive strength (σ_{cf}) on relative density (ρ_{cf}/ρ_s) of brittle foams relies on the fact that collapse occurs when the bending moment being applied to the struts reaches the fracture moment (Fig.2-5):

Fig.2-5 Schematic drawing showing the fracture of a unit cell in brittle open-cell material [75]

$$M_f = \frac{1}{6} \sigma_{fs} t^3 \quad (2.2)$$

where σ_{fs} is the fracture strength of the strut material. Under these conditions, the compressive strength of the foam σ_{cf} can be calculated through the relationship:

$$\frac{\sigma_{cf}}{\sigma_{fs}} = C_1 \left(\frac{\rho_{cf}}{\rho_s} \right)^{3/2} \quad (2.3)$$

where C_1 is a geometric constant characteristic of the unit cell shape that is found to be equal to 0.65 for brittle open-cell foams by fitting the theoretical equation to limited data.

Rice [76] developed a physical property-porosity model based on the concept that the minimum solid area (MSA) (Fig.2-6) normal to the stress should dominate its transmission (i.e. strain, fracture toughness or energy, or strength) through a body. It assumes that mechanical properties are determined by the properties and dimensions of the struts between the pores rather than the thicker cross-sections. The solid spherical particle models were shown to approximate the exponential relation (e^{-bP}) with b values corresponding to unique particle stackings and hence pore structures.

The MSA model has been used for many years to describe individual pore structures, such as uniform spherical pore, cubical pore, aligned cylindrical pore and solid spherical particle. The available collections of pore structures of the MSA models include most, if not all, real pore structures and a number of important physical properties.

Fig.2-6 Schematic illustration of the MSA concept. (a) The cross-section of a dense, uniform body where the transmission from layer to layer, normal to a uniform stress, is the same in every layer; (b) the cross-section of a body identical to that in (a) except it has most of a layer removed, leaving only three small areas of continuity which now dominate the transmission of stress normal to the plane of the slab. Clearly, the average cross-sectional area is not a good indicator of the stress of this body; the limited contact area, i.e. the MSAs, are good indicators. (c), (d) cross-section of particles or bubbles, respectively, where again the minimum areas of the solid cross-sections between pores (cross-hatched) will dominate stress transmission normal to the plane of the slab. Note the horizontal dashed lines indicating the basic, repeat cell structure of the bodies and designated MSA.

2.3.2 Sintering behavior of porous ceramics

Sintering behavior of porous ceramics with pores bigger than $100\mu\text{m}$ has not been widely studied. Several recent studies regarding this topic are reviewed in this section.

Chi *et al.* [77] studied the sintering behavior of porous SiC ceramics. It was found that the introduction of proper amount of dispersant could improve the stability of the slurry and reduce the defect in the final sintered body. Optimizing the Al_2O_3 content in the raw powder could also reduce defects in the final sintered body. Kim *et al.* [78] reported that for sintering porous (Ba,Sr)(Ti,Sb) O_3 ceramic, the porosity decreased, whereas the grain size increased with increasing sintering temperature/time. In Clemmer and Corbins' [79] research work about porous Ni/YSZ composite, it was found that the difference in green tape microstructure could result in different sintering behavior. Higher green density usually led to lower sintering shrinkage. The formation of agglomerates during processing would also decrease the shrinkage. The variation in the green microstructure and density caused the various sintering shrinkage. Senguttuvan *et al.* [80] found that for porous alumina rich cordierite with porosities from 68% to 83%, the sintering temperature did not have significant effect on the porosity, density, permeability or fracture strength.

The maximum pore size in the reviews above was around $10\mu\text{m}$. So far no report has been published for the sintering behavior of porous ceramics with pores larger than $100\mu\text{m}$ (the minimum criteria to achieve bone ingrowth). However, for the strut (the dense part in porous structure), the conventional sintering behavior still can be applied. By optimizing the process parameters such as slurry viscosity (for slip casting), green density, sintering temperature and time, high sintering density and low shrinkage can be achieved.

2.3.3 Fabrication of porous bioceramics

PU sponge

A traditional method to fabricate a porous ceramic structure is to burn off polymer preforms during sintering. Polyurethane sponge is widely used as preform to prepare cellular porous ceramic structures. Kwon *et al.* [81] prepared porous calcium phosphate bioceramics (HA, TCP and HA/TCP) by using polyurethane sponge (45 pore per inch, i.e., 564 μm). The resulting structures (Fig.2-7) had porosities in the range of 65~90% and pore sizes of 400~500 μm . Milosevski *et al.* [82] also studied porous TCP prepared by polyurethane sponge. Similarly, Jun *et al.* [83] reported alumina reinforced calcium phosphate porous implants fabricated by burning off polyurethane sponge. This method usually leads to uniformly distributed and interconnected pores, however, since the ceramic slurry is normally coated onto the PU foam, after sintering, the PU foams is burnt out, leaving holes in the ceramic struts. Poor mechanical properties are to be expected.

Fig.2-7 SEM micrograph (SEI mode) of porous HA prepared by Kwon *et al.* [81]

PVB powder

Polyvinyl butyral (PVB) powder is another polymeric preform widely used to fabricate porous structures, where either slip casting or uniaxial compression method is employed. Liu [84] prepared porous hydroxyapatite via a slip-casting route. The

hydroxyapatite slurry was blended with PVB powders, which after drying was sintered to form porous structures. Liu [85] also reported porous hydroxyapatite via a die-pressing route, where PVB particles were mixed with hydroxyapatite granule and the green pellets sintered (Fig.2-8). By using PVB powders as a preform, pores with different sizes and porosities could be produced, but pore interconnectivity was usually low.

Fig.2-8 SEM micrographs (SEI mode) showing porous HA ceramics prepared at 1200°C for 2h that consist of (a) macropores and (b) micropores [85]

Solidfreeform fabrication

In the past ten years, with the development of computer technology, polymer scaffolds have been designed and used as preforms. Taboas *et al.* [86] developed a porous architecture using an image based design (IBD) method, which allowed creation of complex internal pore architectures and external scaffold shapes to match the implant site requirements. Wax or PSA (polysul-phonamide) molds (Fig.2-9) were created using a 3D printing technique on a Solid Scape, Inc. Model Maker II 3D printer.

Fig.2-9 Optical photo of indirect wax molds (left) fabricated on a Solid Scape MM2 3D printer and cast ceramic molds (right) [86]

Charrière *et al.* [87] also developed hydroxyapatite cement scaffolds with controlled sizes and shapes using a solid freeforminkjet manufacturing process. Fig.2-10 shows a periodic, orthogonal array of cylinders made of a thermoplastic with a diameter of 1mm. The external shape is a cylinder of $18 \times 18 \times 30 \text{ mm}^3$. A slip casting process using a plaster mold was then applied to cast the mixture of dicalcium phosphate and calcite with a dispersing agent in order to obtain the hydroxyapatite cement. The green body was heated at 90°C for 1 hour to melt and remove the thermoplastic from the sample. The resulting hydroxyapatite cement structure is shown in Fig.2-11.

Fig.2-10 Optical photo of negative macroporosity for a cylindrical thermoplastic sample [87]

Fig.2-11 Optical photo of a hydroxyapatite cement sample with designed macroporosity [87]

Solid freeform fabrication methods provide complete control of the porous structural parameters. It is an ideal process to fabricate 3D scaffolds that can be used as a negative for a desired porous structure.

Other methods

Lyckfeldt and Ferreira [88] prepared porous alumina by starch consolidation. By mixing alumina powder with starch in water suspension, pouring the slurries into a mould and heating the green body to 60~80°C, the starch particles swell by water uptake causing the ceramic particles to adhere and, consequently, consolidate into a solid body. After burning off the starch and sintering of the ceramic matrix, a porous alumina material was obtained. Rambo *et al.* [89] developed highly porous yttria stabilized zirconia by infiltration of zirconium-oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) sol into biological template structures derived from rattan and pinewood.

2.3.4 Bone ingrowth of porous ceramics

The advantage of porous materials, in general, is their ability to provide biological fixation to the surrounding bony tissues via the growth of tissues into the pore spaces. Fixation is accomplished by increasing the available surface area for apposition (or bony contact) and by having the interior of the implant accessible due to open pores. Numerous factors affect bone ingrowth into the pore spaces, including porosity, pore size, pore interconnectivity, time of implantation, material biocompatibility, implant stiffness and amount of micromotion between the implant and the adjacent bone.

Lu *et al.* [90] studied the effect of pore neck sizes in hydroxyapatite (HA) and β -tricalcium phosphate (β -TCP) on bone ingrowth. The two bioceramics had the same porosity of about 50%, a mean pore size of 100-300 μm and a mean neck size of 30-100 μm . In vivo, a 20 μm pore neck size only allowed cell penetration and chondroid tissue (a soft tissue) formation. Pore necks larger than 50 μm favored new bone ingrowth inside the pores. Thus there is a pore size requirement to favor particular tissue ingrowth. Chang *et al.* [91] used four kinds of cylindrical-type implants with parallel linear pores (50, 100, 300 and 500 μm) to assess the histological response and the reinforcing effect of bone ingrowth in porous hydroxyapatite (HA) implants. Active osteoconduction was found in the 50 μm -sized cylindrical-type porous HA. Evidence of remodeling of new bone and bone marrow formation within porous HA was found in the larger cylindrical-types (300 and 500 μm). The biomechanical test showed that the ultimate compressive strength increased significantly in the 300 μm -sized cylindrical-type eight weeks after implantation. Here it can be seen that pore size also effects bone development and/or the bone remodeling process, thus affecting the quality of bone repair and regeneration. According to Gauthier *et al.* [92] implants with the 565 μm pore size provided more abundant newly formed bone in both peripheral and deep pores than those with the 300 μm pore size. No significant differences were found between implants with 40% and 50% porosity, suggesting that the influence of macropore size on bone ingrowth

was greater than that of porosity. Hulbert and Klawitter [93] reported that pore sizes of at least 50 μm were required for the ingrowth of blood vessels. Tissue ingrowth into the implants required pore sizes above 75 μm , but continued ingrowth was observed only for pore sizes above 100 μm . Pores sizes above 200 μm decreased the mechanical properties. They further specified three pore size ranges for tissue ingrowth: (1) minimum size for mineralized bone ingrowth, 100 μm , (2) minimum size for nonmineralized osteoid ingrowth, between 40-100 μm , and (3) minimum size for fibrous ingrowth, between 5-15 microns.

2.4 Graded porous bioceramics

Ceramics with graded pore sizes or porosities have been used as functionally graded cermets, for hot gas purification, as liquid filters, and membranes, mandrels for metal casting, and for biomedical applications such as drug delivery systems and dental root implants. Graded porous bioceramics have additional advantages over uniformly porous structures:

1. An implant with graded porosity or pore size resembles the natural structure of bone and the whole bone cross-section from trabecular (cancellous) to cortical bone can be mimicked.
2. Implants can be created with varying porosity and pore size in different regions with specificity to enhance ingrowth of different tissues and cells.
3. Graded porous implants optimize the ability to withstand varying mechanical loads at specific regions.
4. Non-uniform porosity can be used to modify the rate of bone ingrowth through the depth of the replacement and over time. Higher porosity would be used where initial bone ingrowth and maturation occurs (e.g. the surface of an implant), while a lower porosity would be appropriate in regions where bone will take a longer time to develop (e.g. in the interior of an implant).

Although graded porous ceramics have the above advantages, reports on their fabrication and characterization remain limited, as it is challenging to create these materials with sufficient interconnectivity. Only the compressive strength of graded porous bioceramics has been reported to date [94].

Wemer *et al.* [95] produced graded porous hydroxyapatite material by means of tape casting. Macroporosity was generated by incorporating polymeric spacer balls into the slurries for the tapes (Fig.2-12), which were subsequently burnt out during sintering. Temperatures between 1100°C and 1300°C preserved the ceramic matrix, resulting in multi-layer structures of hydroxyapatite with graded macroporosity (Fig.2-13).

Fig.2-12 Schematic illustration of fabricating pore graded multilayers by lamination of individual tapes, manufactured by tape casting (doctor-blade-process) [95]

Fig.2-13 SEM micrographs (SEI mode) of graded HA-multi-layer structures: dried green body with polymeric spacers (left); porous ceramic, sintered for 2h at 1250°C (right) [95]

Tampaeri *et al.* [96] prepared porosity-graded hydroxyapatite by varying the characteristics of starting HA powders and by impregnation of sponges with rheologically optimized slurries. A multiple and selective impregnation route was used: first an HA slurry was used for complete impregnation, subsequently a partial impregnation (only one side of the sponge) was performed using a dilute slurry. After drying and sintering, a porosity graded HA structure was obtained.

Cichoki and Trumble[97] reported porosity-gradient ceramics by colloidal infiltration of deformed polymer sponges. Polyurethane (PU) sponges were sectioned to various thicknesses and shapes. A continuous porosity gradient was produced by compression moulding a wedge-shaped sponge into a planar geometry. More complex shapes and gradients were produced by consolidating premoulded sponge segments in a stepwise fashion. The sponges were inserted into a pneumatic pressure infiltration device and the ceramic slurry was pressure cast into the spaces between the struts of the sponge. After burning off the sponge, a porosity-gradient ceramic structure was obtained.

Ravaglioli *et al.* [94] developed shell-like layered HA structures with a graded porosity by slip casting. The overall porosity achieved was 30~45vol%. Compressive strength tests on cylindrical samples demonstrated a resistance of $\sigma = 31 \pm 11$ MPa. Pompe *et al.* [98] prepared graded porous HA ceramics by sintering laminated structures of HA tapes filled with polymer spheres or combining biodegradable polyesters such as PLA, PLGA and PGA, with carbonated nanocrystalline HA. Vaz *et al.* [99] reported dual-layer HA with differential sizes and porosities using a multiple slip-casting technique. The porosity was controlled by the addition of PVC (polyvinyl polyacrylate).

In summary, porous and graded porous bioceramics for bone replacement have attracted great attention in recent years due to their mechanical and structural advantages compared to their dense counterparts. Conventional methods to prepare porous ceramics include slip-casting of ceramic slurries with polymer particles,

dip-coating polymer foams with ceramic slurry, and die-pressing of ceramic and polymer powder mixtures. Porous structures can be obtained after burn off the polymer preforms. Slip casting and die-pressing can cause low pore interconnectivity in the porous body. Dip-coating can achieve a high open porosity, but low mechanical properties. By using computer designed polymer scaffolds as preforms, well-regulated open porous bioceramics can be achieved. The methods to produce graded porous structures are limited so far. The graded porous structures obtained by mechanical lamination of porous layers with different porosities or pore sizes have a poor interconnectivity between each porous layer. Selective impregnation of polymer foams with a ceramic slurry leads to a porous body with poorly controlled porosities. Besides, the defects in the ceramic struts left by the removal of polymer foams lower the mechanical strengths. Thus, a novel method to produce graded porous structures with high interconnectivity and sufficient mechanical properties is needed.

2.5 Review of bioactive coatings on bioinert substrates

Load bearing bone replacements, such as ceramic and metallic biomaterials, have enjoyed clinical success because of their superior strength, durability and resistance to corrosion in physiological environments. Upon implantation, close contact of an implant with the surrounding host tissue is required for the subsequent ingrowth of bone tissue into the pre-designed cavities on the implant surface. The shifting of relative positions between the implant and the surrounding tissue is highly undesirable and therefore immobilization of a patient is needed before the implant fixation is strong enough to bear a load. However, the most widely used load-bearing ceramics such as alumina and zirconia, and metallic biomaterials such as titanium and its alloys, are bioinert materials. Thus surface modification is desirable to induce bioactivity that can lead to rapid bone development between the implant and the surrounding bone tissue. Bioactive coating materials, such as HA, bioglass and recently developed glass-reinforced HA, are reviewed in the following sections.

2.5.1 Materials and methods used for bioactive coatings

Hydroxyapatite coatings

HA has been widely used as a coating material on metal implants, such as hip joint prostheses. The HA coatings fulfill several functions. First, they provide stable fixation of the implant to bone and minimize adverse reactions by provision of a biocompatible phase. Second, the HA coatings decrease the release of metal ions from the implant to body and shield the metal surface from environmental attack.

The plasma spraying technique is the most popular method to fabricate HA coatings. The coatings have been applied not only on metals, but also on carbon implants [100], sintered ceramics like ZrO_2 and Al_2O_3 , and even polymers (PMMA) [101].

The thickness of the HA coatings is usually in the range of 40~200 μm . The coatings must be thick enough to resist resorption of HA which can be as much as about 15~30 μm per year [101]. It has been noted that the fixation of an implant to the bone can be improved if the HA coating has an appropriate porosity, which promotes bone ingrowth.

Bioactive glass and glass-ceramic coatings

Alternative coatings for titanium based alloys and bioinert ceramics are bioactive glass and glass-ceramics because of their controlled surface reactivity and good bone bonding ability [102]. These materials, when put in contact with biological fluid, are able to provide a strong bonding with the surrounding tissues, via a complex mechanism based on ion leaching, controlled dissolution of the glass surface and precipitation of an apatite layer from the solution. Bioactive glass and glass-ceramic coatings can be achieved by different methods such as conventional enameling [103], sputtering technique [104], vacuum plasma spraying [105], and laser deposition [106].

In vitro tests conducted by Oliver *et al.* [107] showed that bioglass coated titanium alloy elicited a rapid and strong proliferative response by osteoblasts, which spread, formed a close layer and then expressed the specific osteoblastic marker i.e. osteocalcin. *In vivo* tests of a bioactive glass-coated (RKKP bioglaze[®]) zirconia was carried out by Stanic *et al.* [108]. 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.

Glass-reinforced hydroxyapatite coatings

As has been mentioned before, HA has many crystallographic features similar to those of the natural apatite present in bone, but it is limited to low-load applications because of its poor mechanical strength. Thus, glass-reinforced HA composites have been developed by incorporating phosphate-based glasses into the microstructure of HA through a simple liquid-phase sintering process [109,110]. Such composites have higher fracture toughness than sintered HA, and a comparative study of the formation of an apatite layer on the two surfaces has suggested that the composites exhibit an enhanced rate of bone bonding [111]. The glass-reinforced hydroxyapatite has also been used as a coating on titanium based alloys [112,113] as well as bioinert ceramics [114].

Queiroz *et al.* [115] carried out *in vitro* test on glass-reinforced hydroxyapatite and found that the bioactivity of the glass-reinforced HA was higher than HA because a homogeneous CaP layer was formed and the precipitation occurred faster. Salih *et al.* [116] also found that modulation of the glass composition in the composites not only improved mechanical strength, but also enhanced biocompatibility.

2.5.2 Bioactive coatings in porous structures

Bioinert ceramics such as zirconia and alumina are often used to produce porous structures due to their excellent mechanical properties. In order to provide additional bioactivity, a bioactive coating is needed for the porous substrates.

Shi and Jiang [117] coated porous Al_2O_3 with HA by dip coating. Lu and Pilliar [118] applied HA coating onto porous Ti6Al4V by an organic and inorganic sol-gel route. Chen *et al.* [119] developed HA thin films on porous silicon substrates by an aqueous precipitation method with rapid thermal annealing. Kim *et al.* [120] coated porous HA scaffolds with HA/PCL composite coatings for drug delivery.

In summary, hydroxyapatite, bioactive glass and glass-reinforced hydroxyapatite are most widely used as bioactive coating materials to induce bioactivity on bioinert substrates. Among them, glass-reinforced hydroxyapatite has been found to be the most promising coating material that not only improves mechanical strength of HA, but also enhances the biocompatibility.

Chapter 3

Experimental Procedure

3.1 Starting materials

The starting materials used to prepare the porous bioceramics were 3mol% yttria stabilized zirconia powder and alumina powder (AKP-30). Polymethacrylic acid (PMAA) was used to disperse the ceramic slurries. HCl (0.1 M) and NaOH (0.1 M) were used to adjust the pH of the slurries. The polymer preforms used in this study were expanded polystyrene (EPS) beads and polyurethane (PU) foams. Hydroxyapatite (HA) and borosilicate glass powder was used for coating. All these materials will be introduced in detail in the following sections.

3.1.1 Zirconia powder

Zirconia powder used in this study was 3mol% yttria stabilized zirconia (Aldrich Chemical Company, Inc.) with an average particle size of $0.265\mu\text{m}$ (measured by Brookhaven BI-XDC at 2000 rpm at room temperature) and a specific surface area of $4.01\text{m}^2/\text{g}$ (measured by Micrometric ASAP 2000 using nitrogen adsorption at 300°C). The zirconia powder was characterized by X-ray diffraction (Lab XRD-6000 Shimadzu) using the Cu-K_α radiation at 50kV-20mA. The XRD pattern matches the JCPDS (Joint committee on powder diffraction standards) card No. 50-1089 (t- ZrO_2) and No. 37-1484 (m- ZrO_2), indicating major tetragonal phase and minor monoclinic phase.

3.1.2 Alumina powder

Alumina powder used in this study was AKP-30 (Sumitomo, Tokyo, Japan) with an average particle size of $0.357\mu\text{m}$ and a specific surface area of $6.28\text{m}^2/\text{g}$. The XRD pattern of alumina powder matched the JCPDS card No. 10-0173 ($\alpha\text{-Al}_2\text{O}_3$).

3.1.3 Borosilicate glass powder

The borosilicate glass powder was obtained by crushing Pyrex[®] borosilicate glass fragments into glass frits, followed by attrition milling at 100rpm for 24 hours and planetary ball milling at 75rpm for 8 hours. The particle size of the borosilicate glass powder was $0.50\mu\text{m}$ (measured by particle size analyzer). The borosilicate glass had the following typical composition: 80.6wt% of SiO_2 , 4wt% of Na_2O , 13wt% of B_2O_3 , and 2.3wt% of Al_2O_3 (sum $\approx 99.9\%$). The softening point of the glass was 821°C and the annealing point was 565°C . The density of the glass was $2.23\text{g}/\text{m}^3$ [121].

3.1.4 Hydroxyapatite powder

The HA powder used for coating was commercially available HA (Riedel-de Haë[®]) with an average particle size of $0.11\mu\text{m}$. The XRD pattern of HA powder is shown in Fig.3-1, which matches the JCPDS card No. 9-0432. All peaks belong to HA except one reflection at 29.5 degrees (2theta) that most probably belongs to β -tricalcium phosphate (JCPDS card 9-0169).

Fig.3-1 XRD pattern of the HA powder (the numbers are indexes of crystallographic planes)

3.1.5 Dispersant

The polyelectrolyte dispersant (Darvan C, R. T. Vanderbilt) used to disperse the ceramic slurries was a solution of ammonium salt of polymethacrylic acid (PMAA) containing 75wt% water and 25wt% active substance, with a molecular weight of 12000. The pH of the PMAA was 8 (tested by a pH meter Cyberscan 510). Fig.3-2 shows the molecular formula of the PMAA segment.

Fig.3-2 Molecular formula of the PMAA segment

3.1.6 Preforms

EPS beads

The EPS beads with the trade mark of Styropor[®] were kindly offered by BASF Singapore Pte. Ltd. Fig.3-3 shows the unit segment of polystyrene. The average particle sizes of the beads were measured from optical micrographs of the powders by the Stereozoom Microscope (Leica MZ6), followed by analysis using an image processing software (UTHSCSA Image Tool 2.00, a free image processing and analysis program for Microsoft Windows). The average particle size of the beads were 2.95mm, 2.58mm, 2.18mm, 1.85mm and 1.40mm. Scanning electron microscopy (SEM, JEOL, JSM-5310 LV) was also used to confirm the beads were spherical and had a porous structure. The density of the beads was 0.016g/cm³(according to the product specification).

Fig.3-3 Segment of polystyrene

Polyurethane (PU) foam

The PU foam used in this study was commercially available from Foamex Co. and contained about 11 pores/cm. Fig.3-4 shows an optical photograph of the PU foam.

Fig.3-4 Optical photograph showing a PU foam

3.2 Slurry optimization and particle consolidation

3.2.1 Ceramic slurry preparation and characterization

Ceramic slurry preparation

Dilute zirconia (3mol% yttria) and alumina suspensions with solids loadings of 5wt% were used for zeta potential tests. Up to 1.5wt% PMAA was added to the ceramic suspensions. The concentration of PMAA in the suspensions was calculated by the dry weight percentage as shown in Eq.3.1. Solutions of HCl(0.1 M) and NaOH (0.1M) were used to adjust the pH of the suspensions. The pH value was measured by a pH meter (Cyberscan 510).

Concentrated zirconia, zirconia/20wt% alumina (ZA20), and zirconia/30wt% alumina (ZA30) slurries with solids loadings of 50wt% were prepared for viscosity tests by planetary ball milling at 75rpm for 4 hours. Up to 2wt% PMAA was added to the slurries. The pH of the slurries was adjusted to about 9.

$$\text{Concentration of PMAA} = \frac{\text{Weight of dry PMAA powder}}{\text{Weight of dry PMAA powder} + \text{Weight of ceramic powder}}$$

3.1

Ceramic slurry characterization

The zeta potential and the particle size as a function of pH of the dilute zirconia and alumina suspensions were determined using a submicron particle size analyzer with zeta potential option (Brookhaven 90Plus Particle Size Analyzer). All the suspensions were dispersed in an ultrasonic bath for 15 minutes before testing.

The viscosities of zirconia, ZA20 and ZA30 slurries with solids loadings of 50wt% as a function of the PMAA content at $\text{pH} \approx 9$ were measured by a viscosity analyzer (HAAKE Viscotester VT550) with a rotational speed of 200s^{-1} , where s is second. The slurries were magnetically stirred on a hot plate for 15 minutes and ultrasonically dispersed for 30 minutes before testing.

3.2.2 Preparation and characterization of the green compacts

Optimized zirconia, ZA20 and ZA30 slurries were used based on previous experiments. Ceramic slurries with solids loadings of 50wt% were prepared by planetary ball milling at 75rpm for 4 hours. 0.5wt%, 0.7wt% and 0.8wt% PMAA were added to the zirconia, ZA20 and ZA30 slurries for dispersion, respectively. The pH of the slurries was set at about 9. The optimized ceramic slurry was cast in a specially designed device shown in Fig.3-5. To study the kinetics of vacuum casting of a ceramic green body for a fully dense ceramic, the slurry was cast into the plastic container without EPS beads, while different sizes of EPS beads were packed in the container when studying the kinetics of vacuum casting for green bodies containing EPS beads. A vacuum pump with a pressure capacity of 2 MPa (Aspirator A-3S, Eyele, Japan) was connected to the glass flask to facilitate water filtration and the formation of the green compact.

Fig.3-5 In-house designed apparatus for vacuum casting

Characterization of green compacts

The kinetics of vacuum casting of a ceramic slurry with EPS beads was studied. Different sizes of the beads (with average particle sizes of 2.95mm, 2.58mm, 2.18mm, 1.85mm and 1.40mm) were packed in the plastic container. Ceramic slurries were then sequentially poured into the graduated cylinder. The drop of the slurry level Δh within a casting time t was recorded.

The densities of the green compacts prepared by the slip casting of the ceramic slurries with various PMAA contents were measured by a geometry mass method. The weights and volumes of the specimens were measured and the densities calculated. The relative densities of the green bodies were calculated by dividing the measured bulk green densities with their theoretical densities. The theoretical density of the ZA composite was calculated based on the volume percentage of each powder in the mixture using the following equation:

$$\rho_{\text{composite}} = \rho_{\text{zirconia}} V_{\text{zirconia}} + \rho_{\text{alumina}} V_{\text{alumina}} \quad 3.2$$

where ρ_{zirconia} and ρ_{alumina} are the theoretical density of zirconia and alumina and equal to 6.01g/cm³ and 3.98g/cm³, respectively. V_{zirconia} and V_{alumina} are the volume percentage of zirconia and alumina in the composite and can be expressed as

$$\frac{m_{\text{zirconia}} / \rho_{\text{zirconia}}}{m_{\text{zirconia}} / \rho_{\text{zirconia}} + m_{\text{alumina}} / \rho_{\text{alumina}}} \quad \text{and} \quad 1 - V_{\text{zirconia}}.$$

The calculated theoretical densities of the ZA20 and the ZA30 composite were 5.45 g/cm³ and 5.21 g/cm³, respectively. The microstructures of the green compacts were studied by SEM (SEI mode, secondary electron image).

3.3 Sintering of zirconia and zirconia/alumina green compacts without EPS beads

TZP, ZA20, ZA30 disk samples (20mm in diameter and 7-12 mm in thickness) were prepared by vacuum casting of optimized zirconia, ZA20 and ZA30 slurries based on previous studies. The green compacts were dried in air for 2 days. The relative green densities of TZP, ZA20 and ZA30 were 39.7%, 44.8% and 50.7% respectively. Some green compacts were tested on a dilatometer, whereas others were sintered in air at 1400°C, 1450°C and 1500°C with a heating rate of 5°C/min.

A dilatometer (Anter Unitherm 1161) was used to study shrinkage of the TZP, ZA20 and ZA30 samples. Before tests, the diameters and the thicknesses of the disc samples were measured by an electronic caliper. The heating rate of the dilatometer was 5°C/min. The samples were heated up to 1550°C in air. The final densities of the sintered compacts were measured by an electronic densometer (MD 200S). TZP, ZA20 and ZA30 ceramics sintered at 1400°C, 1450°C and 1500°C were polished and thermally etched at 1350°C, 1400°C and 1450°C for 15 minutes to reveal the grain boundaries. The microstructures of the sintered bodies were studied by SEM, FESEM

(Jeol JSM 6340F) and transmission electron microscopy (TEM, JEM 2010). The average grain sizes of both zirconia and alumina were measured by UTHSCSA Image Tool 2.00. The phase compositions of TZP and ZA composites were identified by XRD.

Hardness tests were carried out on polished TZP, ZA20 and ZA30 samples sintered at 1400°C, 1450°C and 1500°C by a Vickers Hardness Tester (Shimadzu HSV20) with a constant load of 5 kg for 25 seconds. The fracture toughness K_{IC} (MPa.m^{1/2}) was calculated by measuring the crack lengths from the hardness tests using the following equation [122]:

$$K_{Ic} = 0.015 \left(\frac{c-a}{a} \right) \left(\frac{E}{H} \right)^{2/3} \frac{P}{c^{3/2}} \tag{3.3}$$

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 length (Fig.3-6), E (GPa) the Young's modulus, H (MPa) the hardness, P (N) the applied load. Young's moduli of 210GPa, 257GPa and 277GPa were used for TZP, ZA20 and ZA30, respectively. The Young's moduli of ZA composites were calculated by the rule of mixture based on the volume percentages of zirconia and alumina in the composites using Eq. 3.2.

Fig.3-6 Schematic showing the indentation impression from a hardness test

3.4 Structures and properties of uniformly porous TZP and ZA20 ceramics

3.4.1 Preparation of uniform pore sized porous structures

An in-house designed apparatus for vacuum casting was used to prepare porous structures. The apparatus is schematically shown in Fig.3-7. The plastic plate with holes on the bottom was used to support the gypsum mould plate (made using the powder/water ratio of 100/60). The holes in the plastic plate were used to remove the water in the ceramic slurry. The EPS beads were packed in the plastic container before casting. Another plastic plate with holes was used to cover the EPS beads. The plate was fastened by two sets of screws and nuts. The pore sizes were controlled by EPS beads sizes and the porosities by adjusting the screws. The relationship between the deformation of the EPS beads and the final porosity is shown in Fig.3-8. While a pressure was applied on the EPS bed, some distilled water was added to saturate the EPS preform in order to prevent cracking in the resulting green body. The whole assembly was then put into a 90°C oven overnight to maintain the deformation of the beads due to creep of polymer. During the casting process, a ceramic slurry was poured into the plastic container to form a green body containing the EPS beads. The optimized ceramic slurries based on previous studies were used for the vacuum casting (zirconia and ZA20 slurries with solids loadings of 50wt%, PMAA addition of 0.5% and 0.7%, respectively, and at pH 9). The green bodies were left in air for 2 days and sintered at 1500°C. The heating rate was 1°C/min to 500°C to burn out the EPS preform, after which, the ramping speed was increased to 5°C/min.

Fig.3-7 In-house designed apparatus used to prepare the porous structures

Fig.3-8 Deformation of EPS beads versus porosity of sintered TZP and ZA20 structures

3.4.2 Characterization of the porous structures

The sintering shrinkage of the porous structures with different pore sizes was measured by the dilatometer. The green bodies containing EPS beads were calcined at 500°C to burn out the EPS beads. Then the porous calcined bodies were tested by the dilatometer using a heating rate of 5°C/min up to 1550°C in air. The morphology of the porous structures was characterized by stereo microscopy (Stereozoom Microscope Leica MZ6) and SEM. The pore sizes were measured by the UTHSCSA Image Tool 2.00.

The total porosity and the open porosity were measured by a geometry mass method involving wax infiltration as follows:

1. Measurement of the weight of the porous structure (m_p).
2. Infiltration of wax into the porous structure.
3. Measurement of the weight of the porous structure containing the wax.
4. Calculation of the volume of the porous structure containing the wax (V_T) (the average density of the porous structure containing the wax was measured using the electronic densimeter MD 200S).
5. Calculation of the volume of the infiltrated wax (V_w), i.e. the open pore volume (The density of the wax was 0.93 (according to the product specification)).
6. Calculation of the total pore volume (V_p) using equation 3.4
7. Calculation of the total porosity and the open porosity using equation 3.5 and 3.6

$$V_p = V_T - V_{TD} = V_T - \frac{m_p}{\rho_{TD}} \quad 3.4$$

$$Total\ porosity = \frac{V_p}{V_T} \quad 3.5$$

$$Open\ porosity = \frac{V_w}{V_T} \quad 3.6$$

where V_{TD} is the volume of the dense ceramic, ρ_{TD} the theoretical density.

The mechanical properties of the porous structures were tested on an Instron Tester (Model 5567). The crosshead speed was 0.5 mm/min. The compressive strengths of porous TZP and ZA20 ceramics sintered at 1500°C with various pore sizes and porosities were measured using rectangular blocks with dimensions of 1 x 1 x 2cm³. The compressive strength of dense ZA20 ceramics was estimated based on the volume percentage of the components using a formula similar to Eq. 3.2. Values of 2000MPa and 4100MPa were used for the compressive strengths of dense TZP and alumina [35].

The diametral strengths of porous TZP and ZA20 ceramics with various pore sizes and porosities were measured. Disk samples with a diameter of 1.7cm and a thickness of 0.8mm were used for the diametral compression tests (indirect tensile tests) (Fig.3-9). The diametral strength (T) of the sample was calculated using the following equation [123].

$$T = \frac{2P}{\pi LD} \tag{3.7}$$

where P is the maximum applied load indicated by the Instron Tester, L the thickness of the sample, D the diameter of the sample. The diametral strengths of dense TZP and ZA20 samples were also measured. Disk samples with a diameter of 1.5cm and a thickness of 0.5cm were used.

The Young's moduli for the porous and the dense TZP and ZA20 ceramics were determined from the elastic stress-strain curves as a result of the diametral compression tests. About 7~10 identical samples were used for each sample type.

Fig.3-9 Schematic showing a disk sample for the diametral compression test

3.5 Structures and properties of non-uniformly porous TZP ceramics

3.5.1 Preparation of graded porous and porous/dense TZP ceramics

Preparation of graded porous TZP ceramics

Graded porous TZP ceramics were prepared following the same route as for uniformly porous structures. The only difference was that before casting, EPS beads with different sizes were packed in the plastic container shown in Fig.3-7 in an ordered manner. The thickness of each EPS layer was controlled by the weight, since the density and the packing method of the EPS beads were same for all the EPS layers. The porosities were controlled by adjusting the applied pressure on the EPS bead beds as described before. Graded porous TZP structures with two and five layers and dimensions of 2 x3 x 4 cm³ were prepared. Table 3-1 shows all the graded porous TZP ceramics sintered at 1500°C for the study.

Table 3-1 Multilayered and graded porous TZP structures prepared for the study

	Pore size of each layer (mm)	Ratio of thickness of each layer	Porosity (%)
Two-layer	2.09 and 1.86	3:1, 2:1, 1:1, 1:2, 1:3	51
	2.09 and 1.54		
	2.09 and 1.29		
	2.09 and 0.98		
Five-layer	2.09, 1.86, 1.54, 1.29 and 0.98	1:1	51
			54
			62
			69

Preparation of porous/dense layered TZP ceramics

Porous/dense layered TZP ceramics were prepared. First a porous layer was formed following the procedure described in section 3.4.1. During the preparation of the porous layer, no extra pressure was applied on the EPS bead bed, i.e., only porous

layer with a porosity of 51% was prepared. Then the plastic plate used to cover the EPS beads was removed. More ceramic slurry was cast to form a dense layer. The thicknesses of the porous and the dense layers were controlled by measurement with a caliper.

Preparation of layer-core TZP ceramics

Porous layer-dense core and dense layer-porous core TZP ceramics were prepared. The dense part was prepared by using a polyurethane (PU) foam as a preform. The foam was first immersed in molten wax. After being solidified, the wax impregnated foams were shaped into cylinders and rings. They were then put into a 90°C oven to remove the wax. The shaped foams are shown in Fig.3-10. The foam was put into a plastic container and then EPS beads were used to fill the rest space (Fig.3-11). The subsequent casting and sintering process was same as described in section 3.4.1.

Fig.3-10 Shaped PU foams: (a) cylinder, (b) ring

Fig.3-11 Schematic showing the arrangement of the preforms: (a) porous layer-dense core TZP ceramic and (b) dense layer-porous core TZP ceramic

3.5.2 Characterization of the non-uniformly porous TZP ceramics

The morphologies of non-uniformly porous TZP ceramics were characterized by Stereo Microscopy and SEM. The grain morphology of the dense part in layer-core TZP ceramics was characterized by FESEM. The compressive strengths of the graded porous TZP and the porous/dense TZP were measured. The original bulk samples with dimensions of $4 \times 4 \times 2 \text{ cm}^3$ were cut into rectangular pieces with dimensions of $2 \times 2 \times 2 \text{ cm}^3$. The compressive strengths were measured by applying a load on the cross sections of the graded porous structure in the transverse and the longitudinal direction, as shown in Fig.3-12. Five samples were used for each sample type.

Fig.3-12 Schematic showing the compressive test for graded porous ceramics in (a) transverse and (b) longitudinal direction

3.5.3 Preparation of HA/glass coatings on dense and porous TZP substrates

An HA/glass slurry with a 50wt% HA content of the mixed powder and a solids loading of 25wt% was prepared by planetary ball milling at 100rpm for 2 hours. A dip-coating process was used. Dense and porous TZP samples were immersed into the HA-glass slurry for 1.5 minutes. They were then centrifuged to move the extra slurry. After drying in air, the coated samples were sintered at 1200°C in air for one hour with a heating and a cooling rate of $5^{\circ}\text{C}/\text{min}$.

3.5.4 Characterization of HA/glass coatings on dense and porous TZP substrates

Optical microscopy and SEM (JEOL, JSM-6310 LV) were used to study the morphologies of as-sintered surfaces as well as the polished coating layers on porous and dense TZP substrates. EDX or EDS (Energy Dispersive Spectroscopy) was used to identify the elements in the coating layers. X-ray diffraction was performed on the as-sintered surfaces of HA/glass coatings on the dense TZP substrates using the thin film mode to identify the phases present in the samples. Vickers hardness tests (HSV-20 Shimadzu) were used to create indentations at the interface between the HA/glass coating layer and the TZP substrate to provide qualitative evaluation of the interfacial bonding.

Chapter 4

Optimization of Ceramic Slurry for Vacuum-Casting

4.1 Introduction

A well-dispersed ceramic slurry is crucial to a casting process and the final sintered ceramics, as it ensures a high packing density compared with a strongly flocculated slurry. The dispersion of a powder in a solvent can be achieved by introducing a surface charge to promote electrostatic stabilization. On the other hand, by attaching polymer molecules of polymeric dispersant to the surface of the particles can prevent the mutual approach of the individual particles and achieve steric stabilization.

In this work, zirconia, alumina and zirconia-alumina mixed slurries were prepared. The influence of chemical composition and pH on zeta potential, and the effect of dispersant content on the viscosity of the slurries were examined. The stability of the slurries was evaluated by rheological measurements and correlated with the dispersant content. The relationship of the stability of the slurries and the green bodies was also studied. The optimized pH value and dispersant content were finally determined for each type of slurry. The kinetics of casting methods (slip casting and vacuum casting) was also analyzed.

4.2 Zeta potential for dilute suspensions

4.2.1 Effect of pH on zeta potential

The efficiency of electrostatic stabilization can be evaluated by measuring zeta potential as a function of pH. The higher the absolute value of the zeta potential, the more stable the slurry. Fig.4-1 and Fig.4-2 show the effects of pH on the zeta potential and the mean particle size for zirconia and alumina powder in dilute suspensions.

Fig.4-1 Zeta potential and the particle size of the zirconia powder in 5wt% suspensions as a function of pH

From Fig.4-1, it can be seen that the isoelectric point (IEP) of the zirconia powder was $\text{pH} = 7.2$. (IEP is the pH at which there is no net surface charge on the particle.) The zirconia particle surface was positively charged when $\text{pH} < \text{IEP}$ and negatively charged when $\text{pH} > \text{IEP}$. Small average particle sizes were observed at both acidic and basic pH, indicating well-dispersed suspensions. However large average particle sizes were found near the IEP. They were the result of flocculation due to no or a low surface charge density. The agglomerates were not much bigger than those tested by the particle size analyzer as mentioned in section 3.1.1.

Fig.4-2 Zeta potential and the particle size of alumina powder in 5wt% suspensions as a function of pH

Fig.4-2 shows that the IEP of the alumina powder was $\text{pH} = 8.5$. Like the zirconia powder, the alumina particle surface was positively charged when $\text{pH} < \text{IEP}$ and negatively charged when $\text{pH} > \text{IEP}$. However, the zeta potential of the alumina powder was highly positive at a low pH, but only slightly negative at a high pH. Agglomeration occurred near the IEP. At pH near 4, the average particle size was the smallest, while large average particle sizes were observed in basic region.

According to the DLVO theory (after the four scientists—Deryaguin, Landau, Venvey, and Overbeek—who were responsible for its development), there exist two forces in any electrostatically stabilized colloidal system: electrostatic repulsion, which opposes agglomeration, and a universal attractive force, which tends to bind particles together. The stability of an aqueous colloidal system can be controlled by generating like-charges of a sufficient number on the surfaces of the suspended ceramic particles. By adjusting pH to a value away from the isoelectric point (IEP), a stable dispersion of dilute suspensions can be achieved. However, concentrated suspensions are difficult to disperse by electrostatic stabilization only. Thus, electrosteric stabilization is needed, as will be seen below.

4.2.2 Effect of PMAA content on zeta potential

Fig.4-3 shows the effect of pH on the zeta potential of the zirconia suspensions added with different amounts of PMAA. The adsorption of PMAA onto the surfaces of the particles resulted in the shift of the IEP to lower pH values. This was because PMAA is an anionic polyelectrolyte. The dissociation reaction of PMAA creates free carboxylic acid groups (RCOO^-), which create negative charges [124]. The dissociation reaction is [125]:

The amount of the dissociated groups increased as the pH increased. Meanwhile, the PMAA changed from relatively neutral to highly negative. The negatively charged PMAA molecules on the particle surfaces led to a negative potential. The IEP of the zirconia powder changed from 7.2 to 3.3 with increasing PMAA amount from 0wt% to 1.5wt%. In particular, the IEP dropped significantly with the addition of 0.5wt% PMAA, but only slightly decreased with further addition. At $\text{pH} > \text{IEP}$, the zeta potential became more negative with the addition of PMAA, due to build up of the double layer which enhanced electrosteric stabilization. At $\text{pH} < \text{IEP}$, the negatively charged PMAA neutralized the positive sites, thus the positive zeta potential values were significantly lowered.

Fig. 4-4 shows the effect of pH on the average particle sizes of the zirconia suspensions containing different amounts of PMAA. The zirconia suspension without PMAA had the largest average particle size at pH around 7.2, while those with different amounts of PMAA had the largest average particle size at pH about 4. For the suspension without PMAA, small particle sizes were obtained in the acidic and basic regions as explained in Section 4.2.1. The addition of 0.5wt% PMAA resulted in a drop of the average particle sizes in basic pH. This corresponds to the shift of IEP shown in Fig. 4-3. In basic pH the surface of zirconia particles was highly negatively charged, leading to a

repulsive force between the particles. This helped the dispersion of the suspension and resulted in a smaller particle size. In acidic pH, the particle size was not significantly reduced because with the addition of PMAA, the IEP shifted to lower pH. The particles were either neutral at IEP or slightly charged near IEP. Thus, the suspension can not be well dispersed. Further PMAA addition did not significantly decreasing the average particle sizes at the basic pH. This was because the adsorption of PMAA had reached saturation. It should be noticed that a minimum amount of polymer should be used to stabilize the slurry, since excessive polymer would have detrimental effect on the microstructure of final ceramics. Results of the zeta potential and the average particle size tests suggest that the saturation point for PMAA adsorption on zirconia particles was about 0.5wt%.

Fig.4-3 Zeta potential vs. pH of the zirconia suspensions with different amounts of PMAA and a solids loading of 5wt%

Fig.4-4 Average particle size vs. pH of the zirconia suspensions with different amounts of PMAA and a solids loading of 5wt%

Fig.4-5 shows the effect of pH on the zeta potential of the alumina suspensions with different amounts of PMAA. The IEP dropped from 8.7 to 3.8. The addition of 0.5wt% PMAA significantly decreasing the IEP. Further addition of PMAA did not shift the IEP noticeably, neither the zeta potential, which suggests that the saturation point of PMAA for the alumina powder was about 0.5wt%. Similar to the zirconia suspension, the addition of PMAA higher than 0.5wt% did not change the zeta potential significantly because the adsorption of PMAA reached saturation. Fig.4-6 presents the effect of pH on the average particle size of the alumina suspensions with different amounts of PMAA. Similar to the zirconia suspensions, the alumina suspensions also showed decrease of average particle size with the addition of PMAA.

Fig.4-5 Zeta potential vs. pH of the alumina suspensions with different amounts of PMAA and a solids loading of 5wt%

Fig.4-6 Average particle size vs. pH of the alumina suspensions with different amounts of PMAA and a solids loading of 5wt%

From the studies of the effect of pH on zeta potential and particle size of the zirconia and the alumina suspensions with different amounts of PMAA, it was concluded that in order to achieve the highest zeta potential (absolute value) with a minimum PMAA addition, highly basic pH values should be used for the zirconia suspensions. However, for the alumina suspensions, the addition of the PMAA dispersant was unnecessary. By adjusting the pH to about 4, the alumina powder could be well dispersed.

Yttria-stabilized zirconia powder was used in this study. Yttria shows acidic dissolution and its presence influences both the rheology of the suspensions and the final microstructure of the sintered ceramics. Therefore, it was important to prevent the leaching of yttria from the zirconia matrix. A basic pH value should be used for the zirconia and the zirconia/aluminamixed slurries. In the following viscosity tests, a pH value near 9 was adjusted in all the slurries.

4.3 Effect of PMAA content on the viscosity of concentrated slurries

Fig.4-7 shows the viscosity as a function of PMAA content in zirconia, ZA20 and ZA30 slurries with solids loadings of 50wt% and pH values near 9. The effect of PMAA additions on the viscosities of three slurries followed similar trends. The viscosities of the slurries without the PMAA were too high to be detected by the viscometer. However, the viscosities of all three slurries dropped abruptly when PMAA was added. The high viscosities at small PMAA concentrations can be explained by insufficient adsorption of the polymer on the particle surfaces.

The lowest viscosity was obtained at about 0.5wt% PMAA for zirconia slurry, 0.7wt% for ZA20 slurry and 0.8wt% for ZA30 slurry. Further addition of PMAA gradually increased the viscosities due to increasing free PMAA molecular chains in the water solution. When the possible sites on the particles for polymer adsorption were

consumed, further PMAA addition resulted in increasing viscosity. High viscosities were observed for the ZA slurries. This was because the alumina powder at pH near 9 was not as negatively charged as the zirconia powder. The van der Waals attractive forces between the zirconia and the alumina particles could increase the viscosities.

Fig.4-7 The viscosity at 200 s⁻¹ as a function of the PMAA content for zirconia, ZA20 and ZA30 slurries with solids loadings of 50 wt% and pH near 9

4.4 Green density vs. viscosity in slip casting

Fig.4-8 shows the relative green densities of the green compacts prepared by slip casting of zirconia, ZA20 and ZA30 slurries with different PMAA contents. Normally, a better-dispersed slurry (i.e. with a lower viscosity) can achieve a higher green density. However, the green densities of ZA composites were higher than those of zirconia. This is because the average particle size of the zirconia and the alumina powder was 0.265μm and 0.357μm, respectively. The mixed powders showed a bimodal distribution (Fig.4-9), which favored a dense packing, since small particles could fill in the interstices of large ones and thus led to a higher green density.

The microstructures of zirconia, ZA20 and ZA30 green compacts with a low and an optimum PMAA addition are presented in Fig.4-10. For each type of the slurry, the relative density changed with the PMAA content. The differences in morphology of the green compacts prepared from the poorly- and well-dispersed slurries were obvious. Fig.4-10(a), (c) and (e) show bigger pores, while Fig.4-10 (b), (d) and (f) show denser packing. It can be concluded that the green compacts prepared from slurries with lower viscosities had higher relative densities. The highest relative green densities for zirconia, ZA20 and ZA30 were 40.3%, 46.1% and 51.2%, respectively. At the optimum PMAA content (corresponding to the minimum viscosity), the adsorbed amount of PMAA was sufficient to promote electrosteric repulsion between the particles, leading to an efficient packing. The green compacts prepared by the slurries with insufficient PMAA had lower packing densities (Fig.4-8). For example, when the PMAA contents in zirconia, ZA20 and ZA30 slurries were lower than 0.1wt%, the relative green densities were 31%, 33% and 33%, respectively. This was because the insufficient adsorption of PMAA resulted in agglomeration.

Fig.4-8 Relative green densities of the green compacts obtained by slip casting of 50wt% zirconia, ZA20 and ZA30 slurries with different amounts of PMAA addition

Fig.4-9 Bimodal particle size distribution of the mixed ZA30 powder

Fig.4-10 SEM (SEI mode, second electron image) micrographs showing the green compacts prepared by slip casting (a) zirconia green compact with 0.05wt% PMAA, (b) zirconia green compact with 0.5wt% PMAA, (c) ZA20 green compact with 0.05wt% PMAA, (d) ZA20 green compact with 0.7wt% PMAA, (e) ZA30 green compact with 0.05wt% PMAA, (f) ZA30 green compact with 0.75wt% PMAA

4.5 Kinetics of vacuum casting

Fig.4-11 shows the drop in the liquid surface of zirconia slurry as a function of vacuum casting time. Delta h (Δh) is the reduced height of the suspension surface which was measured by graduated cylinder. (Section 3.2.2, Fig.3-5). The zirconia slurry had a solids loading of 50wt%, an optimized 0.5wt% PMAA and a pH near 9.

Fig.4-11 The increase of Δh as a function of vacuum casting time for the zirconia slurry cast in the containers with and without EPS beads of different sizes (using optimized zirconia slurry with a solid loading of 50wt% and a PMAA addition of 0.5wt% and a pH near 9)

From Fig.4-11, it can be seen that it took longer to achieve the same green body volume with the EPS beads. In addition, the smaller the EPS size, the longer it took to achieve the same green body volume. The kinetics of the casting can be quantified as a filtration process on the basis of Darcy's equation, which describes the flux of a filtrate volume through a porous bed. By applying mass balance to the system, and integrating Darcy's equation, one can obtain the following equation, relating the thickness of the cake (L) to the casting time (t) [126]:

$$L^2 = \frac{2k\Delta p}{\eta} \left(\frac{\nu_0}{\nu_c - \nu_0} \right) t \quad 4.2$$

where k is the permeability of the porous bed (i.e. the gypsum filter), η the viscosity of the suspending media (i.e., the liquid phase of the slurry), Δp the pressure (i.e., the degree of vacuum), ν_0 the slip density and ν_c the green body density. Since in this study, during the vacuum casting, the slurries were cast into a mould containing EPS beads, the relationship between the cake thickness and the casting time should be converted into the relationship between the reduced slurry volume and the casting time. It was assumed that the dispersion of the ceramic slurries was maintained during casting. Thus the increase of the green solid mass could be related to the reduction of suspension volume, i.e. the change of Δh . The mass balance led to the following:

$$LA_2\nu_c = \Delta h A_1 \nu_s \quad 4.3$$

where ν_s is the volume concentration of the ceramic slurry, A_1 the cross-section area of the graduated cylinder, A_2 the cross-section area of the plastic container (schematically shown in Fig.3-5). The left side of the equation is the green solid mass in the plastic container, while the right side of the equation equals the solid mass of the reduced volume of the slurry.

The modified expression of eq.4.2 is shown as follows:

$$\Delta h^2 = \frac{v_c^2}{v_s^2} \times \frac{A_2^2}{A_1^2} \times \frac{2k\Delta p}{\eta} \left(\frac{v_0}{v_c - v_0} \right) t \quad 4.4$$

From Eq. 4.4, it can be seen that the reduction of slurry Δh was related to $\sqrt{t}$. The results shown in Fig.4-11 correspond to Eq. 4.4. The decrease of the vacuum casting speed due to the existence of EPS beads can be explained as follows. Eq. 4.4 is valid based on the assumption of unidirectional filtration, negligible mould resistance, constant rheological properties of the suspensions, absence of particle settling and constant permeability [127]. However, in practice, a permeability gradient should be expected. The pressure drop over the cake thickness increases with casting time and the available Δp decreases. During the casting process with EPS beads, in order to achieve the same solid green body volume, the thickness of the green body had to be more than that of the EPS-free green body. Thus the permeability was lowered and the casting speed slowed. The increasing cake density and a consequent decreasing cake permeability with casting time were also reported for the pressure casting of SiC bodies [128].

4.6 Summary

In order to determine the optimum slurry for casting, the dispersion of slurries was studied. It was found that zirconia, ZA20 and ZA30 slurries with the PMAA addition of 0.5wt%, 0.7wt% and 0.8wt% and pH near 9 exhibited the lowest viscosities and resulted in green compacts with highest green densities. The green densities prepared by slip casting of the optimized slurries were 40% for zirconia, 46.1% for ZA20 and 51.6% for ZA30 of the theoretical densities, respectively. The ceramic structures to be shown in the following chapters of this thesis were all prepared from these optimized ceramic slurries.

Chapter 5

Dense Zirconia Ceramics and Zirconia/Alumina Composites

5.1 Introduction

Due to the small particle sizes and the vacuum casting process used in this study, the green densities of the zirconia compacts were relatively low. High sintering shrinkage was expected, which could cause defects in the struts if porous zirconia structures were prepared. It was necessary to reduce the shrinkage. On the other hand, the addition of alumina powder could reduce the shrinkage of zirconia by increasing the starting green density and retarding the densification of the composite [129,130,131]. Thus, the sintering shrinking behavior of the monolithic zirconia-alumina ceramic composites was studied in this chapter. The addition of alumina in zirconia was also for the improvement of the mechanical performance. Many reports have shown that zirconia/alumina composites exhibit higher mechanical properties than single phase TZP ceramics [132,133,134]. For example, TZP matrix based composites show higher toughness and strength than those of single phase TZP ceramics. The increased toughness of the composites is due to the microstress-induced strengthening as a result of the addition of alumina particles in the TZP matrix.

5.2 Effect of alumina addition on the densification of zirconia

5.2.1 Densification during heating

Fig.5-1 shows the relative sintering shrinkage ($\Delta L / L_0$) versus temperature for TZP, ZA20 and ZA30 compacts. It can be seen that shrinkage took place above 1100°C, with nearly full densification above 1450°C. However, different sintering shrinkages were noticed for different compacts, as alumina retards densification and reduces shrinkage. Specifically, the pure TZP compact had a sintering shrinkage of 26.87% up to 1500°C. With the addition of alumina, shrinkage was reduced to 23.39% for ZA20 and 20.53% for ZA30, respectively.

Fig.5-1 Relative sintering shrinkage versus temperature during heating up to 1500°C in air with a constant heating rate of 5°C/min for TZP, ZA20 and ZA30 compacts

Since the measured sintering shrinkage was one dimensional, whereas densification is a three dimensional process, shrinkage from the dilatometry should be converted into density in order to compare densification rates. The conversion can be done using the following equation [135]:

$$\rho_t = \frac{\left(1 + \frac{(L_f - L_0)}{L_0}\right) \left(1 + \frac{(\phi_f - \phi_0)}{\phi_0}\right)^2}{\left(1 + \frac{L_0 - L_t}{L_0}\right) \left(1 + \alpha \frac{L_0 - L_t}{L_0}\right)^2} \rho_f \quad 5.1$$

where

ρ_t : Density of the specimen at the sintering time t .

ρ_f : Density of the specimen at the end of sintering.

ϕ_0 : Initial mean diameter of the specimen.

ϕ_f : Final mean diameter of the specimen.

L_0 : Initial thickness of the specimen.

L_t : Thickness of the specimen at the sintering time t .

L_f : Thickness of the specimen at the end of sintering.

α : Anisotropic shrinkage factor.

where α is defined as follows:

$$\alpha = \frac{(\phi_f - \phi_0)L_0}{(L_f - L_0)\phi_0} \quad 5.2$$

where $\frac{L_0 - L_t}{L_0}$ is the relative shrinkage at sintering time t . By dividing both sides of

Eq. 5.1 with the theoretical density of TZP, ZA20 and ZA30 respectively, the relative density can be calculated. The theoretical densities of TZP, ZA20 and ZA30 were 6.03, 5.45 and 5.21 g/cm³ respectively. The calculated relative densities as a function of sintering temperature are shown in Fig.5-2. It can be seen that pure TZP compact started densification at about 1120°C and reached near theoretical density at 1500°C. Since the green densities of ZA20 and ZA30 compacts were higher than that of TZP, it is easy to understand that at the beginning of densification, the relative densities of the ZA composites were higher than that of TZP. However, beyond 1208°C for ZA20 and 1240°C for ZA30, their relative densities were lower than TZP. Near full density

(99.5%) was reached for TZP at 1500°C. With the addition of alumina, the final relative densities reduced to 97.7% for ZA20 and 97% for ZA30. It should also be noticed that beyond 1450°C for ZA20 and 1480°C for ZA30, the relative densities did not increase with the temperature.

Fig.5-2 Relative densities versus temperature during heating up to 1500°C in air at the heating rate of 5°C/min for TZP, ZA20 and ZA30 compacts

Fig.5-3 shows the densification rates of TZP, ZA20 and ZA30 compacts as a function of temperature. The densification rate is defined as $\frac{d(\text{Relative density})}{dt}$, where t is time. Thus, the densification rates can be determined from Fig.5-2 by fitting the curves with functions and differentiating the functions. One has the following equation:

$$\frac{d(\text{Relative density})}{dt} = \frac{d(\text{Relative density})}{dT} \frac{dT}{dt} \tag{5.3}$$

where T is the temperature and $\frac{dT}{dt}$ the heating rate – a constant. In Fig.5-3, a shift of the temperature for maximum densification rate was observed. Increasing the alumina content reduced the densification rate at lower temperature while increase it

at higher temperature. This was due to the high intrinsic sintering temperature of alumina. Compared to alumina, TZP was highly sinterable at lower temperatures. However, at higher temperatures, alumina could be densified due to enhanced atomic diffusion rates, but the dense zirconia could not densify any more since no pore was left.

It should be noted that the densification rate curve of TZP was relatively smooth and only one maximum value was found. However, with the addition of alumina, steps appeared in the curves. When the alumina content was 30wt%, an obvious step appeared at about 1300°C and the maximum value occurred at about 1400°C. This was due to the different sinterability between TZP and alumina. At about 1300°C, TZP matrix reached its maximum densification rate, thus the first step occurred. Beyond 1300°C, the sinterability of TZP decreased while the temperature was still not high enough to densify alumina. Within this temperature range, the curves increased slowly. As the temperature increased, alumina reached its maximum densification rate and the second peak appeared. When the alumina content increased, the densification rate slowed because alumina clusters were easy to form (Fig.5-4). There are three kinds of pores in ZA composite, inter-zirconia particles pores (Pore ZZ), pores between zirconia and alumina particles (Pore ZA) and inter-alumina particles pores (Pore AA). Pores ZZ can be removed during sintering at relatively lower temperature. Pores ZA will not shrink before zirconia particles begin to grow substantially. With the increase of temperature, when the densification process of pure Y-TZP has been completed, pore AA will begin to shrink. With the growth of zirconia particles the coordination number of pore ZA will decrease and they will also become unstable and start to shrink. So the retarded densification of the composite with higher alumina content was understandable.

Fig.5-3 Relative density rate versus temperature during heating up to 1500°C in air at the heating rate of 5°C/min for TZP, ZA20, and ZA30 compacts

Fig.5-4 SEM micrographs (SEI mode) of alumina cluster in ZA30 composite

5.2.2 Densification due to sintering at high temperatures

The microstructures of TZP, ZA20 and ZA30 compacts made from vacuum casting and sintered at different temperatures are presented in Fig.5-5 to Fig.5-7. The morphologies of the TZP samples sintered at 1400°C and 1450°C were different, since

the relative density varied from 95.3% to 98.6% (the density was measured by electronic densometer). After sintering at 1500°C, the relative density of the TZP increased only by 0.9% and there was little difference in the morphology. For ZA composites, the change of morphology was more obvious. At 1400°C, pores could be observed, since the density was only 88.3% for ZA20 and 83.3% for ZA30. At 1450°C, the large pores became less because the densities of both ZA composites were above 90%. When the temperature reached 1500°C, large pores could hardly be found in the polished surface of the dense samples.

Fig.5-5 SEM micrographs (SEI mode) showing the TZP ceramics sintered at different temperatures: (a) 1400°C, (b) 1450°C and (c) 1500°C

Fig. 5-6 SEM micrographs (SEI mode) showing the ZrO₂ ceramic surface.

Fig.5-6 SEM micrographs (SEI mode) showing the ZA20 composites sintered at different temperatures: (a) 1400°C,(b) 1450°Cand (c) 1500°C

Fig.5-7 SEM micrographs (SEI mode) showing the ZA30 composites sintered at different temperatures (a) 1400°C,(b) 1450°C and (c) 1500°C

5.3 Effect of alumina addition on the grain growth of zirconia

The FESEM (Field-Emission Secondary Electron Microscope) micrographs from Fig.5-8 to Fig.5-10 were obtained from polished and thermally etched surfaces of TZP and ZA samples. The dark grains in the ZA composites were alumina while those with lighter contrast were zirconia phase with identification confirmed by EDX. The microstructures were homogeneous in most regions. The grain sizes of alumina and zirconia phases were similar, and confirmed by TEM (Fig.5-11). Again the zirconia and alumina grains were identified by EDX.

Complementary to Fig.5-8, Fig.5-9 and Fig.5-10, Fig.5-12 shows the average grain size of zirconia matrix as a function of sintering temperature for TZP, ZA20 and ZA30. The grain size in zirconia matrix grew with increasing sintering temperature. However, with the addition of alumina, the grain growth was reduced. Fig.5-13 shows the average grain size of alumina phase as a function of the sintering temperature for ZA20 and ZA30 composites. The alumina grains grew larger with increasing sintering temperature. The reduction of the zirconia grain size in the composites is understandable. The TZP matrix grain growth was inhibited by alumina, since the alumina particles in the TZP matrix pinned the grain boundary mobility of the TZP grains, thus hindering the grain growth of the TZP matrix. With more alumina addition, the alumina grain size increased. This was because with the increase of alumina content, the alumina particles tended to segregate. Thus the pinning effect from zirconia particles was reduced and the alumina grain growth was enhanced. It should be noted that the zirconia grain growth inhibited by alumina addition appeared to be marginal. This is because the primary particle size of zirconia used in this study was $0.265\mu\text{m}$. The grain growth inhibition effect was limited. Another factor is that alumina content was not high enough to significantly decrease the grain growth of TZP. Such effect is also reported by Wong *et al.* [136], in whose study, the TZP grain size decreased from $0.32\pm 0.15\mu\text{m}$ to $0.22\pm 0.07\mu\text{m}$ when increasing alumina content from 14wt% to 73wt%.

Fig.5-8 FESEM (SEI) micrographs showing the thermally etched TZP surfaces. The samples were sintered at (a) 1400°C, (b) 1450°C and (c) 1500°C

Fig.5-9 FESEM (SEI) micrographs showing the thermally etched ZA20 surfaces. The samples were sintered at (a) 1400°C, (b) 1450°C and (c) 1500°C

Fig.5-10 FESEM (SEI) micrographs showing the thermally etched ZA30 surface. The samples were sintered at (a) 1400°C, (b) 1450°C and (c) 1500°C

Fig.5-11 TEM micrographs showing grains in (a) TZP, (b) ZA20 and (c) ZA30 sintered at 1500°C

Fig.5-12 Average grain size of the zirconia matrix in TZP, ZA20, and ZA30 as a function of the sintering temperature

Fig.5-13 Average grain size of alumina in ZA20 and ZA30 as a function of the sintering temperature

Fig.5-14 shows the XRD patterns for phase identification. It can be seen that there are two phases in raw zirconia powder: tetragonal zirconia (JCPDS No. 50-1089) and monoclinic zirconia (JCPDS No. 37-1484). After the green zirconia compact was sintered at 1500°C, the tetragonal zirconia phase was retained in all samples. No monoclinic phase was found. The alumina phase in the composite matches JCPDS No. 10-0173 for α -alumina phase. There is a slight shift of TZP peaks in the ZA composites. Namely, the TZP (011) peak shifted from $2\theta = 30.2^\circ$ to 29.66° for ZA20 and to 29.68° for ZA30; the TZP (112) peak shifted from $2\theta = 50.2^\circ$ to 49.76° for ZA20 and to 49.7° for ZA30; the TZP (121) peak shifted from $2\theta = 60.10^\circ$ to 59.62° for ZA20 and to 59.54° for ZA30. The shift of the TZP peaks could be attributed to the lattice distortion due to thermal mismatch of zirconia and alumina (Al_2O_3 having the CTE of $6.6 \times 10^{-6} \text{K}^{-1}$ and TZP having the CTE of $9.8 \times 10^{-6} \text{K}^{-1}$). Such effect was also reported by Lee *et al.* [137]

Fig.5-14 XRD patterns of TZP raw powder, TZP, ZA20 and ZA30 compacts sintered at 1500°C (t: tetragonal zirconia phase, m: monoclinic zirconia phase, A: alpha alumina phase)

5.4 Hardness and fracture toughness of zirconia/alumina ceramics

Fig.5-15 and Fig.5-16 show the Vickers hardness and the fracture toughness of TZP, ZA20 and ZA30 sintered from 1400°C to 1500°C. From Fig.5-15, it can be seen that the Vickers hardness decreased with the increasing alumina content at 1400°C and 1450°C. However, at 1500°C, the hardness increased initially with the addition of alumina, but decreased for ZA30 due to lower density.

From Fig.5-16, it can be seen that with the addition of alumina, the fracture toughness (K_{IC}) of ZA20 sintered at all temperatures increased. However, the K_{IC} of ZA30 increased only when they were sintered at 1450°C and 1500°C, while at 1400°C it was still lower than that of TZP, since the density of TZP at 1400°C was already 95.3%, whereas ZA30 had a density of 83.3%. As the sintering temperature increased, the density of ZA composites increased. Thus, the hardness and the fracture toughness of ZA composites also increased and exceeded those of TZP.

Fig.5-16 indicates that when the density was high enough, the addition of alumina increased the fracture toughness. On the other hand, the XRD results (Fig.5-14) revealed that the t-ZrO₂ was the predominant phase in TZP ceramics and in ZA composites. Thus, a phase transformation toughening mechanism could exist in TZP ceramics and in ZA composites. It is known that the energy for crack propagation can be adsorbed by the stress-induced transformation from the tetragonal to the monoclinic zirconia phase in the wake of the crack tip. The crack can be effectively stopped and the fracture toughness increased. However, Tsukuma *et al.* [138] reported that the addition of Al₂O₃ particles in TZP could also decrease the effect of the phase transformation toughening.

The increase of the fracture toughness in ZA composites could also be attributed to the thermal stresses. Previously, the XRD results showed the shift of the TZP peaks, which suggested the existence of thermal stresses. The residual stresses in the

composites were developed during cooling caused by the mismatch of the coefficient of thermal expansion (CTE). Due to the low CTE of Al_2O_3 ($\alpha_{300-800\text{K}} = 6.6 \times 10^{-6} \text{K}^{-1}$) compared to that of TZP ($\alpha_{300-2000\text{K}} = 9.8 \times 10^{-6} \text{K}^{-1}$), tensile residual stresses were developed in the TZP matrix during cooling. Fig.5-17 schematically shows the thermal stresses in the alumina added-TZP matrix composite. During cooling, the TZP matrix tended to shrink more than the alumina particles. However, the existence of alumina particles prevented the TZP matrix from further shrinking and exerted a compressive stress in the radial direction and a tensile stress in the tangential direction in the zirconia matrix. The increase of the fracture toughness (Fig.5-16) of the ZA composites suggested that the tensile residual stress had a positive toughening effect in the ZA composites. The tensile residual stress could decrease the critical transformation stress of the tetragonal zirconia phase and thus the crack tip transformation would occur at a much lower stress level [139]. Thus, the development of the tensile residual stress was able to contribute to the enhanced stress-induced phase transformation toughening of the composites.

However, addition of more than 20wt% alumina in the zirconia matrix decreased the fracture toughness. This was because the relatively low densities of the ZA30 composites. Furthermore, the increase of the alumina phase content in the composites also lowered the volume of the tetragonal zirconia available for the t- ZrO_2 to m- ZrO_2 phase transformation and thus decreased the fracture toughness.

Fig.5-15 Vickers hardness versus alumina content of the composites sintered at different temperatures

Fig.5-16 Fracture toughness versus alumina content of the composites sintered at different temperatures

Fig.5-17 Schematic diagram showing the thermal residual stresses in the zirconia matrix of the zirconia/alumina composite

5.5 Summary

This chapter mainly dealt with the sintering behavior of zirconia under the influence of alumina addition. The densification of zirconia was hindered and the relative sintering shrinkage was lowered with the addition of alumina. Pure TZP compacts had a relative density of 99.5% at 1500°C, whereas ZA20 and ZA30 composites reached 97.7% and 97% at the same sintering temperature. The grain growth of TZP was inhibited by alumina by 5.3% for the ZA20 composite and by 2.0% for the ZA30 composite sintered at 1500°C. The TZP matrix also inhibited the grain growth of alumina. However, for ZA30, the increased contact between alumina particles led to increased alumina grain growth. The Vickers hardness and the fracture toughness were increased with the addition of alumina sintered at 1450°C and 1500°C. However, at 1400°C, the densities of the ZA composites were low, leading to a low hardness value. The fracture toughness of the ZA composites sintered at 1450°C and 1500°C was increased due to the existence of the residual thermal stresses. Based on these results, TZP and ZA20 were used to prepare the porous structures to be covered the following chapters, since ZA30 exhibited poor mechanical behavior at low sintering temperatures compared to ZA20.

Chapter 6

Structures and Properties of Uniformly Porous TZP and ZA20 Ceramics

6.1 Introduction

It is known that for bone ingrowth into porous structures, interconnected pores with diameters bigger than 100 μ m are required [15]. The mechanical properties of such structures are also important and are controlled by characteristics such as pore size, pore shape and porosity. In this chapter, a vacuum casting method was used to fabricate porous ceramic structures. Spherical expanded polystyrene (EPS) beads were used as preforms to control pore size and porosity. Uniform structures of TZP and ZA20 were developed and the mechanical properties correlated with their porous structures.

6.2 Sintering behavior of the uniformly porous TZP ceramics

Fig.6-1 shows relative sintering shrinkage as a function of sintering temperature for TZP compacts with and without EPS beads. All TZP compacts followed a similar trend, however, the relative sintering shrinkage with EPS beads was lower than that without the beads at all sintering temperatures and decreased when the bead size was smaller. Since the difference between the bead sizes was not large due to the limited availability of the EPS beads and because the vacuum casting process favored large EPS, the difference of relative sintering shrinkages of all the porous structures was not

very large. However, the fact that different porous structures have different sintering shrinkages should be considered when preparing pore size graded structures, as will be discussed in the next chapter.

Fig.6-2 presents sintering shrinkage rate as a function of temperature for the TZP compacts with and without EPS beads. Fig.6-2 was derived from Fig.6-1 by differentiating the relative sintering shrinkages as a function of the sintering temperature (T) using $\frac{dS}{dt} = \frac{dS}{dT} \frac{dT}{dt}$, where T is the temperature, $\frac{dT}{dt}$ is the heating rate (a constant), and $\frac{dS}{dT}$ is the derivative from Fig.6-1. The shrinkage rates (dS/dt) of the TZP compacts with EPS beads were slower than that of the EPS-free sample. Furthermore, the smaller the EPS size, the smaller the shrinkage rate. Nevertheless, the temperatures at which the samples reached their highest shrinkage rates were near the same.

The pores created by burning off the EPS beads resulted in low overall density. With the presence of the pores, the sintering shrinkage of a strut could be limited or restricted by the neighboring struts. Thus, in a porous structure, a lower sintering shrinkage should be expected compared to the EPS-free TZP compacts. But since the TZP compacts were prepared from the same starting material, they exhibited similar sintering behavior. The slight decrease in relative shrinkage and shrinkage rate with decreasing EPS bead size can be explained as follows. In section 4.5.1, it was noted that there was a slight drop of the casting speed with a decrease in bead size. This may result in a slight increase of the green density, leading to a decrease of relative shrinkage and shrinkage rate.

Fig.6-1 Relative sintering shrinkage as a function of temperature of the TZP ceramics with and without EPS beads of different sizes, measured by the dilatometer at a constant heating rate of 5°C/min

Fig.6-2 Sintering shrinkage rate as a function of temperature of the TZP ceramics with and without EPS beads of different sizes, derived from Fig.6-1 and using the constant heating rate of 5°C/min

6.3 Morphology of the uniformly porous TZP structures

6.3.1 Variations in pore size

By using EPS beads of different sizes, uniformly porous structures were prepared. Fig.6-3 shows the porous TZP structures with an average pore sizes from 0.98 to 2.09mm and porosities of about 69%. The spherical pores were interconnected with smaller windows. One can also see that the cell edges, i.e., the struts, were slender due to the high porosity and the pores were uniformly distributed, to yield a foam-like structure. However, the morphology of the porous structure with the pore size of 2.09mm was not as uniform as the rest. This is because small EPS beads are easy to be packed uniformly, while large beads aren't, leading to relatively non-uniform pore morphology and cell edges.

Fig.6-3 Optical micrographs showing the uniformly porous TZP structures sintered at 1500°C and with a porosity of 69%, but different average pore sizes: (a) 2.09mm, (b) 1.86mm, (c) 1.54mm, (d) 1.29mm and (e) 0.98mm

6.3.2 Variations in porosity

By adjusting the applied load on the EPS bead bed, deformation could be controlled and uniformly porous structures with different porosities prepared. Fig.6-4 shows the porous TZP structures with a pore size of 1.29mm but different porosities of 51%, 62% and 69%. It can be seen that the strut size in the porous structure decreased with increasing porosity. Furthermore, the structure of lower porosity was less uniform. For example, in Fig.6-4 (a), there are some areas of the solid TZP matrix. As for a ceramic with the porosity of 51%, no external pressure was applied on the bead bed during the vacuum casting, resulting in loose packing. There was also a possibility that the beads were not densely packed in every layer, leading to voids. Thus, the large strut shown in Fig.6-4 (a) could be formed. However, with the increasing porosity due to a higher applied force, the pores became more regularly distributed, the cell edges were more slender and uniform, and the structure became foam-like.

It was also observed that when the porosities were kept the same, pore windows were similar. When porosity increased, pore window size also increased. For example, for the structure with the porosity of 54%, the window size was about 300 μ m. When the

porosity was 62%, the window size increased to about 500 μ m (Fig.6-5). It should be noted that both pore window were large enough for bone tissue ingrowth.

Fig.6-4 Optical micrographs of uniformly porous TZP ceramics sintered at 1500°C and with a pore size of 1.29mm and porosities of (a) 51%, (b) 62% and (c) 69%

Fig.6-5 SEM (SEI mode) micrographs showing the porous TZP sintered at 1500°C and with pore size of 1.29mm with porosities of (a) 54% and (b) 62%

6.4 Porosity control of uniformly porous structures

For the porous bioceramics in this study, the total porosity and the open porosity were of great interest. Total porosity describes the total pore volume fraction in a porous structure, whereas open porosity indicates the open pore volume fraction. A high open porosity is preferred for bone tissue ingrowth, whereas the total porosity controls the mechanical properties. During the fabrication process, the packing method of the EPS beads, the bead size, and the applied load to deform the beads all affected the total porosity and the open porosity.

During casting, the EPS beads were randomly packed, i.e., packed under gravity and by gentle tapping. The effect of EPS beads sizes on total porosity was studied and the results shown in Fig.6-6. The total porosities did not change significantly with increasing beads size, as they are spherical, leading to close stacking. A particular stacking corresponds to one pore volume fraction. In fact, the total pore volume fraction is 0.52, 0.68 and 0.74 for simple cubic stacking, body centered cubic stacking, and face centered cubic stacking, respectively. For a single cubic unit cell containing one single EPS bead, the volume fraction (leading to final total porosity after sintering)

of the bead in the cubic cell is a constant as long as the sphere is tangential to the cubic cell surfaces. When a load is applied to the bead bed, deformation increases the contact area between the beads. The volume fraction of the bead in the unit cell increases, leading to a higher total porosity. It can be concluded that the load on the bead bed, instead of bead size, controls total porosity.

Open porosity also increased with increasing total porosity (Fig.6-7). Due to the deformation of the EPS beads caused by external load, the beads became much closer. This reduced the probability of the formation of close pores. It should be noticed that the porous structures produced in this study had highly interconnected pores. For instance, the porous TZP with an average pore size of 0.98mm achieved an open porosity of 44% when the total porosity was 51%, and an open porosity of 62% when the total porosity was 69%. More than 86% of the macropores were interconnected.

Fig.6-6 Effect of EPS bead size on the total porosity of the porous TZP sintered at 1500°C. The beads were packed without deformation

Fig.6-7 The total porosity controlled by the applied load versus the open porosity of porous TZP that were sintered at 1500°C and with an average pore size of 0.98mm

6.5 Mechanical properties versus porous structures

6.5.1 Effect of pore size on mechanical properties

Fig.6-8, Fig.6-9 and Fig.6-10 show the effect of pore size on compressive strength, diametral strength and Young's modulus of the porous TZP and ZA20 sintered at 1500°C and with a porosity of 51%. The diametral strengths were measured by the diametral compression tests. The Young's moduli were calculated from the stress-strain curves obtained from the diametral compression tests.

Fig.6-8 Compressive strength versus average pore size of porous TZP and ZA20 sintered at 1500°C and with a porosity of 51%

Fig.6-9 Diametral strength versus average pore size of porous TZP and ZA20 sintered at 1500°C and with a porosity of 51%

Fig.6-10 Young's modulus versus average pore size of porous TZP and ZA20 sintered at 1500°C and with a porosity of 51%

From the figures, it can be seen that all three mechanical properties decreased with increasing pore size. But the decrease in mechanical strengths was rather gradual with the pore size. For the porous TZP, the compressive strength, diametral strength and Young's modulus decreased from 23.6MPa to 15.9MPa, 15.7MPa to 7.1MPa and 2.20GPa to 1.19GPa, when the average pore size increased from 0.98mm to 2.09mm. For the porous ZA20, the compressive strength, diametral strength and Young's modulus decreased from 36.8MPa to 21.8MPa, 17.6MPa to 10.2MPa and 2.25GPa to 1.25GPa, when the average pore size increased from 1.03mm to 2.22mm. The mechanical strengths of the porous ZA20 were higher than those of the porous TZP. This was because tensile residual thermal stresses in the ZA composites decreased the critical phase transformation stress and thus crack tip phase transformation could occur at a much lower stress level, which contributed to the enhanced stress-induced transformation of the metastable tetragonal TZP in the crack tip stress field.

These mechanical property-pore size relationships were quite different from the study reported by Bose *et al.* [140]. In their study, the influence of pore size on the strength

of the porous alumina and TCP (tricalcium phosphate) structures did not show a trend of monotonous increase or decrease. Instead, for a constant pore volume, pore size did not show any effect on the strength degradation behavior. The variation of the strength was due to the change of the pore shape caused during process. However, Liu [85] reported a similar compressive strength-pore size relationship in porous HA. According to the GA [75] model, the following formula can be used for ceramic foams:

$$\sigma = \sigma_0 (1 - P)^{3/2} \quad 6.1$$

where σ is the compressive strength at the porosity P , σ_0 the bending strength of the strut material and $P = 1 - \left(\frac{t}{l}\right)^2$, where t is the average thickness of the cell edge and l the average length of the unit pore cell. From the formula, for a constant porosity, pore size should not have any effect on compressive strength. Specifically, for a porous structure with a constant porosity, when pore size increases, l also increases, which weakens the porous structure and results in the decrease of compressive strength. This theory is comparable with the Graffiths' theory on the rupture of ceramic materials [141]

$$\sigma_f = K / c^{1/2} \quad 6.2$$

where σ_f is the fracture strength, K the fracture toughness of the ceramic material and c the defect size. In porous structures, pores are defects and the origin of failure. The bigger the pore size, the lower the mechanical strength. On the other hand, as l increases, t also increases, which strengthens the porous structure to some degree and mitigates the decrease of compressive strength. The combined effect of pore size and porosity on the mechanical properties of the porous structures will be discussed in section 6.5.3.

6.5.2 Effect of porosity on mechanical properties

The compressive strength, diametral strength, and Young's modulus of the uniformly porous TZP and ZA20 ceramics with similar pore sizes but different porosities were measured. Fig.6-11 to Fig.6-13 show examples of the mechanical properties-porosity relationships of the porous TZP with a pore size of 1.29mm and the porous ZA20 with a pore size of 1.37mm. Both structures were prepared using EPS beads of the same size. The difference in the final pore size was due to different sintering shrinkages. The porosities of the porous TZP and ZA20 varied from 51% to 69%. Again the Young's moduli were calculated from the stress-strain curves obtained from the diametral compression tests.

From the figures, it can be seen that the dependence of the mechanical properties on the porosity followed the same trend: the compressive strength, the diametral strength and the Young's modulus all decreased with increasing porosity. For the porous TZP ceramics with the porosities from 51% to 69% and the pore sizes from 0.98mm to 2.09mm, the compressive strength varied from 23.6MPa to 3.3MPa, the diametral strength from 15.7MPa to 1.5MPa and the Young's modulus from 2.14GPa to 0.24GPa. For the porous ZA20 ceramics with the porosities from 51% to 69% and the pore sizes from 1.03mm to 2.22mm, the compressive strength varied from 36.8MPa to 5.3MPa, the diametral strength from 17.6MPa to 2.5MPa and the Young's modulus from 2.21GPa to 0.30GPa. These data were lower than those of the porous zirconia reported by Kim *et al.* [142], who achieved the compressive strengths from 1.6MPa to 35MPa when the porosities were between 92% and 74% and the pore sizes were up to 600 μ m. The inferior mechanical properties observed were from larger pore sizes. However, the mechanical properties of these porous TZP and ZA20 ceramics were close to those of cancellous bones (2~12MPa for compressive strength and 0.2~5GPa for tensile modulus, (Table 2-1)).

Fig.6-11 Compressive strength versus porosity for the porous TZP and ZA20 ceramics sintered at 1500°C

Fig.6-12 Diametral strength versus porosity for the porous TZP and ZA20 ceramics sintered at 1500°C

Fig.6-13 Young's modulus versus porosity for the porous TZP and ZA20 ceramics sintered at 1500°C

While the GA model is based on micromechanics involving the fracture of struts, a simpler model proposed by Rice can be used to describe the strength-porosity behavior more conveniently. The strength-porosity dependence proposed by Rice [143]:

$$\sigma = \sigma_0 \exp(-bP) \tag{6.3}$$

where σ is the mechanical strength at the porosity P , σ_0 the mechanical strength at the zero-porosity and b is related to the pore characteristics, such as pore shape and pore size. Fig.6-14 shows an example of fitting the compressive strength of the porous TZP with a pore size of 2.09mm with the model (Eq.6.3). Table 6-1 lists the parameters for the curve fitting for all the porous TZP and ZA20 ceramics. The corresponding correlation factor r^2 is also presented in the table. It described how strong the relationship was between the data and the modal.

Fig.6-14 Rice's model fitting of the compressive strength versus porosity for the porous TZP ceramics with a pore size of 2.09mm

Table 6-1 Parameters (σ_0 and b) determined for Eq.6.3 to fit the compressive strength-porosity curves for porous TZP and ZA20 ceramics with different pore sizes

	Pore size (mm)	σ_0 (MPa)	b	r^2
TZP with various porosities	2.09	1841	9.32	0.84323
	1.86	1735	8.99	0.87483
	1.54	1686	8.75	0.84618
	1.29	1649	8.53	0.79846
	0.98	1618	8.31	0.76498
	Dense	2000	-	-
ZA20 with various porosities	2.21	2000	8.70	0.85836
	1.91	1936	8.41	0.84947
	1.63	1889	8.04	0.87462
	1.37	1790	7.72	0.81957
	1.03	1748	7.39	0.78539
	Dense	2576	-	-

The mechanical strength at zero-porosity is expected to be identical for either TZP or ZA20 porous ceramics in spite of different porosities and pore sizes. But, the predicted compressive strengths at zero porosity for the curve fitting were different and lower than the reported value of a dense zirconia (2000MPa) [35]. However, the reported compressive strength was from a fully sintered and defect-free TZP. During the current fabrication of the porous ceramics, the presence of cracks and defects in the struts might result in the low zero-porosity compressive strengths. Liu [84, 85] also reported low zero-porosity compressive strengths and flexural strengths fitted with the Rice's model for large macroporous HA (0.42mm). The corresponding correlation factor r^2 was around 0.8. During the fitting of the compressive strength of the porous ZA20 ceramics, a similar situation to porous TZP ceramics was observed.

6.5.3 Effect of both pore size and porosity on compressive strength

Although the effect of pore size and porosity on mechanical properties have been dealt with separately in the previous sections, it is important to study the two factors together in order to better understand the mechanical property-porosity relationships. The compressive strengths of the porous TZP ceramics with different pore sizes are presented in Fig.6-15. It can be seen that the dependence of the compressive strength on pore size was more pronounced at lower porosity, whereas at higher porosity, the compressive strength became less sensitive to pore size variation.

Fig.6-15 Compressive strength versus porosity for porous TZP ceramics sintered at 1500°C and with different pore sizes

The fact that the mechanical properties were more sensitive to changes in porosity rather than pore size can be explained as follows. According to the GA model (Eq.6.1), for porous structures with a constant pore size, i.e., l is constant, when porosity increases, the cell edge thickness t (or strut) decreases, which leads to a decrease in mechanical strength. For porous structures with a constant porosity, when pore size increases, l increases, which weakens the structures. However, in order to keep porosity constant, t also increases, which means the strut thickness also increases. Due to the opposing effects of l and t , the decrease in mechanical strength due to different pore size is mitigated.

Although Fig.6-15 can be explained by the GA model, the porous structures prepared in this study were different from the foams in the GA model. The cell edges were not as uniform as those in the foams. But the loading and stressing conditions were similar in both types of porous structures. Failure of porous structure results when fracture begins at the most slender part of the cell edge as shown in Fig.6-16. During

the fabrication of the porous structures, the EPS beads were randomly densely packed. The unit cells in the porous structures were not formed by single cubic packing. Instead, they could be packed more densely as shown in Fig.6- 16 (a). When a force, F , was applied on the porous structure, the dense strut transferred the load. The single unit cell marked with a circle would experience the compressive force at the middle of the cell edge, i.e. the most slender part. Like a sample under bending, the cell edge was subjected to a tensile stress. The stress concentration in the pore surface would result in the failure of the unit pore cell.

Fig.6- 16 Crack initiation mechanism for a porous structure under a compressive load: (a) stacked porous unit cells (3D), (b) a unit cell of the porous structure (2D)

For porous structures with same pore size, when porosity increased, the network morphology also changed (Fig.6-4). When the porosity was lower, the porous structure was more likely to have spherical pores in dense cubic unit cells. The pores were connected through a small window between the two unit cells. When the porosity was higher, the connected windows became larger (Fig.6-5), and the cell-edges (struts) became slender. Thus the mechanical properties of the porous structures with higher porosities decreased.

For porous structures with constant porosity, increasing pore size could weaken the porous structure. Furthermore, with constant porosity, the volume fraction of the ceramic struts in a single unit cell was constant. But the bigger the pore size, the thicker the cell edges in the pore unit cell (Fig.6-17). Clearly, a thicker edge could bear more load than a slender one. This is why the decrease in mechanical properties was mitigated even for larger pores.

Fig.6-17 Schematic diagram showing a single unit cell of a porous structure: (a) a unit cell with bigger EPS, (b) a unit cell with smaller EPS

Fig.6-18 and Fig.6-19 show the stress-strain curves of the TZP porous structures from a compressive test and a diametral compression test, respectively. The stress-strain curve from the compressive test appeared to be similar to that reported by Gibson and Ashby [75] in brittle foams. In the initial stage of the test, the compressive stress increased linearly. This corresponded to the linear elastic behavior for the typical fracture of brittle porous structure. When the compressive stress exceeded a given value, crushing of the sample started, resulting in a reduction of stress. The zigzag fluctuations (in the plateau region) indicated the porous structure became progressively damaged. When a cell collapsed, opposing cell walls touched each other and further strain or compression led to a final increase of stress due to the densification of the fragments. It can be seen that the maximum compressive strength was not associated with the failure of a single strut but rather by the propagation of either a macroscopic crack or multiple cracks after damage accumulation reached a critical level. After that, the sample totally collapsed and led to a vertical drop of the

stress, which was the result of unloading of the testing machine. The damage accumulation process was also observed by Brezny and Green [144].

The stress-strain curve from the diametral compression test was smooth. This was because the brittle fracture in the diametral compression test occurred differently from that in the compression test, where the foam was crushed progressively, as compared to the diametral test, where failure occurred by the propagation of a single large crack. In Fig.6-19, the initial stage of the curve (I) was associated with the misalignment of the sample and the presence of a gap between the cross-head plate and the sample. Stage (I) was followed by a linear elastic region (II). At peak stress, the porous ceramic structure collapsed and the stress fell immediately, typical of brittle fracture. Fig.6-20 shows an image of two halves of a porous TZP disk sample after the diametral compression test. The crack from the test was nearly straight and across the center of the sample.

Fig.6-18 Stress-strain curve from a compressive test of a porous TZP sample sintered at 1500°C and with a pore size of 1.86mm and a porosity of 62%

Fig.6-19 Stress-straincurve from a diametral compression test of a porous TZP sample sintered at 1500°C and with a pore size of 1.86mm and a porosity of 51%

Fig.6-20 Optical photo showing two broken pieces of a porous TZP with a porosity of 51% after the diametral compression test

6.6 Summary

This chapter has covered the effects of pore size and porosity. It was found that the relative sintering shrinkage of the porous structures decreased compared to the dense counterparts. Porous TZP and ZA20 structures had high porosities from 51% to 69%, with more than 86% of the pores interconnected. The compressive strength, the diametral strength and the Young's modulus all decreased with increasing pore size and porosity. However the mechanical properties decreased more drastically with porosity than pore size. By adjusting the pore size and the porosity, the porous TZP ceramics achieved compressive strengths of 3.3~23.6MPa, diametral strengths of 1.5~15.7MPa and Young's moduli of 0.24~2.20GPa. On the other hand, the porous ZA20 ceramics had compressive strengths of 5.3~36.8MPa, diametral strengths of 2.48~17.6MPa and Young's moduli of 0.30~2.25GPa. These data were similar to the mechanical properties of cancellous bones (2~12MPa for compressive strength and 0.2~5GPa for tensile modulus).

Chapter 7

Structures and Properties of Non-Uniformly Porous TZP Ceramics

7.1 Introduction

In order to tailor the mechanical properties and mimic the structure of bone, a new route was developed to prepare graded porous TZP structures. These structures included pore size graded TZP, porous/dense layered TZP, porous layer-dense core TZP, and dense layer-porous core TZP. The compressive strength were characterized and correlated with stack of graded layers. The graded structures were considered as a laminated composite consisting of several layers of materials. Finally, hydroxyapatite/borosilicate glass composite material was coated onto the pore walls of the porous TZP structures to provide additional bioactivity.

7.2 Porous TZP ceramics with graded pore size

7.2.1 Morphology

Fig.7-1 shows the cross-sections of the monolayer pore size-graded TZP structures with a total porosity of 51% and 62%, respectively. The pore sizes varied from 0.98mm to 2.09mm and were graded in the vertical direction. It can be seen that with increasing porosity, the pore windows became larger and the struts became thinner.

Fig.7-1 Optical micrographs showing the cross-sections of the monolayer pore size graded TZP ceramics with a porosity of (a) 51% and (b) 62%. The pore sizes varied from 0.98mm to 2.09mm at a sintering temperature of 1500°C.

7.2.2 Compressive strength for porous TZP structures with two porous layers

The effect of stacking of porous layers on compressive strength was studied. In order to simplify the problem, two-layer graded porous TZP were prepared. The compressive strengths were first studied for the porous structures with the pore size stacking of 2.09mm vs. 1.86mm, 2.09mm vs. 1.54mm, 2.09mm vs. 1.29mm and 2.09mm vs. 0.98mm. The thicknesses of the two porous layers were same, which was achieved by controlling the mass of the EPS beads. On the other hand, the compressive strengths of the porous structures with same pore size stacking but various layer thickness ratios (i.e., 3:1, 2:1, 1:1, 1:2 and 1:3) were also studied. The porosities of these porous structures were kept at about 51%. The compressive strengths were measured in the longitudinal direction of the graded porous structures.

Fig.7-2 shows the correlation of compressive strength and pore size stacking for the structures when the two porous layers were of same thickness. Fig.7-3 is the relationship between compressive strength and porous layer thickness ratio.

Fig.7-2 Compressive strength versus porous size ratio of graded porous TZP structures with the 1 : 1 thickness ratio

Fig.7-3 Compressive strength versus porous layer thickness ratio for different pore size stacking. The porosity was kept around 51%

From Fig.7-2, it can be seen that the compressive strength increased with increasing pore size ratio. According to the previous chapter, when porosity was constant, the smaller the pore size, the higher the mechanical strength. When the pore size of one layer was fixed, the compressive strength increased with decreasing pore size in the other layer. It should be noted that when the pore size ratio increased by 90%, the compressive strength increased by only 11%, which again indicated that the compressive strength was insensitive to different pore size.

From Fig.7-3, it is observed that by reducing the thickness ratio of the porous layer with large pores to that with small pores, the compressive strength increased. The effect of the thickness ratio on the compressive strength became more pronounced when two pore sizes were of great difference. For example, the compressive strength of the porous structure with the pore size stacking of 2.09mm vs. 1.86mm increased by only 7% when the thickness of the porous layer with small pore size increased by three times, while it increased by 24% with the pore size stacking of 2.09mm vs.

0.98mm as a small pore resulted in higher compressive strengths.

From these results, it can be concluded that by adjusting the pore size stacking and the thickness ratio, the compressive strengths in the longitudinal direction of the graded porous structures can be tailored. Furthermore, when the pore sizes of the two porous layers were substantially different, the effect of the porous layer thickness ratio on the compressive strength became greater.

7.2.3 Compressive strengths for porous TZP structures with five porous layers and different porosities

The effect of porosity on compressive strength of graded porous TZP with five porous layers was studied. The pore sizes were from 0.98mm to 2.09mm. The thickness of each porous layer was same. The compressive strengths were measured both in the transverse direction and the longitudinal direction (Fig.7-4). The results are shown in Fig.7-5 and Fig.7-6. The compressive strengths of uniformly porous TZP ceramics with a pore size of 2.09mm and 0.98mm are also presented for comparison.

Fig.7-4 Schematic diagrams showing the arrangement of graded porous specimens for compressive tests conducted in the transverse direction (a) and the longitudinal direction (b), where t is the thickness of a porous layer and A the cross-section area.

Fig.7-5 Compressive strength in the transverse direction versus porosity of porous TZP with graded pore size from 0.98mm to 2.09mm compared to uniformly porous TZP with a pore size of 2.09mm and 0.98mm respectively.

Fig.7-6 Compressive strength in the longitudinal direction versus porosity of porous TZP with graded pore size from 0.98mm to 2.09mm compared to uniformly porous TZP with a pore size of 2.09mm and 0.98mm respectively.

From Fig.7-5 and Fig.7-6, it can be seen that the compressive strengths decreased with increasing porosity in both the transverse direction and the longitudinal direction. The anisotropic behavior was obvious. In Fig.7-5, the compressive strength of the graded porous TZP was not much different from that of the uniformly porous structure with a pore size of 2.09mm. This was because when tested in the transverse direction, the porous structures began to fail in the weakest layer, i.e. the layer with the largest pore size. Thus, the compressive strengths were close to those of the uniformly porous TZP with the pore size of 2.09mm. In Fig.7-6, the compressive strength was higher when tested in the longitudinal direction. This was because the porous layers with the smaller pore sizes was stronger and had to share the load. Thus, the compressive strength of the graded porous TZP in the longitudinal direction was higher than that of the uniformly porous structure with the largest pore size.

The rule of mixture can be used to estimate the strength of a graded porous TZP structure in the longitudinal direction. Suppose a compressive force F_C is loaded in the longitudinal direction. The load is shared by each of the porous layers, i.e.,

$$F_C = \sum_{i=1}^n F_i \quad 7.1$$

where F_i is the compressive force on the porous layer i , n the number of different porous layers. In this case, n equals to 5 for the five porous layers. From the definition of stress, $F = \sigma A$, where A is the cross-section area of a porous layer. The above equation can be changed into the following form:

$$\sigma_C = \sum_{i=1}^n \sigma_i \frac{A_i}{A_C} \quad 7.2$$

Since the cross-section area fraction of each porous layer is equivalent to the volume fraction of each porous layer, the above equation becomes:

$$\sigma_C = \sum_{i=1}^n \sigma_i V_i \quad 7.3$$

where V_i is the volume fraction of each porous layer in the graded porous structure. V_i also equals to the thickness fraction of each porous layer in the graded porous

structure. According to Hooke's law, $\sigma = E\varepsilon$, one can replace the stress in the above equation with the product of the Young's modulus and the strain of each porous layer, leading to:

$$\sigma_c = \sum_{i=1}^n E_i \varepsilon_i V_i \tag{7.4}$$

From the above equations, it can be seen that when the compressive force was loaded on the graded porous TZP structure in the longitudinal direction, the compressive stress component shared by each porous layer depended on its own Young's modulus. In other words, the compressive stress on each layer was different, even when V_i was kept same (actually not) and when ε_i was kept same (i.e., isostrain condition). For example, a five porous layer graded TZP with a porosity of 51% consisted of five uniformly porous TZP layers with pore sizes from 0.98mm to 2.09mm. The stress-strain curves of the uniformly porous TZP structures with different pore sizes are shown in Fig.7-7. The measured compressive strength (20.1MPa) of the graded porous TZP in the longitudinal direction is also presented.

Fig.7-7 Strain-stress curves of uniformly porous TZP structures with different pore sizes and a porosity of 51 %.

Since the compressive force (F_C) was loaded on the two parallel surfaces of the porous structure in the longitudinal direction, the elastic deformation (the strain) of the whole porous structure was same; every porous layer was subject to same amount of deformation. The compressive strength for each porous layer was related to its own Young's modulus. According to the rule of mixture, the composite fails when a single component in the composite fails. From Fig.7-7, it can be seen that the porous TZP with a pore size of 0.98mm had the lowest strain upon fracture, 1.07%. Theoretically, the structure should fail when the strain reaches 1.07%. Thus, the fracture compressive strength can be calculated as 18.4MPa, which is close to the measured compressive strength, 20.1MPa.

7.3 Porous/dense TZP structures

7.3.1 Morphology of porous/dense TZP structures

The structures prepared in this study included TZP structures with dense/porous layer, porous layer-dense core and dense layer-porous core. In the case of dense/porous layered TZP structures, a porous layer was combined with a dense layer. The dense/porous layered composites were prepared in order to mimic compact bone/cancellous bone structures and to improve compressive strength.

Fig.7-8 shows the cross-sections of dense/porous layered TZP structures. The porosities of the porous parts were about 51%. The structure with the pore size of 2.09mm showed a cross section with no visible curvature. In other words, the structure had nearly flat top and bottom surfaces. But the structure with the pore size of 1.29mm showed obvious curvature, caused by the different sintering shrinkages of the dense and the porous parts. As mentioned in the previous chapter, the sintering shrinkage of dense TZP was larger than that of porous one, and decreased with decreasing pore size. Thus, in the dense/porous layered structure with the pore size of

2.09mm, the difference of sintering shrinkage wasn't big enough to cause obvious curvature. However, with decreasing pore size, the difference in shrinkage increased, and visible curvature occurred. Different shrinkages can be mitigated by reducing the shrinkage of dense layer, for example, by coarsening the zirconia starting powder. Sintering shrinkage can also be reduced by simply adding alumina into the zirconia matrix, as the shrinkage of ZA composite was smaller than that of pure TZP.

Fig.7-8 Optical micrographs showing the cross-sections of dense/porous layered TZP ceramics with a pore size of (a) 2.09mm and (b) 1.29mm. The porous bodies were sintered at 1500°C and had a porosity of 51%.

Fig.7-9 presents the porous layer-dense core TZP structure and the porous core-dense layer structure. The porous and the dense part were cast simultaneously and no cracks were observed. The denser parts were not fully dense, since they were prepared by infiltrating TZP slurries into PU foams. Fig.7-10 shows an SEM micrograph of the dense part of the dense core-porous layer TZP structure, with the porous network structure due to burning off the PU foam evidently. The pores were actually interconnected in three dimensions, but with small pore channel. This was due to the large sintering shrinkage of TZP and the relative density of the PU foam-derived part

was 93%. Thus, during heating and sintering, the shrinkage behavior of the PU foam-derived dense part was assumed to be similar to that of the dense TZP ceramics.

Fig.7-9 Optical micrographs showing the morphologies of a porous layer-dense core TZP structure ((a) oblique view, (b) top view), and a porous core-dense layer TZP structure ((c) oblique view; (d) top view). The porous bodies were sintered at 1500°C with a pore size of 0.98mm and a porosity of 51%

Fig.7-10 SEM (SEI mode) micrograph showing the dense part of a porous layer-dense core TZP structure sintered at 1500°C

7.3.2 Internal stresses from drying, sintering, and cooling

Qualitative analysis of the internal stresses

Due to the different properties between the dense and the porous parts of the TZP structures, three processes might cause stresses and damage the final products. The stresses could occur during drying, heating and sintering, and/or cooling. First, during drying, the shrinkage of the dense green body was higher than that of the green body containing EPS beads, which could cause internal stress. Second, during heating and sintering, the shrinkage of the dense part was again higher than that of the porous part. At a certain sintering temperature T , the dense and the porous parts in the TZP structure were subjected to internal stresses which were later released by forming curvature and/or cracks in the sintered bodies. Finally, during cooling, the different coefficients of thermal expansion (CTE, $11 \times 10^{-6} \text{K}^{-1}$ for the TZP and $10.7 \times 10^{-6} \text{K}^{-1}$ for the porous TZP with the pore size of 0.98mm) also caused different shrinkages between the dense and the porous parts, which led to thermal residual stress after cooling. The states of these stresses are shown in Fig.7-11, Fig.7-12 and Fig.7-13.

Fig.7-11 shows the internal stresses in the porous and the dense layers caused by different shrinkages. During drying, heating and sintering or cooling, the dense layer tended to shrink more than the porous layer. Thus, the porous layer was subjected to a compressive stress parallel to the layer surface, whereas the dense layer was subjected to a tensile stress along the layer surface.

For the porous layer-dense core TZP structure (Fig.7-12), the inner dense core shrank more than the outer porous layer. Thus, the porous layer was subjected to a tensile stress in the radial direction and a compressive stress in the tangential direction, whereas the dense core was subjected to a tensile strength in both the radial and the tangential directions.

In the case of the dense layer-porous core TZP structure (Fig.7-13), the outer dense

layer shrank more than the inner porous core. Since the porous core resisted the dense layer from shrinkage, the outer dense layer experienced a compressive stress in the radial direction but a tensile stress in the tangential direction, whereas the inner porous core was subjected to compressive stresses in both the tangential direction and the radial direction.

Fig.7-11 Internal stresses existing in the porous/dense laminated TZP structure due to different shrinkages (2D cross section view)

Fig.7-12 Internal stresses existing in the porous layer-dense core TZP structure due to different shrinkages (2D top view)

Fig.7-13 Internal stresses existing in the dense layer-porous core TZP structure due to different shrinkages (2D top view)

Quantitative analysis of the internal stresses

Since the nature (tensile or compressive) of the stresses existing in the porous/dense structures during drying, heating and sintering, or cooling were the same, the stresses may cause curvature in the dense/porous layered TZP structures or cracks in the layer-core TZP structures.

During drying, no visible curvature or cracks were observed in the dense/porous structures. The shrinkage difference caused by drying was not considered here. The sintering shrinkages of both dense and porous TZP ceramics measured in the previous chapter can be used for analysis. For example, the difference in shrinkage between the dense TZP and the porous TZP with a pore size of 0.98mm at 1500°C was calculated to be 3.02%. During cooling, the thermal expansion mismatch strain can be calculated using the following equation [145]

$$S_c = \int_T \Delta\alpha \, dT \tag{7.5}$$

where S_c is the thermal expansion mismatch strain, $\Delta\alpha$ the difference of CTE, T the sintering temperature. S_c of the dense and the porous TZP with a pore size of 0.98mm was calculated to be 0.044%.

From these data, it can be seen that the shrinkage mismatch during sintering mainly contributed to the curvature and the potential cracking in the dense/porous TZP structures. Thus, the internal stresses caused by different sintering shrinkages at 1500°C are analyzed as follows.

I. The case of the dense/porous layered TZP ceramic

The internal stresses in the dense/porous layered TZP can be calculated. The definitions of the parameters involved are schematically shown in Fig. 7-14, where E is Young's modulus, ν the Poisson's ratio, σ the internal stress, h the thickness of the layer, and the subscripts d and p mean the dense layer and the porous layer for the layered TZP structure. Since only tensile stress could result in cracks, tensile stress near the interface in the dense layer is considered.

Fig.7-14 Schematic diagram showing the parameters used to calculate the tensile stress in a dense/porous layered TZP structure (2D cross section view)

The tensile stress in the dense layer near the interface can be calculated using the following equation [145]:

$$\sigma_d = \left(\frac{1}{1 + mn} \right) \left(\frac{E_d}{1 - \nu_d} \right) S \quad 7.6$$

where $m = \frac{h_d}{h_p}$, $n = \left(\frac{E_d}{1 - \nu_d} \right) \left(\frac{1 - \nu_p}{E_p} \right)$, and S is the difference of sintering shrinkages.

A value of 210GPa is used for the Young's modulus of the dense TZP layer, and the

measured Young's moduli of the porous TZP are used (1.19, 1.47, 1.77, 1.97 and 2.2GPa for porous TZP ceramics with a porosity of 51% and pore sizes of 2.09, 1.86, 1.54, 1.29 and 0.98mm, respectively). Poisson's ratio 0.312 is used for the dense TZP [146]and 0.2 for the porous TZP [147].

Parameters that affect shrinkage will affect internal stresses. The internal stresses in the porous structures of different pore sizes are different. Different thicknesses of porous and dense layers also affect internal stresses. From Fig.7-15, it can be seen that the tensile stress in the dense layer is extremely small and much lower than the fracture strength of a dense TZP (700~1100MPa) [148]. Moreover, the stress decreases greatly with increasing porous layer thickness.

Fig.7-15 Calculated tensile stress in the dense layer near the interface of a dense/porous layered TZP structure versus the layer thickness ratio

II. The case of the dense core-porous layer TZP ceramic

The internal stresses in the layer-core TZP structures were calculated and the definitions of the parameters are schematically shown in Fig.7-16.

Fig.7-16 Schematic drawing showing the parameters used to calculate the tensile stress in the layer-core TZP structure (2D top view)

In Fig.7-16, E is Young's modulus, the subscripts i and o mean the inner core and the outer layer, ν the Poisson's ratio, σ the internal stress, r the radius of the layer or the core, and the subscripts θ and r mean the tangential and the radial directions.

The internal tensile stress in the porous layer of the layer-core TZP structure can be calculated using the theory based on Lamé's equations [149]:

$$\sigma_{ri} = A - \frac{B}{r^2}, \quad \sigma_{\theta i} = A + \frac{B}{r^2} \quad 7.7$$

$$\sigma_{ro} = C - \frac{D}{r^2}, \quad \sigma_{\theta o} = C + \frac{D}{r^2} \quad 7.8$$

where A, B, C and D are constants derived from boundary conditions. The boundary conditions used to determine the constants are:

$$r = 0, \quad \sigma_{ri} \neq 0 \Rightarrow A \neq 0, B = 0$$

$$\sigma_{ro} = 0 \quad \text{at } r = r_o,$$

$$\sigma_{ri} = \sigma_{ro}, \quad \sigma_{\theta i} = \sigma_{\theta o} \quad \text{at interface}$$

For the calculation of the stresses in the outer porous layer, the constants C and D are required and are expressed as follows:

$$C = \left(\frac{1}{1-R^2} \right) E_o \frac{S}{3} \left[\frac{E_o}{E_i} (\nu_i - 1) + \left(\frac{1+R^2}{1-R^2} \right) - \nu_o \right]^{-1} \quad 7.9$$

$$D = \left(\frac{1}{1/r_o^2 - 1/r_i^2} \right) E_o \frac{S}{3} \left[\frac{E_o}{E_i} (\nu_i - 1) + \left(\frac{1+R^2}{1-R^2} \right) - \nu_o \right]^{-1} \quad 7.10$$

where $R = r_o/r_i$, S is the difference of sintering shrinkage between the dense and porous layers.

Substitution of C and D into Lamé's equations results in the following expressions:

$$\sigma_{\theta\theta} = E_o \frac{S}{3} \left[\frac{1+R^2}{1-R^2} \left[\frac{E_o}{E_i} (\nu_i - 1) - \nu_o + \frac{1+R^2}{1-R^2} \right]^{-1} \right] \quad 7.11$$

$$\sigma_{r_o} = 2C - \sigma_{\theta\theta} \quad 7.12$$

$$7.13$$

Since the tensile stress σ_{r_o} , if high enough, could cause cracks in the porous layer.

It was calculated and presented in Fig.7-17.

Fig.7-17 Tensile stress in the porous layer in the radial direction at the interface of a porous layer-dense core TZP structure.

In Fig.7-17, the tensile stress increases with increasing the porous layer thickness relative to the core radius. The influence of the pore size in the porous layer on the tensile stress becomes larger when the porous layer radius ratio becomes larger. In each curve, one can find a range of stress values that are lower than the tensile strength of the porous TZP measured in Chapter 6 (7.1MPa, 11.75MPa and 15.7MPa for porous TZP with a porosity of 51% and a pore size of 2.09mm, 1.54mm and 0.98mm, respectively). Beyond that range, cracks may occur in the porous layer.

From these results, it can be concluded that in a porous/dense TZP structure, by controlling the pore size in the porous part and the volume fractions of the dense and the porous layers, the internal tensile stress can be lowered and potential cracks can be avoided. Finally, it is understood that a crack is more difficult to form in a dense core than in a porous layer.

7.4 Porous TZP with HA/borosilicate glass coating

Various porous TZP ceramics have been prepared in this study. However, TZP is bioinert, which is a drawback in spite of the high mechanical strengths. A bioactive coating is needed for the porous substrates for bone bonding. Hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is the main mineral constituent of teeth and bones. It exhibits no cytotoxic effects and shows excellent biocompatibility with hard tissues as well as skin and muscle tissues. These facts make HA the most appropriate ceramic material for bone bonding. HA is often used in the form of coatings. Unfortunately, the interfacial strength between a substrate and HA coating is normally very low, leading to the failure of the coated implant. One option to improve the HA ceramics and the HA coatings is to add a glass as a second phase. In fact, bioglass-reinforced HA ceramics have been recently developed and characterized in terms of mechanical properties [150,151]. In this study, borosilicate glass was added into the HA matrix to enhance the mechanical properties of HA and improve the interfacial bonding between the

coating and the substrate. Borosilicate glass was used because it is bioinert, readily available, and much cheaper than bioactive glass. A dip-coating process was used as it is a simple method of coating porous structures.

7.4.1 Microstructure of the HA/glass composite coating

An HA/glass powder mixture was coated onto the porous TZP structures by dipping the porous TZP substrates in a slurry, having an HA/glass slurry solids loading of 15wt% and an HA to borosilicate glass weight ratio of 1:1. Fig.7-18 shows a coated porous TZP ceramic with a pore diameter of 1.54mm and a porosity of 64%. The HA/glass coating layer was attached to the pore wall surfaces of the porous TZP structure. Although the coating layer was relatively thick, the pore windows were not blocked. Fig.7-19 shows the HA-rich porous coating on the surface, which would provide good mechanical interlocking between newly grown bone and the porous implant.

Fig.7-18 SEM (SEI mode) micrograph showing the HA/glass coating on a porous TZP ceramic. The coating on the TZP structure was sintered at 1200°C for one hour

Fig.7-19 SEM (SEI mode) micrograph showing the as sintered surface of the HA/glass coating layer on the porous TZP structure. The coating layer was sintered at 1200°C for one hour

Fig.7-20 shows the different morphologies of pore wall surfaces of the porous TZP structure before and after coating. Before coating, the pore wall surface was covered with sintered TZP grains with an average grain size around 0.4μm. After coating, the surface of the pore wall became rougher and the grain size was larger. The EDX result confirmed that there are more HA rather than glass at the coating surface.

Fig.7-20 SEM (SEI mode) micrographs showing the pore wall surfaces of porous TZP (a) before coating and (b) after coating. The TZP substrate was sintered at 1500°C and the coating was sintered at 1200°C for one hour

7.4.2 HA/glass coating on flat, dense TZP substrate

Structural analysis of the coating

Since it was difficult to characterize the HA/glass composite coating in a porous structure, the coating layer on a dense TZP substrate was used for fundamental studies. Fig.7-21 shows a cross-section of the coating layer on a dense TZP. From the figure, it can be seen that the coating layer was firmly attached to the TZP substrate. No crack was found on the interface. The average coating thickness was about 50 μ m. X-ray diffraction was done on the surface of the as-sintered coating layer. The XRD result is shown in Fig.7-22. The silica peaks matched the JCPDS No. 39-1425 (phase: cristobalite) and the main phase was HA.

Fig.7-21 SEM (SEI mode) micrograph showing the cross section of the HA/glass coating on the dense TZP substrate

Fig.7-22 X-ray diffraction pattern from the HA/glass coating layer (*: unidentified peak)

The zirconium and the silicon compositional profiles across the interface changed abruptly confirming there was no significant inter-diffusion of zirconium and silicon during sintering (Fig.7-23). Thus, although at 1200°C, the glass was in molten state, the penetration of the glass into the dense sintered TZP substrate was limited.

Fig.7-23 EDS line scans of (a) zirconium and (b) silicon elements across the interface

Interfacial bonding of the coating

Preliminary tests of the coating adherence were performed using a series of indentations near the substrate interfaces on polished cross-sections. Fig.7-24 shows a Vickers hardness micro-indentation impression on the interface between the coating and the TZP substrate. The indentation on the interface did not cause the coating layer to separate from the substrate. In other words, the cracks did not propagate along the interface, instead, they propagated towards the HA/glass composite coating layer. Although this method could not quantitatively measure the interfacial toughness and bonding strength, it provided qualitative evidence that the interface had a sufficient toughness to force the cracks to propagate into the bioactive HA/glass coating layer.

Fig.7-24 Optical micrograph showing the micro indentation on the cross-section of the HA/borosilicate glass coating on the zirconia substrate

The residual thermal stress, σ , in the HA/glass coating due to cooling and different thermal expansions can be estimated by the following equation [152]:

$$\sigma = \frac{E}{1 - \nu} \Delta\alpha \Delta T \quad 7.11$$

where E and ν are Young's modulus and Poisson's ratio of the coating, respectively, $\Delta\alpha$ the difference in CTE, and ΔT the temperature drop during cooling. Since the coating layer was borosilicate glass rich near the interface between the coating layer and the substrate, the properties of borosilicate glass are used to calculate the thermal

stress. The Young's modulus of borosilicate glass is 63GPa (Pyrex[®] glass specification), and the Poisson's ratio is 0.2. The CTE of borosilicate glass is $3.3 \times 10^{-6} \text{K}^{-1}$ (Pyrex[®] glass specification) and $11 \times 10^{-6} \text{K}^{-1}$ for the TZP. The annealing point of borosilicate glass is 565°C, above which the stress could be relieved. Due to the smaller CTE of the HA/glass composite coating, the residual thermal stress in the coating layer should be compressive in nature. As a result, coating would not encourage the formation of cracks in the direction perpendicular to the interface. The calculated thermal stress while a high 330Mpa is not harmful for the coating.

7.5 Summary

This chapter described the morphologies and the mechanical properties of the graded porous and the porous/dense TZP structures, with the former having porosities from 51% to 69% and pore sizes from 0.98mm to 2.09mm, while the dense/porous layered, the porous layer-dense core, and the dense layer-porous core structures all exhibited pore sizes from 0.98mm to 2.09mm and an average porosity of 51% in the porous parts. For the five-layer graded porous TZP ceramics with porosities from 51% to 69%, the compressive strengths were from 16.5~3.3MPa in the transverse direction, and 20.1~4.1MPa in the longitudinal direction. By adjusting the pore size and the thickness of each porous layer, the compressive strength in the longitudinal direction can be tailored and the curvature or cracking of the sintered body can be avoided.

A HA/borosilicate glass composite layer was coated onto the porous TZP structures. The average thickness of the coating layer was 50µm. No inter-diffusion between the zirconia substrate and the coating layer was found, nor any cracking in the coating layer and along the interface. The Vickers hardness tests qualitatively demonstrated good interfacial bonding between the coating layer and the TZP substrate. Due to the low softening point of the borosilicate glass (821°C), sintering at 1200°C lead to a porous HA surface impregnated by borosilicate glass. Thus, porous TZP bioinert ceramics modified with bioactive coating were achieved.

Chapter 8

Conclusions and Future Work

8.1 Conclusions

This thesis describes the preparation and characterization of porous TZP and TZP/alumina composites, while feature uniformly porous, graded porous and porous/dense structures. Vacuum casting was applied for the preparation of the porous structures with expanded polystyrene (EPS) beads of different sizes as a preform. The primary investigations and conclusions were:

- The rheological properties of the ceramic slurries were studied in order to determine the optimum slurries for vacuum casting. It was found that by adding PMAA to zirconia and zirconia/alumina slurries, the isoelectric point (IEP) shifted to acidic pH and the zeta potential was lowered. With increasing dispersant, the viscosities of the ceramic slurries decreased initially, but after reaching a critical point, gradually increased. Zirconia, ZA20 and ZA30 slurries with solids loadings of 50wt%, and PMAA contents of 0.5wt%, 0.7wt% and 0.8wt% exhibited lowest viscosities at $\text{pH} \approx 9$.
- The effects of the rheological properties and the casting methods on the green bodies were studied. The green densities of the samples prepared using optimized slurries were higher than those prepared by poorly dispersed slurries. By slip casting, the green densities achieved 40% for TZP, 46.1% for ZA20 and 51.6% for ZA30 of the theoretical density respectively, and slightly higher than those

prepared by vacuum casting. The relative green densities achieved 39.7%, 44.8%, and 50.7% for TZP, ZA20 and ZA30 after 6 hours of vacuum casting, respectively.

- The sintering behavior of EPS-free TZP ceramics and ZA composites was studied. Since the shrinkage of pure TZP was large, alumina powder of 20wt% and 30wt% was added to alleviate this effect. The densification of the final product was hindered by the addition of alumina and the relative sintering shrinkage was lowered. Pure TZP compacts achieved a relative density of 99.5% at 1500°C, while ZA20 and ZA30 reached 97.7% and 97% at the same temperature. The grain growth of TZP was inhibited with the alumina addition. Such an effect was reduced with further increasing alumina content. The Vickers hardness and the fracture toughness of ZA20 sintered at 1500°C were significantly increased, whereas those of ZA30 were not much improved, especially at lower sintering temperatures (1400°C and 1450°C).
- Uniformly porous ceramics with various pore sizes and porosities were prepared using the vacuum casting process. In the case of TZP ceramics, the pore sizes ranged from 0.98mm to 2.09mm, while for ZA20, the pores varied from 1.03mm to 2.22mm. Both porous structures had porosities from 51% to 69%.
- The effect of pore size on the sintering behavior of the uniformly porous structures was studied. With the existence of pores, the relative sintering shrinkage decreased. Moreover, the smaller the EPS bead size, the lower the relative sintering shrinkage. The shrinkage decreased from 25.97% to 23.84% for the porous TZP ceramics when the bead size decreased from 2.95mm to 1.4mm.
- The total and open porosity were studied. Different sizes of the EPS beads did not affect the total porosity, however, it was modified by the deformation of the EPS beads. Increasing total porosity led to greater open porosity. More than 86% of

the pores were interconnected.

- The mechanical properties of uniformly porous TZP and ZA20 ceramics were studied. The compressive strength, the diametral tensile strength and the Young's modulus all decreased with increasing pore size and porosity. The mechanical properties of the porous structures were more sensitive to porosity than pore size. The porous TZP ceramics achieved compressive strengths of 3.3~23.6MPa, diametral tensile strengths of 1.5~15.7MPa and Young's moduli of 0.24~2.2GPa. On the other hand, porous ZA20 ceramics achieved compressive strengths of 5.3~36.8MPa, diametral tensile strengths of 2.48~17.6MPa and Young's moduli of 0.30~2.25GPa. These data were similar to the mechanical properties of cancellous bones (2~12MPa for compressive strength and 0.2~5GPa for tensile modulus).
- Graded porous TZP ceramics with pore sizes from 0.98mm to 2.09mm and porosities from 51% to 69% were produced. The compressive strengths were from 16.5~3.3MPa in the transverse direction, and 20.1~4.1MPa in the longitudinal direction. The compressive strength of the graded porous TZP in the longitudinal direction was estimated according to the isostrain composite theories.
- Porous/dense layered TZP, porous layer-dense core TZP, and dense layer-porous core TZP were also prepared. The curvature in the layered structures and the internal stresses in the layer-core structures were mainly caused by the different sintering shrinkages between the dense and the porous TZP with different pore sizes. By adjusting the pore size combination and the thickness ratio of the porous layers, the curvature and the stresses in the porous/dense TZP ceramics could be minimized.
- An HA/borosilicate glass composite layer was used as a bioactive coating on the

pore surface of the porous TZP structures to introduce bioactivity. The average thickness of the coating layer was 50 μ m. No cracks were found between the interface. The Vickers indentation tests qualitatively demonstrated good interfacial bonding between the coating layer and the TZP substrate. Due to the low softening point of the borosilicate glass (821°C), sintering at 1200°C, the borosilicate glass impregnated the interior of the HA coating layer, forming a desirable graded coating structure. Thus, porous TZP bioinert ceramics with various configurations could be made bioactive by composite coating.

- The porous ceramics developed in this study can be used as replacement for cancellous bone in the extremities of the long bones. For example, the cancellous bone biopsy specimens taken from the proximal tibias and distal femurs showed compression strengths from 0.5 MPa to 18.1 MPa and a mean value of 5.6 MPa [153]. The 5 layer graded porous TZP has the appropriate compressive property and can serve the purpose. Not only the mechanical properties can be satisfied, the graded structure also mimics the real cancellous bone structure.

8.2 Future work

In this study, uniformly porous and graded porous ceramics were prepared using a novel processing route. In this section, the strengths and weaknesses of the approach are discussed and some suggestions for improvements are addressed:

- **Preform:** A porous structure designed for bone ingrowth must have high porosity, high interconnectivity and a suitable pore size. In order to achieve these properties, expanded polystyrene (EPS) beads were used as a preform instead of the conventional PVA powder. Unlike the irregularly shaped PVA powder, the EPS beads are spherical, enabling the production of porous structures with

uniform spherical pores. Since polystyrene beads are already expanded, they are soft and deformable. This property can be used to produce porous structures with different pore sizes, porosities and connected windows. The disadvantage is that excessive deformation of EPS may break the green bodies after the deformation is recovered. Thus the porosity range was limited and the pore sizes were large, as small EPS beads are light, electrostatic and difficult to handle. To produce porous structures with pore sizes in the range of 100 μm to 900 μm , EPS beads are not recommended. Other polymer preforms such as wax or PMMA beads with diameter less than 900 μm can be combined. The polymer preform must not expand too much during the heating process, even at very slow heating rates (e.g., 0.5 $^{\circ}\text{C}/\text{min}$), since the expansion of the preform during heating will destroy the unsintered green ceramic body.

- *Vacuum casting process:* A vacuum casting process was used in this study to prepare porous structures with high interconnectivity. Conventional slip casting or tape casting process involving blending a polymer preform with a ceramic slurry cannot ensure porous structures with highly interconnected pores. However, vacuum casting can produce graded porous structures with good interconnectivity between each porous layer. The weakness of the vacuum casting process is the long time (e.g., 6 hours). However, in the future, not only porous plates and disks, but also porous hollow cylinders can be produced with a new mold design.
- *Characterization of the porous structures:* For uniformly porous TZP and ZA20 ceramics, the major mechanical properties studied were compressive strength and diametral tensile strength. Young's moduli were calculated from the stress-strain curves of the diametral compression tests. The compressive strength-porosity relationships of the porous TZP and ZA20 ceramics corresponded well with the Rice's model based on the minimum solid area (MSA) theory. The Young's moduli of the porous structures were low but close to those of cancellous bones. This stress matching is important as bone implants with a high Young's modulus

leads to the stress shielding problem that is detrimental to new bone formation. Other mechanical properties such as flexural strength and Young's modulus in bending were not measured due to the difficulty in producing large porous samples required for the three or four point bending tests. This problem was also encountered in the mechanical characterization of the graded porous TZP structures. Limited tests were performed on the graded porous structures. Furthermore, the mechanical properties reported in this study were all obtained in air. Mechanical tests of the porous structures immersed in the simulated body fluid (SBF) (for example) should be conducted in the future.

- *Others:* A bioactive HA/glass composite layer was coated onto the porous TZP structures to provide bioactivity. Although the biocompatibility and the bioactivity of HA is proven, *in vitro* and *in vivo* tests are needed. Finally, the current methodologies are also applicable for producing porous bioactive/biodegradable ceramics, which can be used as tissue engineering scaffolds for bone regeneration.

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