A Novel Ceramic Precursor Route for the Direct Production of Hierarchically Structured Titanium Alloy Foams

Randhir Singh
Department of Materials
Imperial College London

A thesis submitted for the degree of
Doctor of Philosophy
October 2009
Declaration

I hereby certify that the work presented in this thesis is the result of my own investigations carried out at Imperial College London during the period from February 2006 to July 2009, except where otherwise stated.

Randhir Singh
October 2009
Abstract
Titanium alloys find extensive use in the biomedical field, including applications in the form of a porous structure as a scaffold material for bone repair. Scaffold materials have demanding mechanical and biocompatibility requirements, which vary depending on the orthopaedic application. These requirements are determined by both the porous macrostructure of the foams and the strut wall microstructure. Therefore techniques are needed to characterise these structural features and relate them to the mechanical and physical properties. In this thesis new methods were developed to both manufacture titanium alloy foams and characterise them.

Non-destructive X-ray micro-computed tomography (μCT) methods were employed to characterise the pore and interconnect size. The pore and interconnect size dominates the flow properties (permeability) of open-foam structures. Thus, μCT data was meshed and computational fluid dynamics analysis was performed to predict permeability. Direct finite element modelling, continuum micromechanics and analytical models of the foam were employed to characterise the elasto-plastic deformation behaviour. Pore anisotropy was quantified and related to the yield stress anisotropy, allowing identification of initial pore collapse. These results were validated against experimental measurements.

Finally, the conventional production method of porous titanium is achieved through a costly multi-step powder metallurgical (PM) route. A new, potentially low cost, method was developed to produce porous titanium with properties similar or better than the existing titanium foam from a ceramic precursor via an electrochemical route. Two steps were involved: (1) preparing the ceramic precursor foam via a gel-casting route; and (2) reducing the oxide electrochemically via the FFC (Fray, Farthing and Chen) Cambridge process. The results of this preliminary study are very promising, with the foams produced via this method demonstrating mechanical and physical properties comparable to conventionally manufactured foams.
Acknowledgments

First and foremost, my sincere gratitude is to my supervisors Professor Peter D. Lee, Professor Richard J. Dashwood and Professor Trevor C. Lindley for their inspiring guidance ever since my very first day at Imperial College. I feel particularly grateful to Professor Lee (Chapter 3, 4 and 5), Professor Dashwood (Chapter 4 and 5) and Professor Lindley (overall thesis) for spending so much time discussing both scientific issues and helping with the presentation of this thesis.

An early part of the work on an alternative ceramic foam precursor fabrication was carried out at Lehigh University (Professor H. M. Chan, Professor H. Caram and Dr A. Verdooren) over a period of a month. Although this method was not used in the final thesis, I want to thank them for their mentoring on a Modified Motoki method of titania foam fabrication. Financial support and the permission to use the technical facilities in the Departments of Materials Science and in the department of Chemical Engineering at Lehigh are gratefully acknowledged. Of late Dr Julian Jones and Ms Z. Wu have been of paramount importance in optimising the gel casting of titania foams. My colleague Dr G. Poolgasundarampillai was kind enough to offer his help with image analysis and experiments such as permeability measurement and gel casting.

It would have been a nightmare to operate Fray cells without the help from my colleagues Dr K. Rao, Dr R. Bhagat and Ben Jackson. Lately Ben Jackson was quite instrumental in implementing an improved reactor sealing. He has also helped me by reading over a chapter in my thesis, offering very useful tips. Mr T Post is acknowledged for his help on experimental measurement of permeability.

Professor Christian Hellmich at TU Wien was very generous to offer his expertise in ultrasound characterisation and micromechanics modelling of Ti foams. Dr T. Imwinkelried (Synthes, Switzerland) and Dr M. Bram (Forchungszentrum Juelich GmbH, Germany) are thanked for supplying a commercial Ti foam. Professor Kenneth C. Mills (Materials, Imperial College London) was very kind to read over some of the chapters of my thesis and provided very useful tips on writing.

My senior colleagues (formerly Drs. R. C. Atwood and Y Yousef; R Hamilton) have always been a source of inspiration; their ever-willing eagerness to help has kept me going without any delay.
Research and technical staffs - notably Mr Richard Sweeney (XRD), Mr Garry Stakalls (workshop) and Dr Mahmoud Ar dakani (SEM) - have helped me a lot throughout my stay at Imperial.

I would like to tender my deep appreciation for the help I received from my lab-mates Dr D. Ness, Dr D. Fuloria and Dr J. Wang, especially when I started working at Imperial College. Mr S. Abolghasemi, S. Yue, Z. Malik, Y. Lang, P. Ramirez lopez and M. Azeem made my stay more pleasant with their stimulus discussion on all terrestrial issues, provided the company in the college which I will be cherishing for long.

Support from the technical staff for the machining and the SEM characterisation is sincerely appreciated.

My family has always been very considerate. My wife Shalini and the arrival of my daughter Aditi during the course of my stay at Imperial have amplified the sense of fulfilment and joy.

Finally, I am humbled by the financial support from the EC (Commission of European Communities) in the form of a Marie-Curie Fellowship.
# Table of Contents

Declaration......................................................................................................................... 2  
Abstract.............................................................................................................................. 3  
Acknowledgments ............................................................................................................. 4  
Table of Contents ............................................................................................................... 6  
List of Figures ................................................................................................................... 8  
List of Tables .................................................................................................................... 11  
1 Introduction............................................................................................................ 12  
2 Literature review .................................................................................................... 14  
  2.1 Titanium metallurgy and properties - the basics .............................................. 14  
  2.2 Titanium as a bone implant material ............................................................ 16  
  2.3 Metal foam production..................................................................................... 18  
    2.3.1 Overview .................................................................................................... 18  
    2.3.2 Processing of titanium foam ...................................................................... 18  
    2.3.3 Metal foam from ceramics ......................................................................... 22  
  2.4 Ceramic precursor foam fabrication ................................................................ 22  
  2.5 The FFC Cambridge Process: a novel route to titanium metallurgy and  
    processing .................................................................................................................... 24  
  2.6 Foam / scaffold characterisation ...................................................................... 26  
    2.6.1 Immersion gravimetry .............................................................................. 26  
    2.6.2 Scanning electron microscopy (SEM) ....................................................... 27  
    2.6.3 Micro-computed tomography (µCT) ......................................................... 27  
  2.7 Micromechanics of foams ................................................................................ 30  
    2.7.1 Gibson and Ashby model ........................................................................... 31  
    2.7.2 Models from composite theories ................................................................ 34  
    2.7.3 Finite element modelling ........................................................................... 36  
3 Characterisation of titanium foam for biomedical applications –  
    structure and permeability ............................................................................................... 37  
  3.1 Introduction ...................................................................................................... 37  
  3.2 Materials and methods ..................................................................................... 38  
    3.2.1 Titanium foam preparation ........................................................................ 38  
    3.2.2 Scanning electron microscopy (SEM) ....................................................... 39  
    3.2.3 µCT and image analysis............................................................................. 39  
    3.2.4 Permeability measurement ......................................................................... 39  
    3.2.5 Permeability simulation ............................................................................. 40  
    3.2.6 Sources of errors in the permeability simulation ....................................... 43  
  3.3 Results .............................................................................................................. 44  
  3.4 Discussion ........................................................................................................ 48  
    3.4.1 Pore size distribution ................................................................................. 50  
    3.4.2 Interconnect size distribution ................................................................. 50  
    3.4.3 Permeability ............................................................................................... 51  
  3.5 Conclusions ...................................................................................................... 53  
4 Characterisation of titanium foam for biomedical applications –  
    mechanical behaviour ................................................................................................. 55  
  4.1 Introduction ...................................................................................................... 55  
  4.2 Materials and methods ..................................................................................... 57  
    4.2.1 Material and specimen preparation ........................................................... 57  
    4.2.2 Mechanical properties characterisation .................................................... 57  
    4.2.3 µCT characterisation and image processing ............................................. 58
List of Figures

Figure 2.1. Schematic of the Kroll process for Ti sponge production.......................... 15
Figure 2.2. Metal foam production processes and achievable pore size and relative density (after (44)). ........................................................................................................... 19
Figure 2.3. Overview of typical porosity and pore size obtainable from various ceramic foam (macroporous) processing methods (73). ...................................................... 23
Figure 2.4. Schematic of FFC Cambridge process. .......................................................... 25
Figure 2.5. Foam/scaffold characterisation techniques (After Banhart (41)). ................. 27
Figure 2.6. Typical stress-strain curve for an elasto-plastic material such as a titanium foam under monotonic compression test. ................................................................. 30
Figure 2.7. The cubic open-cellular unit cell modelled by Gibson and Ashby (11); (a) open-cell foam under a compressive load, and (b) closed-cell foam showing the cell edge thickness, tc, and cell face thickness, tf. .............................................. 32
Figure 2.8. Micromechanical representation of porous titanium biomaterial: 2D sketch of 3D representative volume element consisting of solid titanium matrix and empty pores. ........................................................................................................ 35
Figure 3.1 Schematic of permeability measurement set-up. Specimen diameter dictated the choice for other components................................................................. 40
Figure 3.2 Measured pressure gradient as a function of superficial fluid velocity for the P65 foam. ......................................................................................................... 41
Figure 3.3. Schematic of the procedure to simulate the flow within a scaffold, leading to the derivation of permeability. The model has a velocity inlet (AB; x = 0) and a pressure outlet (CD; x = LREV). The rest of the solid fluid interface was modelled as wall with no slip condition. The mass flux across the two dashed lines and pressure gradient calculated under steady-state conditions are used to derive the permeability using Darcy’s law (Eq. (3.1) devoid of the last term). ............................................................................................... 41
Figure 3.4. Variation of pressure in flow direction inside the sample with 65% porosity. The pressure gradient was calculated from the inner region of the sample (bounded by the dotted lines)................................................................................. 42
Figure 3.5. SEM micrographs showing wall substructure for bulk porosity of: (a) 51%, (b) 65% and (c) 78%. The darkest regions in all figures show interconnects with the adjoining pore. ............................................................................... 44
Figure 3.6. Portion of μCT image of sample P65 showing interconnected porosity..... 45
Figure 3.7. The 3D μCT images of a single pore (child volume) of (a) P51, (b) P65 and (c) P78, and images of the pore and interconnects obtained using 3D image analysis of (d) P51, (e) P65 and (f) P78................................................................. 46
Figure 3.8. Pore-volume fraction as a function of porosity. ............................................ 46
Figure 3.9. Interconnect-area fraction for the 51%, 65% and 78% porosity samples. .... 47
Figure 3.10. Main components of the permeability tensor vs. the size of the representative elementary volume. The inset picture shows the flow streak lines inside the sample with 65% porosity. .............................................. 47
Figure 3.11. Comparison of experimental and model predicted values of permeability. Cancellous bone permeability is taken from Ref. [43]. *CD = compaction direction. ........................................................................................................ 48
Figure 4.1. A posterior lumbar interbody fusion device made of titanium foam (porosity~65%; implant is 22 mm long, enlarged relative to the spinal column). ................................................................. 56
Figure 4.2. Schematic of the FEM procedure to simulate the monotonic compression deformation. The model has a top node set (AB; \( x = 0 \)) and a bottom node set (CD; \( x = L_{REV} \)) representing respectively the top and bottom face of the cube. The rest of the solid-void interface was modelled as free surface. Total reaction force (stress) developed at the bottom node set as a function of the top node set displacement (strain) was calculated, leading to the derivation of Young’s modulus and yield strength.

Figure 4.3. (a) non-uniform foam-wall as apparent in a 3D tomograph (b) an orthoslice from a 3D tomographic dataset showing intra-strut microporosity and (c) SEM picture showing surface roughness which is beneficial for the cell-anchorage (Sample P65).

Figure 4.4. Engineering stress vs. strain characteristics in compression testing of (a) monolithic and (b) porous titanium (*Compaction direction).

Figure 4.5. Comparison of (a) Young’s modulus and (b) yield strength, of titanium foams in the direction normal to compaction (average of the property along two of the normals), obtained from different methodologies. Note that the Gibson-Ashby model, applicable only to porosity >70%, predicts yield stress scaling as 0.3 times relative density raised to power 1.5, and hence there is large deviations at low values of porosity. The micromechanics and Gibson-Ashby predictions are obtained assuming isotropic porous material behaviour.

Figure 4.7. (a) The moments acting on nodal points such as A, B and C under the application of a force \( F \) on a pore (encircled) and, (b) the segmentation of the large pore into two smaller pores; the latter mask the high aspect ratio of the large pore.

Figure 4.8. True stress-strain curves at nominal deformation of (a) 10%, (b) 20%, (c) 30%, (d) 40% and (e) 50%.

Figure 4.9. Rapid localised collapse at an ellipsoidal pore (dotted) followed by more gradual collapse at a round pore (solid line).

Figure 4.10. (a) Percentage of material deforming plastically as a function of strain and, (b-d) 2D images of the model showing elastically (dark) and plastically (light) deforming material at a strain of 0.038 for P51, P65 and P78 respectively.

Figure 5.1. Overview of metallic titanium foam production.

Figure 5.2. (a) Differential scanning calorimeter characterisation of dried precursor and (b) the four sintering schedules investigated, holding at: 1. 950 °C; (3 h), 2. 1000 °C; (3 h), 3. 1150 °C (3 h), 4. 1250 °C (3 h) and 4. 1450 °C (1 h).

Figure 5.3. (a) Schematic of the modified FFC Cambridge reduction cell: A TiO₂ foam cathode, B Ti cathode for pre-electrolysis, C graphite anode, D alumina crucible, E molten calcium chloride and F ceramic base to adjust the crucible height; and (b) layout for sealing of electrodes: (i) small nut, (ii) thick silicone ring, (iii) double threaded pipefitting, (iv) top plate, (v) ‘O’ ring and (vi) ceramic tube.

Figure 5.4. Procedure to derive 3D pore and interconnect sizes from 2D slice: (a) a filtered slice, (b) after thresholding (a) to label solid and void space, (c) showing the result of watershed segmentation to isolate overlapping pores, (d) isolated pores were labelled to extract quantitative data, (e) subtracting (b) from (c) to isolate individual interconnect and, (f) labelling of the interconnect for further quantification. The procedure was carried out on a number of slices to get a representative number of 2D pores for the analysis.
Figure 5.5 The ceramic foam precursor (left, S_1150) and the reduced metallic foam (right). .......................................................................................................... 84

Figure 5.6. X-ray diffraction data for: (a) TiO₂ powder, (b) sintered oxide foam (1150 °C; 3 h), and (c) FFC reduced foam. .................................................................. 85

Figure 5.7. Reconstructed 3D microstructure of: (a) oxide precursor; (b) reduced titanium foam (S_1150); (c) commercial titanium foam (78% porosity) produced using space holder technique; and (d) human trabecular bone.... 86

Figure 5.8. (a) Cumulative pore size distribution of the precursor and the reduced foams (S_1150) and (b) cumulative interconnect size distribution. Typical tomographic slices of the (c) precursor and (d) the reduced foam illustrating the pores’ spherical nature or the pores. ...................................................... 87

Figure 5.9. Secondary electron image of S_1150 showing the two scales of porosity: (a) precursor; and (b) reduced Ti. Primary pores are in the range of 350 µm, contributing to almost all of the porosity and, the secondary pores, 1-10 µm were within foam wall. ................................................................................ 88

Figure 5.10. (a-c) typical slice of sintered precursors processed under three different conditions: (a) slurry with standard composition and pressure (S_950); (b) the same as (a) but the foam was set under reduced atmospheric pressure of ~30 kPa (S_950_Vac); (c) slurry with low ceramic loading and foam setting standard conditions (1 atm, S_1000_LL); (d) cumulative pore size distribution of the precursors in (a-c); and (e) secondary electron image of the pore wall of S_950. ................................................................................ 90

Figure 5.11. Secondary electron images showing the effect of sintering temperature on cell wall characteristics of precursor: (a) 950 °C for 3h; (b) 1250 °C for 3h; and (c) 1450 °C for 1h. (d-f) Post-reduction (3.10 V; 910 °C for 45 h) microstructure of samples (a)-(c) respectively. Inset in each figure is a higher magnification image of the wall-struts (scale marker = 10 µm). Note that sample S_1250_HT in figure (e) was reduced at 1000 °C and hence exhibited smoothed surface. ........................................................................ 92

Figure 5.12. Comparison of the stress-strain behaviour in the current Ti foam (S_1150) to one produced via a commercial space-holder technique (78% porosity). 93
List of Tables

Table 2.1. Overview of metal foam processing techniques (44) ........................................ 19
Table 2.2. The operating voltage and final oxygen content in the case of three different
titania precursors (duration of electrolysis in all cases is 12 hr) (78) .................. 24
Table 3.1. Structural characteristics of pores and interconnects of titanium foams....... 49
Table 3.2. Experimental and model generated values of the main components* of the
permeability tensor ($\times 10^{-12}$ m$^2$) (Bracketed figures show the calculations
using higher resolution ESRF data) .............................................................. 49
Table 4.1. Density, porosity, ultrasonic velocities and elastic stiffness of pure and porous
titanium ........................................................................................................ 58
Table 5.1. Ingredients used in gel casting of titania foam ........................................... 78
Table 5.2. Details of specimens used in electrolysis ............................................... 79
1 Introduction

Metallic implants are the oldest of biomaterials. The earliest of metallic implants (vanadium steel) were bone fracture plates introduced in the early 1900s [1]. Since the 1970s, titanium alloys have been employed in spinal fusion, skeletal repair and dental implants [2-4]. Polymers, ceramics and their composites are other materials of choice; however, they are normally not preferred for load bearing applications due to their limited strength or poor fatigue properties [5]. Despite the availability of multiple materials for orthopaedic implant application, their fixation to the host bony tissues remains a problem [5]. Over 200,000 spine fusion procedures are carried out each year in USA, and failure due to the lack of solid body reunion is common (>10%) [6]. All scaffolds possess a less than ideal structure, morphology and properties, necessitating further improvements in current scaffold fabrication procedures, characterisation and materials.

A host of techniques are being developed to fabricate porous metallic materials [5]. The current industrial method of porous titanium scaffold fabrication is the space holder technique. The method involves mixing of appropriately sized metal and space holder (e.g. ammonium hydrogen carbonate) powders, pressing the mixture to form a green compact followed by a two step sintering process. The first sintering step removes the space holder. Actual sintering of the porous titanium skeleton is achieved during the second sintering step at much higher temperature [7]. As the technique relies on powder metallurgical processing of a very reactive metal such as titanium, it is costly and offers limited control of its porosity and interconnectivity which is achieved only by selecting a suitable space holder material. The resulting foam wall structure, though highly rough in nature, is good for living cell attachment. However, it results in downgrading its mechanical properties significantly [8].

Key structural macroscopic features deemed crucial for efficient functioning of a scaffold are its pore and interconnect sizes. These are directly correlated to the fluid transport and mechanical properties of the scaffold. Permeability is often taken as a measure of its fluid transport ability [9]. If optimised properly, the aforementioned characteristics will improve the implant durability by cell-proliferation, vascularisation and elimination of stress-shielding, leading to better osteo-integration [10].

The thesis has two-fold objectives. Firstly, to develop micro-computed tomography (μCT) based modelling tools to: (i) characterise the structural features such as pore size,
interconnect size and, pore aspect ratio / orientation and, (ii) model the permeability and mechanical properties employing finite element methods and relate to foams’ morphological characteristics. Most of the modelling results were validated against experimental measurements on commercial Ti foams at varying porosity levels. The mechanical behaviour of these foams is further studied using micromechanics and the semi-analytical models by Gibson and Ashby [11-12] (Chapters 3 and 4). Secondly, and more importantly, the thesis has the objective to develop a novel ceramic TiO₂ precursor route to produce metallic titanium foam by electrochemical reduction of the oxide precursor through the FFC Cambridge process [13]. The FFC Cambridge process is the solid state electrolytic reduction of TiO₂ that serves as a cathode, in a molten calcium chloride or its mixture with other chlorides. The foams were characterised, at each processing stage using scanning electron microscopy (SEM), x-ray diffraction (XRD) and µCT-based methods developed under the first set of objectives (Chapter 5). The ultimate objective of the research was to perfect a novel technique of ceramic foam precursor fabrication that results in a micro-/ macro-structure good for the subsequent electrochemical reduction kinetics as well as the mechanical and transport properties in the reduced foam.

A critical survey of the relevant work with regard to above stated objectives is presented in Chapter 2. The last chapters (#6 and #7) list the important conclusions and future outlook of the project.
2 Literature review
Ceramics, bioactive glasses, polymers and metallic alloys are materials being increasingly investigated in regenerative medicine. These biomaterials, in various forms and treatment conditions, are usually employed to replace or regenerate a variety of tissues such as skin, nerve, bone and cartilage [12]. Ideally a highly porous construct, called a “scaffold”, is employed as a precursor which gives way for: (1) colonisation; and (2) subsequent substitution by biological cells [14-15]. However, in applications involving bone, where the scaffold is required to bear load after implantation, metal-based non-resorbable scaffolds are preferred. The metallic scaffolds offer advantages of high strength over polymers and much superior toughness over the inherent brittleness of ceramics and bio-active glass-based scaffolds [5, 12]. Metallic alloys such as stainless steel (316L), Co-Cr alloys and titanium alloys (commercially pure Ti, Ti-6Al-4V as well as Ni-Ti) are the implant alloys currently being evaluated. Commercially pure titanium (CP-Ti) foam is one of the most promising materials being used in skeletal repair throughout the body [8].

This chapter is organised as follows:
- Section 2.1 surveys the basic titanium metallurgy;
- Section 2.2 examines the characteristic properties of Ti of particular relevance to biomedical applications;
- Section 2.3 and 2.4 present an overview of metal and ceramic foam (macroporous) fabrication techniques;
- Section 2.5 evaluates the feasibility of making titanium foam via a novel electrochemical reduction route;
- Section 2.6 reviews the method for foam characterisation; and finally,
- Section 2.7 introduces the methodologies to model mechanical properties of foam.

2.1 Titanium metallurgy and properties - the basics
Titanium is the fourth most abundant structural metal after aluminium, iron and magnesium [16]. However, it is not used as widely due to prohibitive cost. The Year End price for titanium in 2007 was 6-7 $/lb as against 1.2 $/lb for Al (U.S. GEOLOGICAL SURVEY MINERALS YEARBOOK—2007). The high cost of titanium production is due to high temperature batch processing of the commercial Kroll method of titanium extraction (Figure 2.1). The Kroll process involves multiple distillation steps and
handling of toxic chlorine gas and inert gases such as Ar and N₂. The metal produced by this method is in fine sponge form which is very reactive, posing the problem of explosion hazard in oxygen or air [17]. Titanium sponge is further alloyed with other alloying elements during multiple vacuum arc melting (VAR) yielding Ti slab priced anywhere between 8 $/lb and 20 $/lb depending on demand [18-19].

Titanium alloys are classified into four categories on the basis of their crystal structure. These are: (i) alpha (α), (ii) near α, (iii) α+beta (β) and (iv) β alloys. Alpha (e.g. CP-Ti) and β alloys exhibit hexagonal closed packed (hcp) and body centred cubic (bcc) crystal structure respectively. The (α+β) alloys possess a two-phase structure. Often times, a further classification is used to designate an intermediate alloy ‘near β’ [16]. Typical examples of (α+β) and β alloys are Ti6Al4V (α+β) and Ti8Mo8V2Fe3Al ((α); wt%).

The possibility of the existence of more than one phase in Ti alloys, means they will respond to a range of heat treatments in order to tailor their microstructure and hence their properties. The ability to induce the reversible martensitic transformation by stress, heat and magnetic field gives rise to a shape memory effect and super-elasticity. The range of properties that make titanium unique among structural metals is its excellent corrosion resistance, high specific strength and modulus. With roughly half as dense and strength equal to that of mild steel, Ti has approximately twice the specific strength of mild steel. Moreover, far superior corrosion resistance in virtually all environments.
ensures its use in diverse applications such as in structural, electronic, architectural, aesthetic, jewellery and biomedical fields.

2.2 Titanium as a bone implant material

Commercially pure titanium is one of the accepted materials of choice for implant applications since it has excellent mechanical properties, corrosion resistance and biological properties such as biocompatibility and osteo-conductivity [20-24]. The biocompatibility of a scaffold is its ability to stay in harmony with the neighbouring host tissues, whereas osteo-conductivity is the ability to grow bone tissues over the scaffold surface [5, 25]. However, implants made from monolithic Ti alloys with polymer and/or ceramic coatings have illustrated limited lifetimes due to interfacial instability with host tissues, mechanical mismatch of the elastic modulus, production of wear debris, and inadequate blood supply [21]. Recently, there have been many studies investigating the use of ceramic (e.g. hydroxyapatite and bioactive glass) and polymer materials to form open cell porous scaffolds into which, bone ingrowth and vascularisation can occur. However, these materials have a lower tensile strength and / or ductility than is desired [5] and can resorb more rapidly than bone ingrowth occurs [26]. There is therefore an ongoing search for a material with structure and properties similar to trabecular (cancellous) bone to be used as a scaffold upon which to grow bone either in vitro tissue culture or in vivo implantation [12, 27].

The three major mechanisms of bone resorption are: stress shielding, wear leading to inflammatory responses, and implant loosening [28]. Stress shielding refers to a condition wherein a stiff implant material, far more stiff than bone, takes up the majority of load keeping the surrounding bone tissues relatively free of mechanical stresses. It is well established that the bone tissues model themselves in response to the applied stress (see [11] p. 432), therefore the absence, or reduced magnitude, of the stress leads to bone loss [29].

A benefit of using metallic foams is that Young’s modulus can be fine tuned to match the modulus of the bone in order to avoid the stress-shielding effect of monolithic implants. The mechanical behaviour of a porous scaffold is dependent on the pore volume fraction and size distribution as this determines the size of the struts or walls between the pores which are bearing the load. Depending on the process used in making the foam, its micro-and macro-structure can be tailored to optimise the ‘biofactor’ (cells, genes and/or proteins), delivery and mechanical properties by incorporating well
connected pores [30]. Fatigue and fracture toughness of these scaffolds are also important for their in-vivo durability.

There is considerable uncertainty as to what is the optimum configuration on porosity, pore size and overall topology [5]. The general consensus is that a minimum of 100 μm interconnecting channel between the pores is required for effective bone ingrowth [31-33]. However, there are cases where bone ingrowth has been reported in pores as small as 50 μm. The upper bound on pore size is determined by the tendency of the scaffold to form fibrous tissues which is promoted for large pore size in excess of 500 μm [34-35] to 1 mm [5]. A study by Turner et al. [36] has found no dependence of the cell response on pore shape.

Fujibayashi et al. [37] recently reported that open cell titanium foams are inert. Further, titanium can illustrate good osteoinductive (i.e. ability to generate cells precursor to preosteoblastic cells [25]) behaviour at a non-osseous site by altering the surface oxide using a special chemical and thermal treatment. Scaffolds made from titanium are therefore a promising system for bone implants.

This is not to say that titanium scaffolds once implanted in the body are free of problems. Non-union of the implant with the host tissue, in combination with wear debris appears to be one of the most common causes of implant failures [6]. A histological evaluation of failed titanium mesh cages for posterior lumbar interbody fusion device in humans by Togawa et al. [38] found that all of the 11 cages studied, failed as a consequence of non-union with the host tissues. In a similar study, the same group [39] found that 70 of the threaded metallic cages (from 42 patients) with differing cage design, failed due to a variety of reasons such as failed fusion (23), cage malposition or migration (16), low-back pain (5), progressive spondylosis (2), nerve-root impingement (2), compression fracture at the fusion site (1) and infection (2). Some of the implants failed due to more than one reason. Nonetheless, spinal fusion procedure succeeds in as many as 90% of the cases [6].

Finally, the issue of alloying element cytotoxicity and allergic behaviour is being increasingly taken into consideration in developing novel titanium alloys. In this regard V is being substituted with other less-toxic β stabilising elements such as Fe in Ti6Al4V and efforts are being made to develop new Ni-less shape-memory titanium alloys to replace Ni-Ti. Vanadium has shown to have cytotoxicity. Nickel was found allergic to ever-increasing populations, especially in the female population [40].
2.3 Metal foam production

2.3.1 Overview
A variety of methods are available to produce metal foams [5, 41-42] although the processability of metals to fabricate in the form of a cellular structure is very limited [35, 43]. The difficulty in metal foam processing arises mainly due to: (i) their high strength often associated with high processing temperature and (ii) the very nature of porous materials, entails that conventional mechanical forming methods (exploiting their excellent plasticity) are ruled out. Highly reactive metals with high melting points, such as titanium, present added obstacles since they require a controlled atmosphere during most of the processing (melting and powder processing). Nine metal foam processing methods are, listed in Table 2.1 [44]. Achievable pore sizes and relative densities of foam characteristics of these methods are shown in Figure 2.2. Note that the porosity-relative density fields for each processing method are only typical values. Novel approaches, within each group, have expanded the capabilities of these methods to produce an ever-more diverse range of pore size and relative density. For biomedical applications, as noted in the previous section, pores are required to be in the range of 100-400 μm. Except for a very few, but equally critical, applications in orthopaedic surgery [5], highly open porosities are desired to allow bone ingrowth. From Figure 2.2 it is clear that most of the processing methods produce closed-cell morphologies and not all processes are suitable for Ti foam processing (Table 2.1).

2.3.2 Processing of titanium foam
The highly reactive and high melting point of titanium makes it virtually impracticable to employ a melt processing route for foam production. The commercial routes to make open-cell titanium foam are (i) the space holder technique [3, 7] and (ii) vapour phase or electrochemical deposition onto polymer foam [44]. The space holder method is a powder metallurgy (PM) route for foam production. Metal powders smaller than the space holder particles, are mixed with the latter, compacted and finally, sintered. This is normally operated as a two step process. Firstly, the fugitive space holder particles are removed at low temperature (200 °C) and secondly, the titanium powder is sintered at high temperature (1200 °C). The space holder technique has a major limitation in controlling the pore morphology and interconnect size, two of the structural features of a porous material influencing its suitability for biomedical applications. The cell wall
thickness is non-uniform which results in a significant downgrading of the foam’s mechanical properties.

**Table 2.1. Overview of metal foam processing techniques** [44].

<table>
<thead>
<tr>
<th>Foam making process</th>
<th>Processed metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Gas bubbling in molten metal</td>
<td>Al, Mg [45-46]</td>
</tr>
<tr>
<td>2. In-situ foaming by a foaming agent</td>
<td>Al [42, 47]</td>
</tr>
<tr>
<td>3. Foaming in mushy state of metal-foaming agent (TiH$_2$) compact</td>
<td>Al, Zn, Fe, Pb, Au [48]</td>
</tr>
<tr>
<td>4. Lost wax technique</td>
<td>Al, Mg, Ni-Cr, stainless steel, Cu [41, 49]</td>
</tr>
<tr>
<td>5. Vapour phase deposition or electrodeposition of metal onto a precursor</td>
<td>Ni, Ti [50-51]</td>
</tr>
<tr>
<td>6. Ar entrapment at high pressure and high temperature followed by its expansion at low pressure</td>
<td>Ti [20, 52]</td>
</tr>
<tr>
<td>7. Hollow sphere sintering</td>
<td>Ni, Co, Ni-Cr alloys [53-54]</td>
</tr>
<tr>
<td>8. Space holder technique</td>
<td>Al [55], Ti [7]</td>
</tr>
<tr>
<td>9. Gas dissolution in molten metal followed by its’ evolution during solidification</td>
<td>Cu [56], Ni [57], Al [58], Mg [59]</td>
</tr>
</tbody>
</table>

Metal deposition onto a polymer precursor and the subsequent removal of the polymer (by burning while sintering the deposited metal) results in pore and interconnect size

![Diagram](image-url)  

**Figure 2.2.** Metal foam production processes and achievable pore size and relative density (after [44]).
dictated by the precursor. However, it results in internally hollow cell struts, sometimes with additional defects, such as cracks, when removing the polymer. Recently, many other techniques have been reported for making porous titanium. One such technique is freeze casting, developed originally for ceramic processing. In this technique a slurry is prepared by placing metal powder in a non-dissolving liquid, frozen and freeze-dried to remove the carrier liquid. Freezing dendrites of the liquid force the metal powder into interdendritic spaces. On freeze-drying a negative replica of the frozen dendrites is obtained. High temperature sintering in an inert atmosphere is required to consolidate the foam. Chino and Dunand [60] fabricated a porous titanium structure with 57-65% porosity. They used water as a carrier fluid and applied directional solidification in the freezing process which yielded a highly anisotropic pore network with pore dimensions of 100 μm in diameter and several millimeters in length. It was unclear whether the pores were interconnected in 3 dimensions (3D). Yook et al. [61] used a camphene / TiH₂ based slurry to make porous titanium. Use of hydride as a precursor to titanium minimised the problems of oxygen contamination. Constant temperature freezing at 33 °C for 24 h resulted in isotropic pore morphology with a typical pore size of 100 μm. The porosity attained was 45 and 63% for a slurry loading of 15 and 25% respectively. The microstructure suggested a semi-closed-cell structure had been formed. Thus two of the parameters of the process, the solidification condition and the slurry loading, significantly control the final pore morphology. It is possible that pore size could be increased by altering the cooling rate and thus altering the inter-dendritic spacing.

Titanium foams have also been produced by controlled expansion of argon gas at high temperature [2]. The Ar gas is entrapped or locked in a can containing Ti powder at high pressure (3.3 atm) and temperature (890 °C). It is then consolidated using hot isostatic pressing (HIPing) to a pressure of 100 MPa at the same temperature for a period of 125 min. The foaming of the consolidated preform was achieved by heating a smaller specimen in an evacuated quartz tube at 960 °C for 24 h.

Combustion synthesis has been employed to make Ti alloy foam of composition 50Ni-50Ti (atomic percentage). In this process the alloy components react exothermically forming the final intermetallic compound. For 50Ni-50Ti alloy the reaction is [5]:

\[
\text{Ni} + \text{Ti} \rightarrow \text{NiTi} + 67 \text{kJmol}^{-1}
\]  

(2.1)

The steps involved in this process are mixing of powders, cold compaction, preheating in an inert atmosphere and triggering the reaction to foam it. Li et al. [62-63] have
produced a 50Ni-50Ti shape memory alloy with 54% porosity. The final porosity was determined by the initial porosity in the starting, un-foamed compact (40%), the presence of volatile / adsorbed species and the transient liquid phase. One advantage of the process is high purity of the final product due to very high reaction temperature and short reaction time. However, the need for an exothermic reaction between the powder ingredients seriously limits the compositional range of potential alloys.

Rapid prototyping (RP) has also been employed to make porous titanium foam. This technique is deemed capable of controlling the pore size, shape and the interconnectivity. Hence it is thought to have a good chance of providing the next major improvement in orthoprosthesis-scaffold design by matching mechanical properties to the host bone [5]. One major advantage of the technique of rapid prototyping lies in the fact that complex parts (in this case scaffolds) can be built directly from computer-generated models without the need for a tool or subsequent machining. It relies on layered manufacturing, i.e., the model to be built is represented as a stack of 2D slices with finite thickness and each layer / slice is built over the underlying layer, slice by slice thus creating the prototype of a computer model.

Two of the RP techniques used in making porous titanium are laser-engineered net shaping (LENS®) [64] and selective electron beam melting (SEBM) [65]. In the LENS® process, the interlayer fusion is achieved by laser beam, unlike the use of electron beam in the Arcam AB’s SEBM process. After fabricating a layer the laser head is moved up, a new layer of loose powder laid and fusion welded selectively to the base layer. This process is repeated until a complete structure is produced. Xue et al. [64] fabricated a range of porous microstructure with titanium powder via the LENS® process. The pore size ranged from 100 μm to 800 μm and porosity 17-58%. The study of in vitro response of these foams to human osteoblast cells (OCP1), suggested that a critical pore size of 200 μm or higher is required for bone ingrowth. However, the microstructure contained partially sintered titanium particles which might not be good for wear resistance.

In the SEBM process a 3500 W electron beam with a spot diameter of 0.1 to 0.4 mm was employed to achieve the inter-layer fusion. By varying the line offset and interlayer distance Heinl et al. [65] fabricated titanium foams with porosities of 25 to 60%. They used a minimum line offset of 0.5 mm. If it were the limit of the process, this could seriously restrict the minimum size of the achievable pore size and cell wall thickness.
Finally, there are techniques suitable for modifying the surface structure of titanium. These include plasma spraying, fibre sintering and titanium rod sintering etc, however, these techniques have rarely been used [37] for the production of bulk foam. These are closer to coating technologies used to make the titanium surface osteoconductive [66] by introducing surface porosity and surface coating with another bioactive material.

2.3.3 Metal foam from ceramics
There are some advantages in producing metal foams from a ceramic precursor. By integrating all of the processes, including high temperature reduction, involved in making the end product (i.e. foam), the process economics could become more attractive. Moreover, novel foam structures, characteristic of the ceramic precursor route may not be achievable, should the metal foam be fabricated from its elemental state. For example, Verdooren et al. [67-69] produced iron foams from naturally occurring mineral haematite and high-strength, closed-cell, ferrous-alloy foams. They produced iron oxide foams using a ceramic slurry that foamed and then set so as to result in precursor foams with uniform pore size,. These oxide precursor foams were subsequently reduced using a non-flammable Ar-4%H₂ mixture as a reductant at 1240 °C for 36 hours [67-68]. One of the aims of this project was to make porous titanium from its oxide precursor foam. Section 2.4 surveys the available methods to fabricate ceramic TiO₂ precursor foam. Section 2.5 reviews the novel electrochemical technique, the FFC Cambridge process [13], to reduce the precursor foam to metallic titanium foam, since there are no suitable reductants, except metals, to reduce it chemically.

2.4 Ceramic precursor foam fabrication
Porous TiO₂ structures find numerous applications such as in sorption media, photocatalysis, water and gas purification filters and sensors. Recently, it was deemed as a potential tissue-engineered, bone-implant material [70]. Depending on the application, various pore sizes, types and morphology are required in the foam to optimise efficiency. Several methods are used to produce ceramic foams as reviewed in [71-73]: for example, the polymeric sponge method, bubble generation or direct foaming (into an aqueous and organic-based slurries) method, chemical leaching, solid state sintering, sol-gel processing, and numerous other novel techniques such as combustion synthesis, expansion of supercritical fluid suspension, etc. These methods can produce either closed or open cellular foam in various shapes and sizes which are generally the characteristic of the method used in the production.
Figure 2.3 summarises the macroporous (pore diameter > 50 nm) ceramic foam processing techniques, and pore size and porosities characteristics which can be achieved with the major processing routes [73].

The direct foaming method generally involves preparation of suitable slurry and then triggering the foaming and the setting mechanism, simultaneously. It can produce closed or reticulated (open-cell) foam structures, though closed cell structures are more common [71]. Foam generation, stabilisation and its permanent setting mechanism give rise to numerous techniques within the direct foaming method. One of the techniques falling into the class of direct foaming methods is the gel casting technique [74]. In this method a water-based slurry contains a monomer, an optional cross linker, surfactants, initiator and catalyst. The foam stabilisation is accomplished with the aid of surfactants and a more permanent stability to the foam is realised by an in-situ polymerisation reaction. The gel casting technique produces closed cell morphology on foaming. However, drying and sintering of the foam result in rupture of the thin wall between the neighbouring pores resulting in highly interconnected foam. In this project the gel casting technique was used to make the precursor TiO₂ foam (Chapter 5).

![Graph showing the relationship between porosity and average pore size for various ceramic foam processing methods](image)

Figure 2.3. Overview of typical porosity and pore size obtainable from various ceramic foam (macroporous) processing methods [73].
2.5 The FFC Cambridge Process: a novel route to titanium metallurgy and processing

The FFC Cambridge process (named after its inventors Fray, Farthing and Chen at the Materials Department of Cambridge University, England) is the process of electrolytic reduction of titanium dioxide to metallic titanium in molten calcium chloride [13]. The process seems to offer advantages of speed and economics over the conventional pyrometallurgical routes (the Kroll / Hunter / Armstrong processes) of titanium metal production [75-76]. It lends itself for the production of other individual or mixed oxide powders of Al, B, Cr, Fe, Nd, V, [13, 77] Mo and W [77]. Recently, three kinds of cheap titania sources, have become available from industry; these are titania dust, meta-titanic acid and titania-rich slag which have all been reduced successfully to titanium [78]. The operating voltage and final oxygen content in the case of the three different precursors are recorded in Table 2.2. The energy efficiency (calculated as the ratio of the theoretical energy required to reduce a given amount of titanium dioxide divided by the energy consumed during actual experiment) was less than 40% in all the cases. The reduction process was found to be independent of the morphology and the crystal structure of the precursor. More importantly, metallic impurities (Al and Mn) in the titania-rich slag precursor were found to decrease (or were removed completely) at the completion of the reduction process. However, impurities, such as Si and Fe, remained virtually at the same level after the electrolysis.

Table 2.2. The operating voltage and final oxygen content in the case of three different titania precursors (duration of electrolysis in all cases is 12 hr) [78].

<table>
<thead>
<tr>
<th>Precursor type</th>
<th>Cell voltage (V)</th>
<th>Final oxygen content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titania dust</td>
<td>2.9-3.1</td>
<td>&lt;3000</td>
</tr>
<tr>
<td>Metatitanic acid</td>
<td>2.9-3.1</td>
<td>3000</td>
</tr>
<tr>
<td>Titania-rich slag</td>
<td>3.1</td>
<td>4500</td>
</tr>
</tbody>
</table>

A schematic of the FFC Cambridge process is shown in Figure 1.4. Pellets of TiO₂, or its mixture with other metal oxides, form the cathode, carbon / graphite is used as the anode whilst and molten calcium chloride serves as the electrolyte in the electrolysis cell. The reduction mechanism at the cathode is subject of much debate. According to Chen et al. [13] it proceeds via progressive oxygen de-ionisation of TiO₂ cathode. Ono and Suzuki [79], on the other hand, proposed a different mechanism, termed “secondary reduction” [80-81]. The latter is a two-step reduction process in which Ca²⁺ ions, present in the melt, are first reduced to calcium metal at the cathode; the calcium metal then reduces TiO₂ metallo-thermically to titanium.
Another approach used to reduce titanium dioxide using calcium is an electronically-mediated reaction (EMR) [82-84]. The molten calcium chloride solution serves as an oxygen / calcium ion conductor. Titanium dioxide, in the form of powder or perform, and a reductant (molten Ni-Ca alloy) are charged into a reactor, and are kept isolated, electronically, from each other. Like the cementation process, no external voltage is needed; however, an external circuit between the feed and the reductant must be closed. The standard Gibbs free energy change for the reaction (2.2) drives the reduction process [84]:

$$\text{TiO}_2(s) + 2 \text{Ca}(l) \rightarrow \text{Ti}(s) + 2 \text{CaO}(s); \Delta G^\circ = -240.60 \text{kJ} \quad (2.2)$$

In the study by Park et al. [84], the EMR ratio (defined as the ratio of actual charge passed through external circuit to reduce the TiO$_2$ to the theoretical charge required to reduce the given amount of TiO$_2$) was found to be very low even though the reduction proceeded almost to completion (purity was greater than 99.5%). The external circuit voltage (0.1 V) was found to be less than the theoretical electromotive force (0.62 V). One possible reason for the low EMR ratio might be the existence of electronic short circuiting in the molten salt due to presence of the metallic calcium.

The process seems attractive due to the fact that, unlike the FFC Cambridge process, it is not generating any greenhouse gases. Also, there was no electrolysis carried out which could result in some power saving; however, electrolysis of the CaO / CaCl$_2$ would be required to replenish the consumed calcium. Research on Ti extraction from its oxide is currently a very active area of research. A study conducted by EHK Technologies for US Department of Energy and Oak Ridge National Laboratory in 2004 identified more than a dozen emerging technologies for Ti extraction [18]. However, it is only the FFC Cambridge process that appears to lend itself easily for the reduction of TiO$_2$ precursor.

**Figure 2.4. Schematic of FFC Cambridge process.**
foam into metallic Ti foam retaining the shape of the precursor. Therefore in this project, 
the reduction of gel cast oxide foams via the FFC Cambridge process is investigated.

2.6 Foam / scaffold characterisation
Cellular materials (honeycombs or foams) can be characterised in many ways by a 
variety of characterisation techniques. In all cases, the objective is to determine the 
structural, physical and mechanical properties of the foam and to arrive at a link among 
these i.e. to establish structure-property correlations. Gibson and Ashby [11] have 
identified some of the useful features (e.g. material, density and nature of porosity etc) 
that, when determined, characterise the foam structurally. Based on the beam theory and 
dimensional arguments, they developed simple and widely used micromechanical 
models to predict the mechanical behaviour of foams. Many of the useful mechanical 
properties are easily expressed in terms of the structural parameters and the cell wall 
material properties. In biomedical applications however, an ideal scaffold is required to 
have a ‘hierarchical’ porous structure so as to result in strong osteo-integration with the 
host tissues. The term ‘hierarchical’ refers to the fact that features from the nanometre to 
the millimetre level will determine the in vitro and in vivo functioning of the scaffold. 
This coupled with the fact that actual scaffolds are often semi-closed cell structures 
requiring added structural parameters to describe their structures, has led to 
identification and subsequent quantification of additional microstructural characteristics. 
These include parameters such as interconnect size [85-86] and interconnectivity [85, 
87-88], surface area to volume ratio [88] and a measure of distance of an interior pore 
from the surface [85].

The common techniques used to characterise foam are presented in Figure 2.5. The 
following techniques used to characterise titanium foams in this project are described in 
the following subsections: immersion gravimetry, scanning electron microscopy (SEM) 
and X-ray tomography. Characterisation techniques for properties such as the 
permeability and compressive mechanical behaviour are described in Chapters 3 and 4 
respectively.

2.6.1 Immersion gravimetry
Immersion gravimetry may be used to determine the overall density (total porosity 
which can be calculated theoretically) and closed porosity and is based on Archimedes’ 
principle of buoyancy. The technique is particularly useful for making measurements on
irregular dimensioned specimens. Open cell foams, where the fluid can permeate into the interior region of the specimen, can be sealed using a resin or polymer.

### 2.6.2 Scanning electron microscopy (SEM)
SEM is a powerful 2D characterisation technique having a far higher resolution than optical imaging techniques. As it becomes clear that the features at scales from nm to mm level are important in influencing the bio-mechanical performance of the scaffold [30], SEM imaging may provide vital information regarding pore size, interconnects, and strut thickness. However, the technique requires sectioning of the samples and hence is destructive. Moreover, specimen sectioning can damage/deform the cell walls, thereby, compromising the result. It is worth noting that only superficial areas are imaged and careful sampling is required to derive any useful parameter [88]. Apart from structural characterisation, SEM, in combination with X-ray energy dispersive spectroscopy (X-EDS), is used to provide chemical microanalysis and phase identification.

### 2.6.3 Micro-computed tomography (µCT)
X-ray micro-computed tomography is a relatively new, non-destructive, 3D imaging tool that finds applications in many diverse fields such as medicine, geosciences, materials, quality control and the food industry. Since its invention in 1968 by Hounsfield [89] for medical imaging, it has seen tremendous development in terms of its capability and
application. There are numerous recent reviews detailing its diverse use and new developments in the field [89-94].

**Computed tomography: principle and types**

X-ray computed tomography relies on taking 2D radiographic images of an object from multiple directions and then reconstructing the 3D image by deriving the attenuation properties of the volume—represented by a set of regular, continuous cubic volume elements called voxels. Voxels are the 3D analogue of pixels. The attenuation characteristic (which is closely related to the local material density of the object) is computed at each voxel one slice at a time. The 3D volume is represented as a stack of 2D slices whose axis runs perpendicular to the beam direction.

Common elements of X-ray radiography are an X-ray source, the object to be imaged and a series of detectors which measure the transmitted X-ray intensity [91]. Industrial tomography units have a similar, but more sophisticated, configuration to make multiple radiographs from different radial directions of the object. CT scanners can be grouped into four categories based on their spatial resolution and the size of objects suitable for scanning [91]. These are conventional (resolution ~10^-3 m), high-resolution (~10^-4 m), ultra-high-resolution (~10^-5 m) and micro-computed (~10^-6 m) tomography, in order of achievable fine resolution. It is noted that there is a trade off between the size of the scanned object and the achievable resolution.

**Contrast, resolution and image artefacts**

The ability to identify various features of interest in an image depends strongly on the contrast and resolution of the imaging technique. Contrast is a measure of how well a feature is distinguishable from its surrounding background whereas the resolution is defined as the minimum distance between two identical points which can be perceived by the instrument as discrete objects. The two parameters are not completely independent of each other; a pair of high contrast features can be differentiated at much closer distance than the same-sized, low-contrast features [93]. Often improving one parameter adversely affects the other. For example, in the case of X-ray tomography the contrast between two features / phases increases as the energy of the incident radiation is reduced, i.e., as wavelength of X-ray is increased. However, resolution is inversely proportional to the wavelength of the radiation. Penetration depth of the radiation is also adversely affected by lower energy incident radiation. The spatial resolution of CT images is determined by the size and type of X-ray source and detector, the distance
between source, object, and detector, the imaging optics, the signal to noise ratio [93] and the ability to collimate the source [90].

Image artefacts are normally produced during image acquisition. Commonly occurring artefacts in CT scanning are beam hardening, ring artefacts, streaking and partial volume effects [91]. Beam hardening results in a reduction in intensity at the centre of an object compared to the intensity at the edge. It is caused by the preferential absorption of low intensity radiation before it traverses the whole specimen thickness. This is not the case along sections of specimen (e.g. region projecting as edge in the transmission) offering short path along beam direction. Thus, the interior region of the specimen does not see the soft radiation and appears darker (i.e. lower attenuating) when compared to the outer region of the sample. Obviously, this can be eliminated by the use of mono-chromatic radiation such as that from synchrotron generated X-ray radiation. In case of white radiation, its effect may be minimised by: (1) pre-hardening of the beam using an attenuating filter (normally aluminium, copper or brass); (2) using smaller samples; and (3) correction during image reconstruction [91].

The main source of the ring artefacts is defective pixels. The ring artefacts are more amenable to correction than beam hardening; they are easily identified on sinograms appearing as straight lines and hence are amenable to remediable correction. Streaking is caused when a highly attenuating feature / object is surrounded by relatively low-attenuating matrix. Bright rays emanate from the object into the matrix to very short distances giving it a star like appearance. Lastly, the partial volume effect is caused when a voxel is composed of more than one material in the sample. However, in the reconstructed data it has to be represented by a single value, an average of the attenuation from the whole voxel. Ironically, this effect is utilised in resolving features with sub-voxel accuracy [91].

In order to obtain a reconstructed image free of any artefacts the following procedure is suggested: (1) proper selection of scanning configuration; (2) use of a suitable X-ray source and detector; (3) careful calibration; and (4) attention to the origins and modes of artefact suppression [91].

* It is a 2D representation of the raw data such that each line contains a single set of detector readings for a view, and time progresses from top to bottom. This image is called a sinogram, as any single point in the scanned object corresponds to a sinusoidal curve.
2.7 Micromechanics of foams

The reliable mechanical behaviour of foams is always desirable for any application—even when they are used for non-structural purposes—to use them effectively and efficiently [11]. Monotonic compression testing of foams is the simplest and the most common of the mechanical tests performed to characterise the mechanical behaviour of foams. A typical compression stress-strain curve for elasto-plastic metal foam is shown in Figure 2.6. It shows three distinct regions: linear elasticity at low stresses; followed by a relatively long collapse plateau; and finally a densification region where the stress rises steeply. These are caused, respectively, by the elastic bending and stretching of the cell edge and face. The cell edge bending occurs by the formation of plastic hinges and the cell face stretching is a response to the compression of the solid itself once the strain exceeds a critical value causing opposing cell walls to touch each other.

The main macroscopic parameters controlling the mechanical behaviour of a porous scaffold are the pore volume fraction, nature of porosity, i.e. open or closed, and the cell wall material properties. Furthermore, the ‘complex micro-architecture’ [8] of the foams significantly influence its mechanical performance; this micro-architecture includes the presence of curves and wiggles, the closed pores in the cell wall, inhomogeneities arising from non-uniform pore size, and strut-thickness. The various approaches to model the mechanical behaviour of the foam are described in the following sections.

There are many modelling approaches to relate the mechanical properties of foams to

![Figure 2.6. Typical stress-strain curve for an elasto-plastic material such as a titanium foam under monotonic compression test.](image-url)
their microstructure. They can be grouped mainly in three categories; (1) those based on modelling the deformation of a unit cell (porous) and then extending the result to 3D foam, (most notably the Gibson and Ashby model) (2) those based on composite theories, and (3) finite element modelling. These approaches to model the mechanical behaviour of the foam are described below.

2.7.1 Gibson and Ashby model
The Gibson and Ashby micromechanical models [11], developed using the beam theory and the dimensional analysis, take the relative density, the nature of porosity and the cell wall material properties to predict the mechanical behaviour of cellular solids. The models assume uniformity in relative density, the absence of curves and wiggles along the cell wall, and the absence of any axial or shear displacement of cell edge. The model is based on a porous cubic element termed a cell. The relative density should be less than 30% of solid cell wall density to hold true to the underlying assumptions. Actual foam structures in real applications rarely conform to this requirement and hence predictions tend not to conform to the measurements. Nevertheless, the model is very useful in evaluating the various mechanical characteristics of the cellular solids and forms a qualitative measure for the deviation of the real foam structure from the ideal, which theoretically would yield the best properties. It is very frequently employed in the analysis of the mechanical behaviour of the foams because of its simplicity.

The model is based on a cubic unit cell shown in Figure 2.7. Neighbouring unit cells are joined in a staggered manner. The cell is characterised by its edge thickness, $t_e$, the cube length, $l$, and the face thickness, $t_f$. Cell edge bending and cell face stretching are assumed to be the main deformation mechanism in the elastic regime for open-and closed-cell† foams, respectively. For other more complex non-regular cell geometries, it is argued that a dimensionless form of the results would be applicable as long as the deformation mechanism is the same.

Consider the deformation of a cell (open cell foam) when a compressive force, $F$, is applied as shown in Figure 2.7(a). No shear displacement is allowed, and axial compression of the vertical struts will contribute little towards the displacement / strain compared to the displacement / strain contribution due to bending of the horizontal struts. The deflection, $\delta$, (due to the bending) will be proportional to $F l^3 / E_s I$, where $E_s$ is the

† If all the solid in the cell is confined into cell edges leaving the cell faces void, it is called open-cell foam. However, if the solid material is distributed between cell edges as well as cell faces, it is designated as closed-cell foam. Foams can be semi-open/closed.
modulus of the cell wall material and ‘I’ is the second moment of inertia of an individual edge related to cell dimension by:

\[ I \propto t_e^4 \]  

(2.3)

The cell relative density is:

\[ \frac{\rho}{\rho_s} \propto \left( \frac{t_e}{l} \right)^2 \]  

(2.4)

where \( \rho \) and \( \rho_s \) refer to the density of the foam and the solid material of the cell (edge/face). Writing the macroscopic stress, \( \sigma \), as proportional to \( \propto (F/l^2) \) and strain, \( \varepsilon \), as \( \propto (\delta/l) \), Equations 2.3 and 2.4 result in the elastic modulus, \( E \), of the foam as:

\[ \frac{E}{E_s} = C_1 \left( \frac{\rho}{\rho_s} \right)^2 \]  

(2.5)

where \( C_1 \) (\( C_1 \approx 1 \) [11]) is a constant catering for all of the geometrical constants of proportionality.

Likewise, the shear modulus, \( G \), and Poisson’s ratio, \( \nu \), of an open cell foam can be shown to be given by Equations 2.6 and 2.7 respectively [11]:

\[ \frac{G}{E_s} = C_2 \left( \frac{\rho}{\rho_s} \right)^2 \]  

(2.6)

and
\[ \nu = \frac{C_2}{2C_2} - 1 = C_3 \]  
(2.7)

where \( C_2 \) and \( C_3 \) are constants (\( C_2 \approx 3/8, C_3 \approx 1/3 \) [11]). The corresponding equations for Young’s modulus, shear modulus and Poisson’s ratio for a closed cell foam, incorporating cell face stretching in addition to cell edge bending, are:

\[ \frac{E}{E_s} = \phi^2 \left( \frac{\rho}{\rho_s} \right)^2 + (1 - \phi) \frac{\rho}{\rho_s} \]  
(2.8)

where \( \phi \) is the fraction of material concentrated in cell edge.

Likewise, the shear modulus, \( G \), and Poisson’s ratio, \( \nu \), of an open-cell foam can be shown to be given by Equations 2.9 and 2.10 respectively [11]:

\[ \frac{G}{E_s} = \frac{3}{8} \left\{ \phi^2 \left( \frac{\rho}{\rho_s} \right)^2 + (1 - \phi) \frac{\rho}{\rho_s} \right\} \]  
(2.9)

and

\[ \nu = \frac{1}{3} \]  
(2.10)

Plastic collapse of the metal foam occurs when the moment exerted by the force through the cell edge exceeds the fully plastic moment of the cell edge. The plastic collapse strength of a foam, following similar arguments as above, can be shown to equal:

\[ \frac{\sigma_{pl}}{\sigma_{ys}} \approx 0.3 \left( \frac{\rho}{\rho_s} \right)^{3/2} \]  
.....(open - cell foam)  
(2.11)

and

\[ \frac{\sigma_{pl}}{\sigma_{ys}} \approx 0.3 \left( \phi \frac{\rho}{\rho_s} \right)^{3/2} + 0.4(1 - \phi) \frac{\rho}{\rho_s} \]  
.....(closed - cell foam)  
(2.12)

where \( \sigma_{pl} \) and \( \sigma_{ys} \) are the plastic collapse strength of the foam and the yield strength of the cell wall material respectively.

It should be pointed out that when the density is not too small and the cell corner accounts for a significant amount of material, a density correction applies in the above equations. Also, in the case of a closed cell having a fluid in the void that can not escape during the deformation, there is a contribution to the modulus and strength values of the foam arising from the fluid pressure [11].
2.7.2 Models from composite theories

Porous materials represent an extreme in composite mechanics; foams are composite materials with infinite phase contrast. Bounds in their elastic moduli are therefore far apart, reflecting a maximised influence of the microstructure on the mechanical response of the material. Metal foams are of additional interest because the ductility of metals also makes these materials an attractive test bench of the non-linear deformation theory [55]. This allows the micromechanical models developed for modelling the elastic and elasto-plastic behaviour of composites, to be extended to model the mechanics of metal foams by considering the void space as a second phase with zero modulus. The most notable of composite theories used in modelling foam [8, 55] are based on the Eshelby theory [95-96] of internal stress around an ellipsoidal inclusion. One of the approaches to model elasto-plastic deformation behaviour of foam is based on extension of continuum micromechanics theory of solids to porous materials and capitalizing on the Eshelby theory.

In continuum micromechanics of porous materials, the material is understood as a macro-homogeneous, but micro-heterogeneous body filling a REV with characteristic length $l_{REV}$. $l_{REV} \gg d$, $d$ standing for the characteristic length of inhomogeneities within the REV, and $l_{REV} \ll L$, $L$ standing for the characteristic lengths of geometry or loading of a structure built up by the material defined on the REV. In general, the microstructure within each REV is so complicated that it cannot be described in complete detail. Therefore, quasi-homogeneous subdomains with known physical quantities (such as volume fractions, elastic or strength properties) are reasonably chosen. They are called material phases. The ‘homogenised’ mechanical behaviour of the overall material, i.e., the relation between homogeneous deformations acting on the boundary of the REV and resulting (average) stresses, or the ultimate stresses sustainable by the REV, can then be estimated from the mechanical behaviour of the aforementioned homogeneous phases (representing the inhomogeneities within the REV), their volume fractions within the REV, their characteristic shapes, and their interactions. Consider an REV of titanium-based biomaterial with characteristic length $l_{REV} = 1$ mm and with volume $V_{REV}$, hosting spherical, empty pores with characteristic size $d = 350-400 \mu m$ $\ll l_{REV}$ with volume $V_{por}$ and volume fraction $\phi$ ($= V_{por}/V_{REV}$). These pores are embedded in a solid matrix with volume $V_S$ and volume fraction $(1 - \phi)$ (see Figure 2.8).

In order to account for the connectivity of pores, a differential homogenisation scheme was employed, yielding the (homogenised) properties of the porous titanium
biomaterials, as functions of the titanium elasticity and the porosity (see [97-100] for details):

\[ g_1 = \frac{(1 + 4 \mu_S / 3 k_S)(\mu_{\text{hom}} / \mu_S)^3}{2 - (1 - 4 \mu_S / 3 k_S)(\mu_{\text{hom}} / \mu_S)^{3/5}} - (1 - \varphi)^6 = 0 \]

\[ g_2 = \frac{\mu_{\text{hom}}}{\mu_S} - \frac{(1 - 4 \mu_{\text{hom}} / k_{\text{hom}})^{5/3}}{(1 - 4 \mu_S / k_S)^{5/3}} = 0 \]  

where \( k_S (= C_{1111} - 4/3 C_{1212}) \) is the bulk modulus and \( \mu_S \) is the shear modulus of the pure titanium (as determined by the ultrasonic experiments described in the Appendix A and listed in Table 4.1); \( k_{\text{hom}} \) and \( \mu_{\text{hom}} \) are the homogenised bulk and shear modulus of the porous titanium biomaterial.

It has been recently shown that functions like Equation 2.13 give access to measures for stress and strain peaks in the microstructures (called higher order averages), which would lead to plasticity and failure of the overall material. For metallic materials, the spatial average over the squares of the equivalent deviatoric strains is an appropriate measure for microstrain peaks leading to microplasticity. Their combination with a von Mises criterion or the microstresses leads to the following relation between the pure shear stress at yield of pure titanium, \( \tau_y \), and the overall uniaxial strength of the porous titanium biomaterial, denoted as \( \Sigma'_{\text{pred}} \) (see [97-100] for details):

\[ \Sigma'_{\text{pred}} \]
\[
\begin{align*}
\sum_{\text{pred}}^y &= \left[ 9(2\nu_{\text{hom}} - 1)^2 \frac{\partial k_{\text{hom}}}{\partial \mu_S} + 4(2\nu_{\text{hom}} + 1)^2 \frac{\partial \mu_{\text{hom}}}{\partial \mu_S} \right]^{1/2} (1 - \varphi)^{1/2} E_{\text{hom}}^y \\sum \left( \frac{2\nu_{\text{hom}} - 1}{2\nu_{\text{hom}} + 1} \right)^{2} \frac{\partial \mu_{\text{hom}}}{\partial \mu_S} \mu_S \right. \\
&+ 3(2\nu_{\text{hom}} - 1)^2 \frac{\partial k_{\text{hom}}}{\partial \mu_S} + 4(2\nu_{\text{hom}} + 1)^2 \frac{\partial \mu_{\text{hom}}}{\partial \mu_S} \mu_S \\
\end{align*}
\] 

(2.14)

where \( E_{\text{hom}} = 9 k_{\text{hom}} \mu_{\text{hom}}/(3k_{\text{hom}} + \mu_{\text{hom}}) \) is Young’s modulus of the homogenised porous titanium biomaterial, and similarly \( \nu_{\text{hom}} \) is its Poisson’s ratio.

In this thesis, the continuum micromechanics-based approach has also been used to model the mechanical behaviour of Ti foam (see Chapter 4).

### 2.7.3 Finite element modelling

The Gibson and Ashby micromechanical models and the models from composite theories tend to simplify the real microstructure of foam. However, direct finite element modelling (DFEM) is based on the real 3D structure of the foam and makes no assumption about its structure and hence tends to be more accurate. However, it comes at a cost of the time-consuming tasks of characterising the internal, complex geometry of the foam and the subsequent analysis (employing commercially available FEM packages). This methodology is increasingly being used by various groups who have investigated the compressive damage behaviour in bone [101], titanium [8], aluminium [102-104] and polymer [105] foams. In this thesis the DFEM methodology was employed to model the monotonic compression behaviour of foams (Chapter 4). As the 3D meshed model is representative of the real foam structure derived from the \( \mu \)CT data, the FEM model is expected to yield accurate results.

\[ \text{‡ The micromechanics model development and its implementation was carried out by Professor C. Hellmich (TU Wein, Austria). The results of micromechanics modelling of commercial titanium foam were further discussed further in Chapter 4.} \]
3 Characterisation of titanium foam for biomedical applications – structure and permeability*

In this chapter, the pore and interconnect size of a commercial titanium foam were determined using 3D micro-computed tomography (μCT) based techniques. A computational fluid dynamic procedure was developed to simulate the permeability. The permeability calculations were validated against experimental measurement. Characterisation (including modelling) of mechanical properties will be the subject of the next chapter.

3.1 Introduction

The advantages of using Ti scaffold have been discussed in Section 2.2. With regard to porous scaffold, it is generally agreed that the minimum pore and interconnect size required for effective bone ingrowth is 100 μm [5]. There is therefore a need for effective methods to quantify the size distribution of pores and interconnects. The size of interconnects also affects the flow properties, which are important for cell seeding and nutrient delivery for in vitro / in vivo bone ingrowth and vascularisation [106-108]. Permeability is one measurement by which the flow properties (crucial to the in-vivo performance of a scaffold as a bone implant) may be measured. Permeability depends upon the scaffold’s internal topology. If the topology can be quantified, the Navier-Stokes equations can be used to compute the permeability [109]. It is also possible to calculate the permeability analytically as a function of the material’s porosity, surface or interconnect size depending on the simplifying assumptions used [110-111].

The precise 3D quantification and characterisation of Ti foams [85-87] has received only limited attention despite the importance of the size and morphology of both pores and interconnects in influencing biological and mechanical performance of these foams as scaffold. In an evaluation of the biological performance of scaffolds, conventional techniques based on 2D image analysis and mercury intrusion porosimetry can be insufficient to estimate permeability and pore size. Shen et al. [112] performed 2D image analysis on Ti foams and then transferred the results into 3D models for the purpose of simulating foaming and mechanical properties. Although they performed a 3D tomographic scan of an experimental foam, they compared the results only qualitatively rather than quantitatively. Recently, Otsuki et al. [85] have presented the

*Note, portions of this chapter have also been published in Singh R, Lee PD, Lindley TC, Dashwood RJ, Ferrie E, Imwinkelried T. Acta Biomater 2009;5:477-487.
most detailed analysis of a Ti foam to date; they used image analysis of \( \mu \)CT data to calculate the path length from pores on the interior to the outer surfaces (using a method based on percolation theories [113] developed for analysing rock samples). Using iterative dilation, they ranked the pores by the minimum interconnect size along the connecting path. However, the individual quantification of pore and interconnect size and morphology was not determined, hence their distributions can not be plotted. Although it has not been applied to Ti foams, Atwood et al. developed an algorithm that detected individual pores and interconnects and applied it successfully to bioactive glass foams [86]. This technique uses a watershed algorithm [114] and a custom distance map to first isolate and label individual pores, followed by the subsequent identification of the areas connecting them. In the field of porous rock characterisation, Lindquist et al. [115] developed a technique based on medial surface/axis thinning algorithms [116] to perform similar characterisation of individual pores in open cell structures.

In this chapter, a state of the art \( \mu \)CT unit was used to characterise the structure of porous titanium scaffolds at three porosity levels, namely, 51, 65 and 78%. Image analysis techniques [86] were then applied to derive size distributions of pores and interconnects. A new method to compare the size distributions of interconnects in different materials is presented. The permeability of titanium fusion implant scaffolds are derived via simulations from the \( \mu \)CT data for the first time, and validated against experimental measurements, as well as analytic approximations. The characterisation of both the structure and permeability is then compared to the properties of bone and those required for an ideal scaffold.

### 3.2 Materials and methods

#### 3.2.1 Titanium foam preparation

The open cell titanium foams were supplied by Synthes (GmbH, Switzerland). These were produced using powder metallurgy combined with the space holder method [3, 23-24]. The titanium powder used was Grade 4 commercially pure (CP) titanium having a log-normal particle size distribution with an average \( d_{50} \)-value of 25 to 40 \( \mu m \). Ammonium hydrogen carbonate (\( \text{NH}_4\text{HCO}_3 \)) was used as the space holder material, sieved to obtain the desired particle size distribution (425 and 710 \( \mu m \) sieves).

The titanium powder was then mixed with the space holder substance and subsequently cold-isostatic pressed at 300 MPa into blocks measuring approximately 70x45x50 mm. This green compact was then held at 95°C for 12 h in a convection oven to allow
complete gaseous decomposition of the ammonium hydrogen carbonate. The foams were then sintered at 1300°C for 3 h under argon atmosphere [117].

Differing amounts of space-holder substance were used to obtain three different porosity levels, namely 51, 65 and 78% (designated as samples P51, P65 and P78 respectively).

3.2.2 Scanning electron microscopy (SEM)
Samples of each type of foam were examined in the SEM (5610LV, JEOL) in order to characterise the structural features at both the macro and micro scales. The distribution and morphology of both the pores and the cell walls were studied in detail. The SEM analysis was performed to reveal the surface roughness and the sub-surface architecture within the wall which is at a smaller scale than which could be resolved from the μCT data.

3.2.3 μCT and image analysis
Cylindrical specimens 5 mm in diameter and 10 mm in length were produced using electric discharge machining (EDM), with the centre-line axis both parallel and perpendicular to the compaction direction. These cylinders were then scanned using a commercial μCT unit (Phoenix-X-ray Systems and Services GmbH) at 5.5 μm (P51 and P65) and 5.75 μm (P78) voxel resolutions. Reconstructed images, consisting of 1024×1024×512 voxels, were collected from each sample and were processed and analysed using commercial image analysis software (Amira 4.0 and VG-Studio MAX 1.2). Algorithms developed in-house (described elsewhere [27, 86]) were applied to quantify the individual pore size in an open-cell foam and the size of the interconnects between them.

3.2.4 Permeability measurement
The main components of the permeability tensor were experimentally measured for each sample assuming the flow was governed by the Dupuit-Forchheimer equation. The law relates the superficial (or ‘Darcian’) velocity $\vec{v}$, to the pressure gradient ($\partial P/\partial x$):

$$-\frac{\partial P}{\partial x} = \left(\frac{\mu}{k_1}\right)\vec{v} + \left(\frac{\rho}{k_2}\right)|\vec{v}|^2$$  \hspace{1cm} (3.1)

where $\mu$ and $\rho$ are the dynamic viscosity and the density of the fluid and, $k_1$ and $k_2$ are the Darcian and non-Darcian permeabilities of the porous media [118].

Permeability experiments were performed using cylindrical specimens 16 mm in diameter and 8 mm in height for samples of foams P51, P65 and P78, derived for all
major directions (x, y and z; z always being in the compaction direction). The schematic of the experimental set-up designed to carry out the measurement is shown in Figure 3.1. The curved surface of the cylindrical specimen was sealed by inserting it into a heat-shrinkable tube to give it a close fit. The rubber tube was further secured tightly to the specimen by an outer cylindrical steel strap. The other end of the heat shrinkable tube was fixed onto a polyvinyl chloride (PVC) pipe. The PVC pipe was held straight and received a fixed flow rate of demineralised water. The end of the tube with the specimen served as outlet for the fluid (demineralised water) while the inlet at the other end of the tube, was connected to a water supply line. The fluid pressure and the flow rate were controlled by the degree of tap opening. The hydrostatic head at the inlet served as measure of inlet pressure. The outlet pressure was assumed to be one atmosphere. The flow rate was measured using a graduated cylinder at the outlet, readings being recorded at regular intervals until the flow stabilised. Steady-state flow rate as a function of applied pressure differential was measured and least-square fitted to Equation 3.1 to derive the Darcian permeability.

It is clear that the range of experimental pressure difference applied resulted in non-Darcian- i.e. non-linear-flow (Figure 3.2). It is for this reason that the experimental values of permeability were derived from the Dupuit-Forchheimer equation (instead of just using Darcy’s Law; see Appendix B), because it corrected for the non-linearity.

3.2.5 Permeability simulation

The principal components of the permeability tensor were calculated from the µCT datasets by first discretising the volume into meshes and then solving the Navier-Stokes equations [119] using a commercial, computational fluid dynamics (CFD) package. The

![Figure 3.1 Schematic of permeability measurement set-up. Specimen diameter dictated the choice for other components.](Image 237x91 to 386x286)
steps involved in these simulations were:

1. Importing the raw data into a filtering and segmentation package (ScanIP, Simpleware Ltd., Exeter, United Kingdom) and then:
   i. Applying a 3x3x3 median filter to reduce noise.
   ii. A flood-fill thresholding algorithm [114] was then applied to distinguish the interconnected porosity from the wall.
   iii. The following boundary conditions were applied (see Figure 3.3): a fixed velocity at the inlet ($V_x = 10^{-4}$ ms$^{-1}$, $V_y = V_z = 0$ ms$^{-1}$); a pressure outlet; and no-

![Figure 3.3](image)

Figure 3.3. Schematic of the procedure to simulate the flow within a scaffold, leading to the derivation of permeability. The model has a velocity inlet (AB; $x = 0$) and a pressure outlet (CD; $x = L_{REV}$). The rest of the solid fluid interface was modelled as wall with no slip condition. The mass flux across the two dashed lines and pressure gradient calculated under steady-state conditions are used to derive the permeability using Darcy’s law (Eq. (3.1) devoid of the last term).
flow \( (V_n = 0 \text{ ms}^{-1}) \) along all other faces. Note \( x \) is the direction in which permeability is calculated and \( V_n \) is the velocity component normal to the face.

iv. A fully fluid buffer zone (approximately 60 µm thick) was added to the downstream surface of the foam to allow application of a pressure outlet boundary condition.

2. The fluid (pore) regions were then meshed using ScanFE (Simpleware Ltd., Exeter, United Kingdom) and exported in the correct format for the CFD solver.

3. The mesh was then imported into FLUENT (ANSYS, Inc., PA, U.S.A.) and solved assuming steady state flow using the boundary conditions listed above and fluid properties defined such that the interstitial Reynolds number \[118\] had a very low value (<0.001).

4. The pressure gradient \( (\Delta P/L, \text{ where } L \text{ is the thickness of the region bounded by the two dashed line in Figure 3.3 and } \Delta P \text{ is the pressure difference across it}) \) was calculated as the slope of average pressure on planes normal to \( x \) (i.e. the flow direction) vs. \( x \). A typical, calculated, pressure gradient in the flow direction is shown in Figure 3.4.

5. The Darcian permeability was calculated employing Darcy’s law (Equation 3.1 devoid of the last term on the right hand side) in the central region of thickness where the flow is stable; this region is shown in Figure 3.4, where a region, approximately 0.4 mm thick was excluded for both the inlet and the outlet sides to

![Figure 3.4](image-url)  
*Figure 3.4. Variation of pressure in flow direction inside the sample with 65% porosity. The pressure gradient was calculated from the inner region of the sample (bounded by the dotted lines).*
calculate the gradient. Further discussion about the entry/exit effect leading to non-linear behaviour in the vicinity of inlet and outlet is discussed in Appendix B.

The CFD simulation was performed on successively larger and larger ‘child’ volumes (i.e. a sub-region extracted from the full 3D reconstructed µCT dataset) until a representative elementary volume (REV) was reached. An REV is defined as the smallest sized element / model that manifest the macroscopic properties of the bulk foam. This is represented as the length, $L_{REV}$, in Figure 3.3.

The permeability of each sample was also calculated using the Kozeny-Carman equation [120]:

$$K = \frac{(1 - g_s)^3}{5S_s^2}$$  \hspace{1cm} (3.2)

where $g_s$ is the volume fraction of solid and $S_s$ is the solid-pore interfacial area per unit volume (measured from the µCT data).

### 3.2.6 Sources of errors in the permeability simulation

Deviation between the measured and the modelled values of permeability can arise from:

1. Insufficient voxel resolution in the µCT data to resolve the surface roughness;
2. Threshold value selection during µCT data processing; and
3. Numerical simulation errors (e.g. insufficient discretisation or domain size).

With regard to point 1, the problem of resolution is evident when comparing that of the high resolution SEM micrographs of wall roughness (e.g. Figure 3.5) to the typical modelled surface (e.g. Figure 3.6). The voxel size of the µCT is limited to approximately 5 µm by the field of view required to obtain a sufficiently large representative volume. With a voxel size of 5 µm, only features greater than 10 µm are resolved, whilst the SEM micrograph shows features smaller than this. The permeability is inversely dependent on the surface area (Equation 3.2); therefore, the simulated permeabilities are expected to overestimate the ease of flow (i.e. predict a permeability that is higher than that measured). Equation 3.2 predicts that a 10% underestimate in the roughness (decrease in $S_s$) would increase the predicted permeability by ~20%.

With regard to point 2, because the thresholding of the µCT data uses the average value within a voxel, the thin walls around the interconnects may be classified as a pore rather than a strut. This misclassification would lead to an overestimation of interconnect size and hence a larger predicted permeability.
With regard to point 3, different levels of resampling (element size) were tested. It was found that the predicted permeability for the mesh size used, was less than 25% larger than the finest element sizes tested, illustrating the importance of surface roughness. Note that this was in addition to the REV studies to ensure that the domain simulated was representative of the macroscopic foam properties (see Section 3.4.3).

3.3 Results
An orthographic view of a thresholded, child volume of the 65% porous sample is given in Figure 3.6, showing the typical structure of this foam. This figure shows that the material has a highly-interconnected, porous structure, but it is difficult to quantify the

![Figure 3.5. SEM micrographs showing wall substructure for bulk porosity of: (a) 51%, (b) 65% and (c) 78%. The darkest regions in all figures show interconnects with the adjoining pore.](image)
pore sizes and morphologies. The wall thickness also varies; with potentially isolated, small pores in the thickest sections.

Using in-house algorithms (described in the methods section), each individual pore in this open-cell foam was isolated and quantified, together with their interconnecting flow regions. Three dimensional μCT views of the scaffold surrounding typical pores for each of the three samples (P51, P65 and P78) are shown in Figure 3.7(a-c). The renderings of the pore in the centre of each region and the interconnecting flow passages (Figure 3.7(d-f)) are also shown.

Figure 3.8 shows the pore-volume-fraction distribution as a function of diameter (on a log scale). The equivalent pore diameter is defined as the diameter of a sphere whose volume equals the pore volume (disregarding its shape).

As a first approximation, the interconnect size was calculated as the diagonal of an excrived 3D box. However, this method tends to overestimate the interconnect diameter. In order to derive a more accurate measure of interconnect diameter a multiplicative correction factor of 1.22 was derived following the procedure outlined by Jones et al. [121] and applied to the interconnect results presented here.

Figure 3.9 shows the interconnect-area-fraction distribution as a function of corrected interconnect diameter (on a log scale). The microstructural characteristics of pores and interconnects and the associated scatter are given in Table 3.1.

![Image](image.png)

Figure 3.6. Portion of μCT image of sample P65 showing interconnected porosity.
SEM micrographs (Figure 3.5) of the samples revealed that there were two populations of porosity present: (i) microporosity less than 10 \( \mu \text{m} \) in diameter within the cell walls and (ii) inter-strut macroporosity over 100 \( \mu \text{m} \) in diameter. The percentage of closed

Figure 3.7. The 3D \( \mu \text{CT} \) images of a single pore (child volume) of (a) P51, (b) P65 and (c) P78, and images of the pore and interconnects obtained using 3D image analysis of (d) P51, (e) P65 and (f) P78.

Figure 3.8. Pore-volume fraction as a function of porosity.
porosity within the struts was analysed using Archimedes method (Table 3.1). The amount of closed microporosity within the struts was less than 1% in all samples, and hence was considered negligibly small when compared to the macroporosity. The permeability values predicted from the computational fluid dynamics simulations for various representative elementary volume (REV) are shown in Figure 3.10 for
sample P65. A comparison of the experimental versus simulation-predicted results for the main components of the permeability tensor is plotted in Figure 3.11. Table 3.2 gives the measured and calculated permeability tensor components (main) and their average values (in brackets) for all specimens.

### 3.4 Discussion

Two of the key microstructural features required in the characterisation of a foam or scaffold are the pore and interconnect size. These are shown qualitatively in the μCT images of the scaffold surrounding typical pores in Figure 3.7(a-c), as well as in the SEM images in Figure 3.5. Many qualitative trends are apparent from these two figures. Firstly, although there is a clear reduction in the wall thickness with increasing percentage porosity, the pore size does not show any clear trends. Since the pore size is governed by the size distribution of the space holder particles, consistency of pore size would be expected.

Secondly, the number of interconnects (the window between neighbouring pores) appears to increase significantly with increasing foam porosity, as does the size of the interconnects. These trends are also qualitatively supported when examining the renderings of the pores and their interconnecting flow passages in Figure 3.7(d-f). The first trend, the increase in coverage, can be quantified by the ratio of the surface area of
Table 3.1. Structural characteristics of pores and interconnects of titanium foams.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Total Porosity (%)</th>
<th>Closed Porosity (%)</th>
<th>Number Counted</th>
<th>Mode, (µm)</th>
<th>Median, (µm)</th>
<th>Mean, (µm)</th>
<th>Mean–σ (µm)</th>
<th>Mean+σ (µm)</th>
<th>Number Counted</th>
<th>Mode, (µm)</th>
<th>Median, (µm)</th>
<th>Mean, (µm)</th>
<th>Mean–σ (µm)</th>
<th>Mean+σ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P51</td>
<td>51</td>
<td>0.99</td>
<td>112</td>
<td>589</td>
<td>453</td>
<td>336</td>
<td>211</td>
<td>536</td>
<td>369</td>
<td>288</td>
<td>98</td>
<td>95</td>
<td>43</td>
<td>207</td>
</tr>
<tr>
<td>P65</td>
<td>65</td>
<td>0.32</td>
<td>172</td>
<td>438</td>
<td>361</td>
<td>312</td>
<td>197</td>
<td>496</td>
<td>393</td>
<td>254</td>
<td>111</td>
<td>105</td>
<td>44</td>
<td>249</td>
</tr>
<tr>
<td>P78</td>
<td>78</td>
<td>0.08</td>
<td>202</td>
<td>488</td>
<td>345</td>
<td>334</td>
<td>241</td>
<td>463</td>
<td>388</td>
<td>263</td>
<td>61</td>
<td>70</td>
<td>34</td>
<td>145</td>
</tr>
</tbody>
</table>

Table 3.2. Experimental and model generated values of the main components* of the permeability tensor (×10⁻¹² m²) (Bracketed figures show the calculations using higher resolution ESRF data).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Direction</th>
<th>Experimental (Darcys)</th>
<th>CFD Predictions (Darcys)</th>
<th>Kozeny-Carman (Darcys)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P51</td>
<td>Average</td>
<td>6.9±0.3</td>
<td>20±7</td>
<td>214±18</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>7.4±0.4</td>
<td>23±5 (10.9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>y</td>
<td>7.9±0.4</td>
<td>18±10 (9.9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>z</td>
<td>5.3±0.3</td>
<td>18±7 (4.9)</td>
<td></td>
</tr>
<tr>
<td>P65</td>
<td>Average</td>
<td>126±6.3</td>
<td>137±45</td>
<td>305±17</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>117±5.9</td>
<td>132±50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>y</td>
<td>163±8.2</td>
<td>163±36</td>
<td></td>
</tr>
<tr>
<td></td>
<td>z</td>
<td>97.6±4.9</td>
<td>117±50</td>
<td></td>
</tr>
<tr>
<td>P78</td>
<td>Average</td>
<td>470±23</td>
<td>624±201</td>
<td>462±23</td>
</tr>
<tr>
<td></td>
<td>x</td>
<td>679±34</td>
<td>647±211</td>
<td></td>
</tr>
<tr>
<td></td>
<td>y</td>
<td>389±19</td>
<td>693±214</td>
<td></td>
</tr>
<tr>
<td></td>
<td>z</td>
<td>341±17</td>
<td>531±179</td>
<td></td>
</tr>
</tbody>
</table>

*‘z’ being always in the compaction direction.
interconnects on any pore divided by the surface area of the pore (including regions touching both struts and interconnects). This ratio increases from 12.8% coverage for sample P51 to 34.7% for P65 and 61.7% for P78. For the foam with 78% porosity, the amount of interconnect area has increased by almost 5 times from the foam with 51% porosity. This suggests that flow in the high porosity foam will be significantly easier. The second trend, the increase in the size of the interconnects, will be shown later to be a minor quantitative effect. These quantitative algorithms are relatively straightforward if the pores are closed. However, in the case of highly interconnected pores, the use of more complicated mathematical-morphological operators is required to classify the porous areas into pore and interconnect. More details about the technique can be found in references [27, 86], with the results of this analysis discussed below.

3.4.1 Pore size distribution
It has been reported that the pore size in a scaffold for the range of 200-500 µm is the optimum size for the functioning of osteoblasts [22]. In this study, the modal pore size was found to be greater than 300 µm in all the samples, ranging from 438 to 589 µm (see Figure 3.8 and Table 3.1). No obvious trend was apparent between the pore size and total porosity. As the space holder material and the sieving fraction used in making all the samples was the same, the average pore size remained almost constant in all the foams, irrespective of their level of porosity. This illustrates the ability of the space-holder technique of Ti-foam production to control the size, and possibly morphology, of the pores by controlling the size and shape of the particles in space-holder powder.

3.4.2 Interconnect size distribution
Tissue-scaffolds and other materials allowing bone ingrowth are typically characterised only by their percentage porosity and pore size. However, the interconnects also play an important role, although, most prior studies have only analysed them in qualitative manner [e.g. 122]. A few prior quantitative analyses on two dimensional histological sections have been performed, for example Lu et al. [123] concluded that interconnections must be over 50 µm in diameter to favour new bone-ingrowth inside the pores they connect. These interconnects provide the passages for cell seeding and subsequent bone ingrowth, as well as routes for the vascularisation required to keep the tissue healthy. Therefore, the importance of quantitatively characterising the size of the interconnects between the pores is also a key characteristic of scaffold materials. This has been proposed by Lee and co-workers [86, 121] for bioactive glass scaffolds and by
Moore et al. [87] for biodegradable polymer scaffolds. More recently, Otsuki et al. [85] also suggested the importance of quantifying interconnect size for Ti based scaffolds.

Figure 3.9 shows the results of applying the algorithms for quantifying the interconnect size in three dimensions. This involved a novel method to compare the size distribution of interconnects in different materials through using an “area fraction” distribution. This method is considered to be more appropriate for the comparison of interconnects in different materials than the use of standard number density histograms because the sizes are weighted by their cross-sectional area. Cross-sectional area weighting is appropriate since seeding, vascularisation, and nutrient flow are all dominated by the larger area interconnects. This weighting is similar in methodology to the well established use of volume-fraction distributions in particle analysis, where volume fraction is used since it allows direct assessment of the degree of reaction between particle and matrix. It is suggested that a similar case is true for interconnects in scaffolds, i.e. an area-fraction distribution realistically presents the fraction of interconnects of a given size as a percentage (or fraction) of the total area of interconnects. This eliminates the undue weighting of a mean or median by the large number very small interconnects that do not contribute to processes such as flow or vascularisation.

The usefulness of weighting by the total area of interconnects is shown by re-examining the qualitative conclusion made earlier based on visual examination of the interconnects in Figure 3.7, where the average size appears to increase with increasing percentage porosity. Quantitative analysis of the area-fraction distributions (Figure 3.9) shows that the size distribution is nearly identical for all three levels of porosity, with the modal size ranging from 254 to 288 μm. Figure 3.9 illustrates that the relative area contributed by interconnects with a diameter of less than 50 μm is negligible. Statistical analysis of the data revealed that more than 90% of the total interconnect area was provided by interconnects greater than 100 μm in diameter, illustrating that for all three foams seeding and subsequent vascularisation should be possible. The high value for the ratio (of interconnect to pore surface area) should ensure that flows in high porosity foams are significantly easier.

### 3.4.3 Permeability

An ideal scaffold for tissue-engineered bone implantation must allow sufficient fluid flow for cell nutrition, cell multiplication and cell migration to promote uniform colonisation. Permeability of the porous scaffold is often taken as a measure of its ability
to fulfil these requirements and the permeability correlates with the scaffold-bone interface/interior healing process [124]. Therefore, the simulation of the permeability of the three scaffold materials will be discussed first and then validated against experimental measurements.

**Modelling**

The predicted main components of the permeability tensor resulting from the computational fluid dynamics simulations of the μCT data for sample P65 are given in Figure 3.10. The permeability is plotted as a function of the amount of scaffold simulated, allowing the minimum representative elemental volume to be determined. Figure 3.10 illustrates that the region of scaffold simulated should have an edge length of at least four pores (or 5 interconnects) in the flow direction for the REV used. This required the REV should be at least 3-5 times the flow-region-characteristic-length scale (e.g. pore size), and thus agrees well with prior studies in other materials [e.g. 109, 121].

**Comparison with measurement**

The measured and predicted permeability in the directions parallel and normal to the foam compaction direction are compared in Figure 3.11. The permeability predicted by computational fluid dynamics simulations of the μCT data agree well with those measured. However, for all samples the predicted permeability is greater than that measured. The possible sources of error for these predictions have been discussed in Section 3.2.6, and all error sources lead to higher values of the predicted permeability, and are thus in agreement with our findings. The largest deviation is for the lowest porosity (sample P51). In this sample there is the lowest ratio of interconnect area to pore surface area (12%), hence any misclassification due to thresholding will cause the greatest simulation errors. One method for reducing the error would be to take higher resolution scans. To test this, a P51 sample was scanned at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and the interconnect distributions were characterised for comparison. Using the higher resolution, the distribution was shifted to smaller sizes since the very fine wall thickness surrounding each interconnect was more accurately resolved. The ESRF data gave mean, median and mode values of 50 μm, 42 μm and 236 μm as compared to the laboratory μCT values of 95 μm, 98 μm and 288 μm (Table 3.1). The ESRF data was meshed and permeability analysis was performed, with the predicted values given in Table 3.2. The comparison with experiment was significantly improved, reducing the average error from 190% down to 27%. In summary, the major source of error in the permeability calculations is most
likely to arise from the limitations on scan resolution. However, this error is only large in the P51 case where the interconnects are the smallest and dominate the flow. The μCT calculated permeability values are in good agreement with the experimental values at high porosity, validating our permeability simulation approach, but illustrating that an appropriate scan resolution is required.

All three main components of the model-predicted, permeability tensor are listed in Table 3.2 for all three samples, together with the experimental measurements and Kozeny-Carman values. Good agreement is evident for all components, illustrating that the simulations correctly predict the anisotropy in the permeability. This anisotropy is thought to occur because of non-uniform compaction during a pre-compaction stage prior to cold isostatic pressing of the powders, thereby causing anisotropy in both pores. If the forces are not perfectly isostatic, the spaceholder particles will rotate to align normal to the largest force. The calculated and measured values of the permeability were found to be the smallest in the compaction direction; the remaining two normal directions exhibited similar values.

It is worth noting that the experimental values in Table 3.2 were calculated using Dupuit-Forchheimer’s expanded form of Darcy’s law (Equation 3.1), which has additional terms to account for inertia losses. The interstitial Reynolds numbers \(Re\) were 0.1 to 20, hence the use of the Dupuit-Forchheimer correction is appropriate [110]. Using this correction increased the permeability calculated from the measurements by 20-40\%, depending on the \(Re\) number. The Kozeny-Carman relation, which is a semi-empirical and is applicable to isotropic porous media, was found to give similar results to the CFD simulations at higher porosity levels (see Table 3.2).

Finally, it is worth comparing the measured and model calculated permeability values of these porous titanium foams to those of healthy cancellous bone (233×10^{-12} to 465×10^{-12} m² measured in different orientations [9]). The comparison is shown in Figure 3.11. Foams with porosity in excess of 65\% have permeability similar to that for healthy cancellous bone.

### 3.5 Conclusions

This chapter demonstrates the applicability of μCT and novel image analysis routines for the non-destructive quantification of several key characteristics determining the biocompatibility of scaffold materials, specifically: pore size distribution; interconnect size distribution and flow permeability. This method was validated on three different
titanium foams with porosity levels of 51, 65 and 78%. The modal values of pore (and interconnect) size are 589 (288), 438 (254) and 488 (263) μm for samples with 51, 65, and 78% porosity, respectively; exceeding the interconnectivity requirement for biocompatibility.

The μCT data was used to perform computational fluid dynamics simulations of nutrient flow to select the foam best matched to cancellous bone. The CFD predictions of the permeability matched best with the experimental values at higher porosity (as good as within 1% of experimental in case of P65). The main source of error in permeability simulation was the limited resolution of 3D μCT data. The permeability value for 65% porous foam found to be similar to those found in healthy cancellous bone. Hence, of the three commercial space holder foams tested, the P65 foam is the most suitable for bone implant applications based on the two criteria used in this study.
4 Characterisation of titanium foam for biomedical applications – mechanical behaviour*

In the previous chapter, the structural and fluid transport properties (i.e. permeability) of a biomedical Ti scaffold were studied. Understanding the mechanical properties of a scaffold is equally important, especially for load bearing implants. This is the subject of this chapter.

4.1 Introduction

In load-bearing applications, metallic scaffolds offer the advantages of high strength (compared to polymer scaffolds) and good toughness (compared to inherently brittle ceramic-based and bioactive glass-based scaffolds) [5, 12, 40]. By producing these implants in an interconnected porous form, there are three main benefits: (1) proliferation of cells into the structure is facilitated; (2) vascularisation is promoted; and (3) the structure can be tuned to match the modulus of bone to reduce stress-shielding effects [125].

The main macroscopic parameters controlling the mechanical behaviour of a porous scaffold are the pore volume fraction, nature of porosity (i.e. open or closed), and the properties of the foam walls (termed struts). For the foams used in this study, which are produced via a powder metallurgy (space-holder) method, there can be considerable variation in the size and orientation of the pores and hence the foam strut. Gibson and Ashby [11] have developed a number of micromechanical models to predict the mechanical behaviour of foams as function of their characteristics, such as the relative density, the nature of porosity and the foam strut material properties. These models assume uniformity in the porosity, which should be greater than 70%. In addition, the models assume idealised smooth struts and the absence of any axial or shear displacement of the foam edge during loading. Real foams rarely conform to these requirements; therefore, the accuracy of these models can be compromised [126]. Nevertheless, their models are useful in evaluating the various mechanical characteristics of porous solids, estimating properties such as Young’s modulus and yield stress. Continuum micromechanics [127], using an Eshelby-type matrix-inclusion approach [128], has also been applied to predict the mechanical behaviour of biomaterial structures [97, 129]. This technique allows more characteristic features of the

* A version of this chapter has been submitted for publication. Singh R, Lee PD, TC Lindley, C Kohlhauser, C Hellmich, M Bram, T Imwinkelried, RJ Dashwood, Acta Biomater.
Another approach is to use direct finite element modelling (DFEM) of the 3D structure of the foam. This avoids the simplifying assumptions about the foam structure used in analytic models. This methodology has recently been used to investigate damage under compressive loading in bone [101], titanium [8], aluminium [102, 104, 130], polymer [105] and bioactive glass [27] foams. However, the characterisation and meshing of the complex internal geometry of a foam and subsequent analysis employing commercially available FEM packages is computationally intensive.

In this chapter the link between mechanical properties and microstructure will be characterised using a commercially pure titanium foam as an example. This foam was developed for spinal fusion in a posterior lumbar interbody fusion device (Figure 4.1) by Synthes GmbH (Oberdorf, Switzerland) [3, 117]. These implants are mainly used in the surgical treatment of degenerated discs of the lumbar spine where the goal of the surgery is to restore the initial height of the intervertebral disc space. The foam must withstand the compressive loading to relieve pressure from the spinal chord, and allow a bony bridge to form between the two adjacent vertebrae.

Three different levels of porosity (51, 65 and 78%, henceforth designated as P51, P65 and P78) were studied using static compression tests to measure key elasto-plastic properties. A non-destructive methodology is presented to predict these properties with greater accuracy than traditional analytic solutions. This methodology combines X-ray micro-tomography (\(\mu\)CT) with DFEM. Interrupted compression testing and subsequent \(\mu\)CT characterisation was performed in the 65% porosity sample to investigate its post yield behaviour. These results illustrated that collapse of many isolated pores occurs first before the onset of the traditional banded failure [11]. The latter mechanism was

![Figure 4.1. A posterior lumbar interbody fusion device made of titanium foam (porosity~65%; implant is 22 mm long, enlarged relative to the spinal column).](image)
proposed by Gibson and Ashby for homogeneous idealised structures. Using in-house algorithms for quantifying the pore size and their orientation, these parameters were related to the onset of collapse of individual pores.

4.2 Materials and methods

4.2.1 Material and specimen preparation

Commercial titanium foams were supplied by Synthes GmbH (Oberdorf, Switzerland) with porosities of 51%, 65% and 78% (P51, P65 and P78). These foams were fabricated using commercial grade-4 titanium (CP4-Ti) powder via a space holder technique, as detailed elsewhere [3, 7, 131]. As shown in the previous chapter, the pore and interconnect sizes were found to be almost independent of relative density in these materials since the same space-holder particles were used in all cases. However, foam strut thickness decreases with increasing porosity. Two monolithic titanium specimens were also made following the same processing route (minus space holders) to evaluate the foam strut properties of the porous titanium.

4.2.2 Mechanical properties characterisation

Due to difficulties in specimen preparation no tensile/fatigue testing was carried out. Three types of tests were performed to characterise the mechanical properties: (i) static compression tests to 60% strain to obtain characteristic mechanical behaviour, (ii) interrupted compression tests (in 10% strain increments) followed by μCT to relate mechanical behaviour to foam microstructure, and (iii) ultrasound tests to determine Young’s modulus as this was not possible to measure using static compression tests. Static and interrupted compression tests were performed on cylindrical specimens (16φ ×8 and 5φ ×8 mm). Static tests were carried out on specimens machined with their longitudinal axis aligned with each of the three orthogonal directions (i.e. parallel to the pre-compaction direction and in the 2 perpendicular directions) to characterise the anisotropy in the mechanical properties. The ultrasound testing specimens were 10φ×18 mm. Monolithic CP-Ti specimens of dimension φ10×20 mm were tested in compression to derive the modulus, and the yield strength (as a function of strain) of the foam strut.

A 100 kN load cell servo-hydraulic universal testing machine (Zwick, GmbH, Ulm, Germany) was used to perform the static compression testing. The tests were carried out in displacement control mode with an initial strain rate of 0.001 s⁻¹. PTFE
(polytetrafluoroethylene) tape was employed to minimise friction between the platens and specimen surface. A linear voltage displacement transducer (LVDT) was used to measure the cross head displacement. To correct for machine compliance, a steel block of large cross sectional area and of known modulus was tested in compression, following a similar methodology to that detailed in [132]. The yield strength of the foam was taken as the stress at the intersection between regression lines corresponding to the linear elastic region and the plateau region of the stress-strain curve. However, it should be pointed out that the method cannot correct for the ‘contact compliance’ between the test specimen and the machine platen and hence the results are still not appropriate for the accurate measurement of elastic modulus of foams, as has been observed previously [133]. Therefore, the ultrasound technique was preferred for modulus measurements.

The experimental procedure of ultrasound method of modulus measurement* is described in the Appendix A. The typical values of the measured modulus are listed in Table 4.1.

Interrupted compression tests were performed in a screw-driven 10 kN Zwick machine using successive small deformation stages of 10% nominal strain. The displacement was recorded by applying a clip gage over the test platens. This series of tests was performed to relate the mechanical behaviour to the morphology of the cells within the foam by performing µCT after each step.

The mechanical properties such as Young’s modulus and yield strength were also calculated employing micromechanics of porous material§.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g cm⁻³)</th>
<th>Porosity (%)</th>
<th>Velocity, vL (km/s)</th>
<th>Velocity, vT (km/s)</th>
<th>C₁₁₁ (GPa)</th>
<th>C₁₂₁₂ (GPa)</th>
<th>Young’s Modulus, E (GPa)</th>
<th>Poisson’s ratio, ν</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP-Ti</td>
<td>4.42</td>
<td>0</td>
<td>6.00 ± 0.03</td>
<td>3.11 ± 0.03</td>
<td>159.1 ± 1.5</td>
<td>42.6 ± 0.9</td>
<td>112.3</td>
<td>0.317</td>
</tr>
<tr>
<td>P51</td>
<td>2.18</td>
<td>50.6</td>
<td>4.23</td>
<td>2.06</td>
<td>39.1</td>
<td>10.9</td>
<td>28.5</td>
<td>0.307</td>
</tr>
<tr>
<td>P65</td>
<td>1.59</td>
<td>63.9</td>
<td>3.36</td>
<td>1.46</td>
<td>18.0</td>
<td>3.82</td>
<td>10.4</td>
<td>0.365</td>
</tr>
<tr>
<td>P78</td>
<td>1.01</td>
<td>77.1</td>
<td>2.13</td>
<td>1.02</td>
<td>4.59</td>
<td>1.14</td>
<td>3.03</td>
<td>0.336</td>
</tr>
</tbody>
</table>

### 4.2.3 µCT characterisation and image processing

All the foams were scanned using a commercial lab-based X-ray micro-computed tomography (µCT) unit and subsequently, the raw data was processed using commercial image analysis packages (Amira 4.0 and VG-Studio MAX 1.2) as well as in-house algorithms which have been described elsewhere [86, 121, 134] in detail and hence are only outlined below. The aforementioned procedure was required to isolate individual

---

* The experimental set up was built and the actual measurement was carried by Professor C. Hellmich (TU Wein, Austria).

§ The results of micromechanics modelling were provided by Professor C. Hellmich (TU Wein, Austria).
pores from their interconnecting neighbours. Each pore was then represented by an equivalent ellipsoid having the same inertia tensor as the pore. The voxel-set representing a pore was arranged in a 3xN matrix and the inertia matrix of the pore was calculated. The eigen value decomposition of the inertia matrix gave access to the magnitude and direction of the major axis of the equivalent ellipsoid. The preferential orientation of the space-holder particles was thus characterised in this way by the orientation of major axis of the equivalent ellipsoid. Additionally the eigen value was related to the anisotropy observed in the mechanical properties of the foam.

µCT was also employed to scan the interrupted test specimen at each step of deformation starting from 0% nominal strain. Fiducial marks were added to the specimen to facilitate registration using a minimal amount of Cu dag at three locations. The amount of the applied copper was dictated by its resolvability in the transmission image, which was used as a visual guide to align the specimen at the same location and orientation as the previous scan. This scheme of scanning allowed easy comparison and registration (based on ITK [114] image processing tools) of the images obtained at successive stages of deformation. All the scans were performed at 6.5 μm resolution using X-ray radiation at 80 keV and a filament current of 100 μA.

### 4.2.4 Analytical modelling
The relationships between the relative properties and the relative density ($\rho_{\text{app}}/\rho_s$) for open-cell foam as predicted by the Gibson-Ashby model [11] are:

$$\frac{E_{\text{app}}}{E_s} = \left( \frac{\rho_{\text{app}}}{\rho_s} \right)^2$$  \hspace{1cm} (4.1)

and,

$$\frac{\sigma_{\text{app}}}{\sigma_s} = C \left( \frac{\rho_{\text{app}}}{\rho_s} \right)^{3/2} \left[ 1 + \left( \frac{\rho_{\text{app}}}{\rho_s} \right)^{1/2} \right]$$  \hspace{1cm} (4.2)

where, $E$, $\sigma$ and $C$ refer to Young’s modulus, the yield stress and a constant (~0.23); the subscript ‘app’ and ‘s’ refer to the properties of foam and the foam strut material, respectively. The second bracketed term in Equation 4.6 is a density correction term for foams with relative density greater than 0.3.
4.2.5 Finite element modelling in ABAQUS

The solid titanium network from the μCT datasets was segmented and meshed in a commercial FEM meshing package, ScanFE (Simpleware Ltd., United Kingdom) and imported into the FEM analysis package ABAQUS. Two sets of boundary conditions were applied: (1) a node set representing the top face of the model was defined (AB in Figure 4.2) and a maximum displacement (equivalent to 12-15% strain) was given to this node set, AB, along $z$ in multiple steps, and (2) a node set representing the bottom face (CD) of the model was defined and its’ freedom of movement along $z$ was restricted (see Figure 4.2). The total reaction force at the bottom face as a function of displacement or equivalently strain was calculated. The modulus was calculated by linear extrapolation of the elastic regime and the yield stress was determined by following the procedure employed in experimental measurement from the stress-strain curve. A representative elementary volume (REV) was established by performing a sensitivity analysis over

![Figure 4.2. Schematic of the FEM procedure to simulate the monotonic compression deformation. The model has a top node set (AB; $x = 0$) and a bottom node set (CD; $x = L_{REV}$) representing respectively the top and bottom face of the cube. The rest of the solid-void interface was modelled as free surface. Total reaction force (stress) developed at the bottom node set as a function of the top node set displacement (strain) was calculated, leading to the derivation of Young’s modulus and yield strength.](image-url)
multiple volumes of increasing size unless the modelled properties, such as Young’s modulus and yield stress, remained constant within <10%. All the volumes were grown from a fixed centroid during the REV analysis.

4.3 Results
Figure 4.3(a) shows the highly interconnected pores within the 65% porosity (P65) foam.

Figure 4.3. (a) non-uniform foam-wall as apparent in a 3D tomograph (b) an orthoslice from a 3D tomographic dataset showing intra-strut microporosity and (c) SEM picture showing surface roughness which is beneficial for the cell-anchorage (Sample P65).
The structure within the wall struts of this foam is shown in a 2D orthoslice from μCT (Figure 4.3(b)) illustrating some fine intra-strut micro-pores as a result of incomplete sintering. The foam struts have significant surface roughness as seen in Figure 4.3(c) which can be beneficial to cell attachment [3].

The stress-strain curve from the monolithic titanium material (Figure 4.4(a)) was used to derive the flow stress of the foam strut material as a function of strain for input into the FEM simulations. The equivalent stress-strain curves for the foams with the three levels of porosity are shown in Figure 4.4(b). The initial non-linear behaviour of these foams is due to the contact compliance of the machine. Owing to the small length of the specimen and the localised plastic deformation occurring in the beginning of the test at the contact point between the specimen and the test platen, the initial non-linearity in the stress-

![Figure 4.4. Engineering stress vs. strain characteristics in compression testing of (a) monolithic and (b) porous titanium (*Compaction direction).](image-url)
strain curves could not be corrected by employing the procedure outlined in Section 4.2.2. As a result of the compliance complication, an ultrasound method was employed to measure the Young’s modulus of the foams. This modulus data is plotted, together with the yield stress measured from the compression tests, in Figure 4.5, as a function of relative density (1 - fractional foam porosity).

The stress-strain curves exhibited three regimes of deformation, as is typical for metal foams [11]: (i) an initial linear elastic region, (ii) a plastic collapse plateau region, and (iii) a densification region. The foams also displayed noticeable mechanical property anisotropy at all porosity levels with the strength and modulus values being lower in the pre-compaction direction (CD).

![Graph](image)

Figure 4.5. Comparison of (a) Young’s modulus and (b) yield strength, of titanium foams in the direction normal to compaction (average of the property along two of the normals), obtained from different methodologies. Note that the Gibson-Ashby model, applicable only to porosity >70%, predicts yield stress scaling as 0.3 times relative density raised to power 1.5, and hence there is large deviations at low values of porosity. The micromechanics and Gibson-Ashby predictions are obtained assuming isotropic porous material behaviour.
Figure 4.5 gives the Young’s modulus and yield stress values simulated using the semi-analytical Gibson-Ashby [11] model, micromechanical model and direct FEM. The FEM results are presented as mean ± standard deviation of 3 independent simulations on REVs from different regions. The influence of the size of the REV is shown in Figure 4.6(a). The simulated properties stabilise once the cubic edge length spanned 4-5 times
the foam’s characteristic length scale (i.e. its pore diameter). Therefore, a region of at least the minimum of this size was used for all simulations. Note that even after the values plateau, there is a variation in the properties in the different directions. This dependency of the properties on pre-compaction direction can be explained in terms of the preferential orientation of the equivalent ellipsoids representing the pores.

Figure 4.6(b) shows that for most pores the major axis aligns normal to CD. This anisotropy in the porosity is reflected in the anisotropy in properties (Figure 4.6(c), where the anisotropy ratio is defined as the yield stress normal to the CD divided by that in the CD). Mechanical properties such as yield stress and Young’s modulus were lower in CD than in normal to CD. This is due to the largest of pore axes aligned normal to CD, as analysed in the discussion section below. The extended Gibson-Ashby model relates the yield stress anisotropy to the pore aspect ratio. Note that the image analysis can in some cases underestimate the major axis length (and hence anisotropy) by classifying a large pore (such as the one circled in Figure 4.7(a)) as two smaller pores (Figure 4.7(b)).

Figure 4.7. (a) The moments acting on nodal points such as A, B and C under the application of a force $F$ on a pore (encircled) and, (b) the segmentation of the large pore into two smaller pores; the latter mask the high aspect ratio of the large pore.
Assuming conservation of volume, the true stress-strain curves for a series of interrupted tests on P65 are given in Figure 4.8 and the corresponding µCT images are shown in Figure 4.9. The collapse of a high aspect ratio pore (dotted line) with its major axis oriented normal to the loading direction can be clearly observed. This figure also shows a near spherical pore (solid line) which resists deformation more efficiently. The fraction of wall material (as predicted by the direct FEM method) that has plastically deformed as a function of strain is plotted in Figure 4.10(a) for the three levels of porosity. The location and severity of plastic strain, for each level of porosity, is shown in Figure 4.10(b-d) at a global total strain of 4%.

4.4 Discussion

4.4.1 Monotonic compression testing and elastic behaviour of the foams
The mechanical properties of the foams, as obtained from experiments and modelling, are summarised in Figure 4.4 and Figure 4.5. The key observations from these two figures are: (1) the foams are anisotropic and (2) the direct FEM approach, among all the investigated modelling tools, predicts best the mechanical properties of the foams over the full range of relative densities.
As well as providing the closest prediction for both modulus and the yield stress, the direct FEM approach also correctly predicts the systematic experimental trend of increasing yield stress anisotropy which increases with porosity (Figure 4.6). The

Figure 4.10. (a) Percentage of material deforming plastically as a function of strain and, (b-d) 2D images of the model showing elastically (dark) and plastically (light) deforming material at a strain of 0.038 for P51, P65 and P78 respectively.
micromechanics and Gibson-Ashby models predict an upper bound on modulus. For yield strength, the micromechanics model provides an upper bound. This over-prediction is not surprising considering the inability of the micromechanics model to correctly account for the interactions between the interconnected porosity treated as inclusions. The Gibson-Ashby model underestimates the yield strength at high relative densities (>0.3) where many of its mechanistic assumptions become invalid.

Mechanical methods for determining Young’s modulus of foams are inherently difficult [126]. Ideally a long gauge length tensile sample would be employed in combination with highly accurate extensometry. Tensile foam samples are impractical due to difficulties in gripping; hence compression specimens are used. This immediately limits the gauge length that can be used due to buckling considerations. Furthermore, extensometry is difficult in foams owing to problems such as localised surface deformation and attachment of clip gauges. Contact compliance, which causes inelastic phenomena at the beginning of the test [129, 133], is also a problem. For these reasons, an ultrasound method was used for modulus measurement; this technique is increasingly becoming the accepted methodology for accurately measuring the moduli of porous materials [8, 129, 135-136].

Direct FEM simulation, incorporating elasto-plastic material behaviour (i.e. the local plasticity was allowed), predicted moduli that correlate well with the ultrasonic measurements (Figure 4.5(a)). Thelen et al. [8] hypothesised that the underestimation of modulus during compression testing is due to local plasticity in these porous materials. Interestingly the amount of local plasticity can be predicted from the FEM simulations. Although the FEM simulations do show that local plasticity is occurring (Figure 4.10), the models were rerun using only elastic material behaviour, and the modulus predictions were almost unchanged, still matching the ultrasound measurements (Figure 4.5(a)). Therefore, it is hypothesised that the low values of modulus measured during compression testing are due to contact compliance and the non-planar surfaces of the sample, rather than local plasticity. (Note in the FEM simulations the surfaces were maintained as perfectly planar.) This is not the case for unloading, as found by McCullough, Fleck and Ashby [133].

Although the FEM method gave the closest match to experimental values for both modulus and yield strength, there was still a significant difference in yield stress for the P51 sample (~40%). The deviation in yield strength values also appeared to follow a trend; the FEM under-predicted the properties at the lowest relative density (P78) whilst,
these values were increasingly over-predicted as the relative density increased (e.g. for P65 and P51). Two potential reasons for this trend are: (1) the properties used for the foam struts may be non-representative; and (2) the meshing accuracy is limited by the scan resolution. The same mechanical properties were used for the foam struts in all cases, as obtained from testing a monolithic Ti specimen processed in a similar fashion to the foam but with no space-holders. However, the level of microporosity within the foam struts was twice as high as in the monolithic sample (~1% as compared to ~0.5%). Although this difference was considered negligible because a prior study [137] illustrated levels of microporosity of less than 5% did not significantly alter uniaxial loaded mechanical properties. However, since the struts are loaded in bend, these micropores might be acting as stress concentrators initiating yield at lower loads [138]. Another reason why the struts may have different properties than the monolithic sample could be minor variations in the interstitial concentration which can have a large effect on properties [16]. The microstructure and the oxide content of struts in aluminium foams with similar densities have been found to affect considerably the deformation mechanism of these foams, manifested also in their macroscopic mechanical behaviour [139].

With regard to meshing accuracy, the μCT voxel size of ~5 μm was re-sampled to 16 μm before meshing to keep the maximum number of elements to under 5 million. This re-sampling will remove fine internal defects and surface roughness in thicker struts (i.e. P51&P65), overestimated the strength. However, in very thin struts where the minimum thickness is on the order of the voxel size (i.e. P78, see Figure 4.10(d)), the struts may become stepped in thickness with very thin (or non-existent) connecting points, underestimating the strength. Of the two hypotheses, the mesh resolution reasoning best matches the results, unfortunately due to computational costs, higher resolution was not possible.

Lastly, the Young’s moduli and yield stress (experimental) for the three foams were found to be in the range of 3-29 GPa and 10-180 MPa, respectively. This moduli range has a sizeable overlap with that found in trabecular through to cortical bone [11], indicating the suitability of these foams for implant applications while minimizing stress-shielding. The yield stress is far superior to bone of similar relative densities.
4.4.2 Relationship between mechanical property and morphological anisotropy

An anisotropy in mechanical properties arises during the manufacturing of the foams. The pre-compaction step (where the powder mix is packed prior to cold-isostatic pressing) imparts a preferential orientation to the space holder particles (Figure 4.6(b)). The mechanical properties are lowest in the compaction direction (Figure 4.4(b)) due to the fact that elastic as well as plastic deformation is dominated by wall strut bending, as explained below.

Since the major axes of the pores are predominately inclined normal to CD, the wall struts are therefore elongated normal to CD. As shown schematically in Figure 4.7(a), the load required to deform these longer struts is lower due to the increased bending moment on struts AB and BC due to their longer lengths. This reduces the mechanical properties in CD, as well as other properties such as permeability, as was found in a prior study [134].

By employing beam theory, Gibson and Ashby [11] characterised anisotropy in an idealised tetragonal open-cell structure. Dillard et al. [140] extended this model to an orthorhombic unit cell and successfully quantified the effect of pore anisotropy on modulus in an open cell nickel foam. In this study, their analysis is extended to simulate the effect of anisotropy on yield stress, validating it on titanium foams.

Following the procedure outlined by Gibson and Ashby for a tetragonal unit cell, it is possible to show that the yield stress anisotropy ratio for an orthorhombic unit cell (dimensions \(a, b\) and \(c\), \(a<b<c\)) in the directions \(c\) and \(a\) (\(\sigma_c/\sigma_a\)) can be written as:

\[
\frac{\sigma_c}{\sigma_a} = Q^{1.5} \left( \frac{1 + R}{Q + R} \right)
\]

(4.3)

where, \(Q\) and \(R\) equal \(c/a\) and \(b/a\) respectively. For the case of a tetragonal based unit cell structure \((b=a)\), this reduces to \(2Q^2/(1+Q)\) as found by Gibson-Ashby [11].

For the ensuing analysis, the parameters \(a, b,\) and \(c\) are taken as half the mean of all major axes of the fitted pore ellipsoids. Each axis is mapped to the nearest coordinate axis, transforming \(a\) to CD, with \(b\) and \(c\) normal to CD. The CD and two normal semi-axis lengths are: P51 - 162, 273 and 282 μm; P65 - 191, 198 and 224 μm; and P78 - 196, 220 and 239 μm. Note the length in the CD direction is significantly shorter, confirming the reasoning outlined above for the measured mechanical property anisotropy.

The result of applying Equation 4.9 is compared to both the experimental and direct FEM values in Figure 4.6(c). The extension of the Gibson-Ashby model has correctly
predicted the trends in yield stress anisotropy for P65 and P78. However, at the low porosity associated with P51, the assumptions underlying the Gibson-Ashby approach are not appropriate. The small under-prediction of yield anisotropy in P65 and P78 was attributed to an underestimation of the pore aspect ratio for larger pores (Figure 4.7(a)), due to their segmentation into two smaller pores (Figure 4.7(b)). The former behaves mechanistically as a single pore; however, both the analytic approaches will consider them as two separate pores with far smaller aspect ratios.

The FEM predicted values show a better match, but there is still some discrepancy. There were a number of limitations to the direct FEM approach which could explain this. Firstly, while the REV analysis suggests that a domain of 1.65 mm$^3$ is sufficient for mean value predictions (Figure 4.6(a)), closer inspection suggests that a larger REV is required for a stable prediction of anisotropy. The REV used in this study was between 4 to 5 cells across (for computational efficiency), while Gibson and co-workers [141-142] suggested a minimum REV of 6 and 8 times the characteristic cell diameter be used.

Secondly, in the current work a free boundary condition was applied to all surfaces normal to loading. A prior FEM study [143] on titanium foam constrained the lateral surface nodes to a plane deforming outwards proportionally to the displacement applied on top surface nodes. Such a boundary condition is realistic for a monolithic material and hence reasonable for their foam which had a very low level of porosity (~15% porous titanium). Another approach which can correct the free-surface effect would be to use the imbedded micro-cell model [138]. In this analysis, an REV representing all the microstructural features of the material is imbedded into a bulk material having the average property of the material being studied. While this strategy has been shown to produce more accurate results at reduced computational cost in monolithic (but multi-phase) materials, meshing the interface between a foam and monolithic surround is non-trivial. Other possible sources of errors could be due to μCT and FEM mesh limitations.

### 4.4.3 Interrupted compression testing and foam failure behaviour

Deformation in cellular structures is highly inhomogeneous. Even for homogeneous cellular materials, post-yield deformation becomes highly localised and progresses via the formation of bands of plastically collapsed cells normal to the applied load [104]. Interrupted compression testing (Figure 4.8) was combined with μCT (Figure 4.9) and direct FEM (Figure 4.10) to determine the onset of plastic deformation and post ‘yield’ behaviour for the highly inhomogeneous foams under investigation.
Unlike homogeneous cellular materials where the collapse of the first pore is followed by the collapse of its neighbours normal to loading direction, termed banding [11], failure in the current foam was observed to occur at a large number of isolated pores. This was then followed by the more traditional banding, although the banding was not as well defined due to heterogeneity in pore size. An interesting result of having applied principle component analysis (PCA), is that one can predict which isolated pores will collapse first. For example, in Figure 4.9, the dotted pore has a high aspect ratio of 1.73 (average is 1.57) and long length normal to loading of 945 μm (average 529±204 μm). Thus, the dotted pore is among 5% of the largest pores (+2σ). Therefore, this pore can be predicted to have a very high bending moment and hence be amongst the first isolated pores to collapse [104], as observed. The well rounded and shorter length, pore (solid line in Figure 4.9) resisted deformation until much higher strains, supporting the conclusion observed by Bart-Smith et al. [104], that the shape of the pore is important in determining the deformation of the foam. Therefore, the PCA technique developed in this chapter can be used to predict the potential failure locations. Similar behaviour has been observed in a syntactic foam, which was also non-homogeneous [144].

The relative extent of local plastic deformation in the three foams was assessed using direct FEM. Figure 4.10 illustrates that localised deformation was more pronounced in the higher porosity foam (P78) where less material underwent plastic deformation irrespective of the level of nominal strain. In contrast to the two denser foams, which behave similarly to each other, P78 deforms significantly more homogeneously with widespread plastic deformation even at modest strains (>5%). The highly localised deformation observed in P78 is consistent with the assumptions in the Gibson and Ashby model that assumes deformation is localised to strut-nodes. As Gibson and Ashby state, this assumption breaks down rapidly as the level of porosity decreases. The direct FEM method does not have any such limitations and is able to correctly characterise the intermediate porosities desirable for highly loaded implant applications.

### 4.5 Conclusions

A generic non-destructive methodology based on μCT data was used to both determine the mechanical properties of titanium foams and to characterise their deformation behaviour. Although the procedure is applicable to most foams and composite materials, it is demonstrated here for commercial titanium foam used for biomedical implants. A number of techniques for predicting the mechanical properties of foams with porosity
levels of 50-80% were investigated: analytic, micromechanics and direct FEM. The direct FEM approach provided the most accurate predictions for Young’s modulus, yield strength (modulus within 5% of experimental values for P51 and P65) and post yield behaviour. The Gibson-Ashby analytic model gave a reliable prediction for yield strength and its anisotropy by extending it to the more general case of an orthorhombic unit cell. A computational methodology was developed to extract parameters for this extended Gibson-Ashby model from μCT data of foam.

The post yield behaviour of the 65% porosity foam was characterised using interrupted compression testing in combination with μCT. The use of principle component analysis provided a powerful tool to predict the most vulnerable regions in these foams. The results illustrated that the localised collapse of large and unfavourably orientated pores occurs at dispersed points throughout the volume, which is critical in understanding the failure mechanisms in metallic foams in general and porous implants in particular.
5 A novel ceramic precursor route to make Ti foam*

In the previous two chapters μCT based modelling methodologies were developed to: (i) characterise the structure and permeability of a porous scaffold (Chapter 3); and (ii) simulate some of the mechanical properties, including the foam progressive deformation behaviour under compression (Chapter 4). These were validated on commercial Ti foam that finds applications in spinal fusion devices. In this chapter, a novel ceramic precursor route to make porous titanium is established. Having successful produced Ti foams via a novel route, their properties were characterised using the techniques developed in the previous two chapters and compared with the existing commercial foam.

5.1 Introduction

Porous titanium structures are currently produced through multi-step powder metallurgical (PM) routes. Examples of these techniques include: space-holder or sacrificial template method [7, 21-22, 145-147]; polymer replication [148]; controlled expansion of entrapped argon gas in a Ti preform at high temperature and pressure [20]; freeze-casting [60]; laser processing [64]; and rapid prototype methods including selective electron beam melting [65]. All of these techniques require expensive Ti-powders as their starting material, and in general yield a single scale of porosity.

In this chapter the use of the Fray, Farthing and Chen (FFC) Cambridge process [13] is explored. This technique provides a means of producing a near-net shape metal product directly from an inexpensive metal-oxide precursor. During the FFC Cambridge process a TiO\textsubscript{2} cathode is progressively reduced and deoxidised in a molten calcium chloride salt. At the cathode the titanium oxide is reduced to titanium and the oxide ions dissolve into the calcium chloride. These oxide ions migrate to a carbon anode where they undergo an electrochemical reaction with the C anode, to yield CO / CO\textsubscript{2}. Since its discovery, significant research has focused on applying this technique to the production of titanium and its alloys [77-78, 149-152]. A study conducted for the US Department of Energy in 2004 identified more than a dozen emerging technologies for Ti extraction [18]. However, only the FFC Cambridge process lends itself to the production of Ti foams via the reduction of a porous TiO\textsubscript{2} precursor. This process (see Figure 5.1) also has other benefits, such as the ability to produce conventional or unique alloys by blending the relevant oxides [77].

* The work presented in this chapter is being considered for patenting and subsequent to that will be submitted for consideration of publication in Acta Materialia.
To the author’s knowledge, there has only been one prior attempt to produce titanium foams via the FFC Cambridge process [153]. In that study, Centeno-Sanchez et al. [153] produced the ceramic precursor using a space-holder technique. Whilst, the level of interconnectivity, mechanical properties, and permeability were not analysed, this study demonstrated that reduction of a porous ceramic precursor was possible. Due to the limitations of the space-holder technique [73] the pore walls were irregular in thickness. Alternative methods for producing the porous ceramic are required.

One such technique involves the preparation of a slurry mix, mechanical foaming and setting by gelation (e.g. in situ polymerisation). Although not previously applied to TiO$_2$, in other ceramic systems, this technique, termed gel casting, has been shown to be an effective method [73] for producing highly interconnected open-foams.

In this chapter, a novel route for the production of titanium foams with interconnected pore networks is presented. A method for gel casting of a TiO$_2$ foam precursor was developed, the oxide foam was then reduced using the FFC Cambridge process. Using a variety of 2D and 3D characterisation techniques, in combination with physical and mechanical testing, the evolution of both the microstructure and properties was tracked. This characterisation will show that the hierarchical porosity with these Ti foams can be tailored to match the mechanical and physiological requirements. Large, highly interconnected, pores in the range of 100 to 850 $\mu$m were produced with independently varied microporosity with their walls on a scale of 1 to 10 $\mu$m. The microporosity within

---

**Figure 5.1. Overview of metallic titanium foam production.**
the strut walls is also open and well connected. Sound walls can also be produced, although the novelty of the process is the controlled microporosity which has not been achieved yet via other routes. The tailorable fine intra-wall porosity has many potential applications, including infiltration with a bioactive glass or polymer composite.

5.2 Experimental
New titanium foams were produced by reducing a titanium oxide foam using the FCC Cambridge process. The titanium oxide foam was produced using the gel cast foaming process, which dictated the macropore structure of the final foam. The titanium foams were then characterised using SEM and μCT. Mechanical and fluid transport properties were also assessed.

5.2.1 Gel casting of precursor foam
A gelling system based on methacrylamide (monomer), N,N'-methylenebysacrylamide (cross-linker) and ammonium persulphate (APS; initiator) was employed in this work to make the precursor titania foam. All the reagents (Table 5.1) were from Sigma-Aldrich, USA. Initial TiO$_2$ powder particle size plays an important role in determining the rheology of water based slurry system. The oxide particles had a $d_{50}$ of 0.93 μm when measured by laser diffraction (CILAS 1064 Laser Particle Size Analyser). The standard composition in Table 5.1 corresponded to a slurry composition loaded with maximum possible titania while keeping unchanged remainder of the reagents. A slurry with a low ceramic content (~34 wt.% TiO$_2$, cf. a standard of ~48 wt.%) was used to investigate the effect of ceramic loading on pore wall characteristics and on foam integrity.

Obtaining an optimum slurry composition required a series of informed trial and error experiments. The first composition* of slurry set so quickly that the foaming was not possible. Then the slurry compositional optimisation focussed on lengthening the induction time (the time between addition of initiator and catalyst and significant polymerisation to the point where the freshly foamed slurry, still transferable to a mould, could stand by itself). Hence, the induction time provided a useful window for foam generation [73]. Four strategies were followed to increase the induction time: (1) to reduce the amount of the monomer and cross linker while keeping their ratio unchanged; (2) reduction of initiator and catalyst, broadly commensurate with the reduction in the amount of monomer; (3) increase of distilled water and (4) increase in slurry TiO$_2$

*TiO$_2$ powder (14 g), Distilled water (20 ml), monomer (9 g), cross linker (3 g), APS (6 ml), Dispex (2 drops), Triton (0.1 ml) and TEMED (7 ml). This composition was recommended by Dr Julian R. Jones.
loading. The relative degree of change in the above parameters was dictated by the batch size (two moulds of casting) of foam production and the minimum usage of reagents excluding the TiO$_2$ powder. The quantity of monomer and cross linker had the greatest impact on induction time, and these were decreased, with concurrent increase in distilled water and TiO$_2$ loading, until an induction time of one minute was obtained. This induction time was found to be a potential minimum time required for foam generation.

The reagents were mixed in the order they are listed in Table 5.1, with the initiator and catalyst being added immediately prior to foaming by vigorous agitation for 60 s. The foamed suspension was cast into 60 ml autoclavable straight edge polymethyl pentene moulds (Nalgene Labware, UK). The moulds were sealed and allowed to gel at room temperature for 24 h. The gelled foams were 44 mm in diameter and varied from 20 to 40 mm in height. Drying of the foam was carried out at 60 ºC for at least 18 h, followed by a similar time at 100 ºC. Differential scanning calorimetry (Figure 5.2(a)) was used to determine the appropriate sintering schedule for dried precursor (Figure 5.2(b)). It was found that accelerated drying and decomposition of the polymer occurred over a range

![Differential scanning calorimeter characterisation of dried precursor and four sintering schedules investigated.](image)

**Figure 5.2.** (a) Differential scanning calorimeter characterisation of dried precursor and (b) the four sintering schedules investigated, holding at: 1. 950 ºC; (3 h), 2. 1000 ºC; (3 h), 3. 1150 ºC (3 h), 4. 1250 ºC (3 h) and 4. 1450 ºC (1 h).
of temperatures from 100 ºC to 700 ºC. Therefore, the selection of the initial ramp rate to the sintering temperature was critical in order to avoid crack formation. Heating at 0.5 ºC/min to 350 ºC, followed by a one hour hold, was found to be appropriate for removal of the majority of the polymer without cracking. The samples were then ramped at 3 ºC/min to the sintering temperature (950-1450 ºC) and held for three hours, followed by a furnace cool.

A series of samples was produced using these base conditions with individual processing conditions varied (Table 5.2).

### 5.2.2 Reduction of the precursor foam via the FFC Cambridge process

A schematic of the experimental setup used for the reduction of the samples is shown in Figure 5.3(a). The cell design is essentially the same as used in previous investigations [80-81, 149] except for improved sealing (replacement of silicone bungs) where the electrodes enter the retort Figure 5.3(b). The current design is able to ensure a stable airtight seal whilst still allowing movement of current collectors keeping their separation constant.

The reduction cell consists of a programmable vertical tube furnace housing an Inconel® reaction vessel with a water cooled top plate. The molten calcium chloride was contained in an alumina crucible (92 mm diameter OD, 86 mm diameter ID, 100 mm high). Prior to electrolysis the as-received anhydrous calcium chloride (Fluka) was heated at 0.1 ºC/min to 300 ºC and held at this temperature for at least 5 h prior to raising the temperature of the salt to the reaction temperature of 900 ºC at 3 - 4.5 ºC/min. The salt was then left to soak at this temperature for a minimum of 30 min. During

<table>
<thead>
<tr>
<th>Material (function)</th>
<th>Amount, g or ml (Standard)</th>
<th>Amount, g or ml (Low loading)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂ powder (main component)</td>
<td>33</td>
<td>14</td>
</tr>
<tr>
<td>Methacrylamide (monomer)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>N,N'-Methylenebysacrylamide (cross-linker)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Distilled water (carrier)</td>
<td>25</td>
<td>14</td>
</tr>
<tr>
<td>Triton X 100 (Surfactant)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Dispex (Surfactant)</td>
<td>2 drops</td>
<td>2 drops</td>
</tr>
<tr>
<td>N,N,N',N'-tetramethyl ethylene diamine (TEMED) (catalyst)</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Ammonium Persulphate (APS) solution (initiator; 0.52 g/ml)</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>
Table 5.2. Details of specimens used in electrolysis.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Parameter/properties studied</th>
<th>Post-reduction porosity, %</th>
<th>Pre-(post-)reduction wt, gm: [ wt% loss]</th>
<th>Reduction temperature (salt), °C</th>
<th>linear shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_950</td>
<td>Sintering temperature</td>
<td>82 [μCT]</td>
<td>2.700 (1.591) [41.1]</td>
<td>910</td>
<td>16.8</td>
</tr>
<tr>
<td>S_1150</td>
<td>Sintering temperature</td>
<td>81 [bulk]</td>
<td>3.817 (1.905) [50.1]</td>
<td>910</td>
<td>17.1</td>
</tr>
<tr>
<td>S_1450</td>
<td>Sintering temperature</td>
<td>80 [μCT]</td>
<td>2.875 (1.607) [44.1]</td>
<td>910</td>
<td>20.7</td>
</tr>
<tr>
<td>S_1000_LL</td>
<td>Ceramic loading</td>
<td>88 [bulk]</td>
<td>0.528 (0.242) [54.2]</td>
<td>910</td>
<td>NA</td>
</tr>
<tr>
<td>S_1050</td>
<td>Post-reduction properties</td>
<td>78 [bulk]</td>
<td>3.282 (1.728) [47.3]</td>
<td>910</td>
<td>16.8</td>
</tr>
<tr>
<td>S_1250_HT</td>
<td>Reduction temperature</td>
<td>82 [bulk]</td>
<td>2.680 (1.414) [47.2]</td>
<td>1000</td>
<td>39.1</td>
</tr>
<tr>
<td>S_1350</td>
<td>Post-reduction properties</td>
<td>73 [bulk]</td>
<td>2.780 (1.473) [47.0]</td>
<td>910</td>
<td>NA</td>
</tr>
</tbody>
</table>
heating, electrolysis, and cooling the salt was held under argon to maintain an inert atmosphere. The argon was dried and oxygen gettered by passing through silica gel, molecular sieves and heated (>500 °C) titanium turnings.

Prior to the reduction experiments, pre-electrolysis at 2800 mV was performed using a graphite anode (10 mm diameter Tokai Carbon EC4) and a titanium (3 mm diameter CP-Ti rod) cathode to remove any electroactive impurities. Pre-electrolysis was continued until the background current reached a level ~130 mA (typically 60 – 90 min). After pre-electrolysis the TiO₂ foam cathode (suspended from a CP-Ti rod current collector) was immersed into the salt and electrolysis commenced. During reduction the cell voltage was ramped up to 3.1 V over the course of 2 h and then held at this level for the remainder of the reduction (45 h total). For all experiments the anode consisted of 10 mm diameter rods of Tokai Carbon EC4. After reduction the sample was withdrawn to the top of the retort (~450 °C) and the furnace was switched off and allowed to cool down to 110 °C. At this point the lid was removed from the retort and the samples removed.

Figure 5.3. (a) Schematic of the modified FFC Cambridge reduction cell: A TiO₂ foam cathode, B Ti cathode for pre-electrolysis, C graphite anode, D alumina crucible, E molten calcium chloride and F ceramic base to adjust the crucible height; and (b) layout for sealing of electrodes: (i) small nut, (ii) thick silicone ring, (iii) double threaded pipefittings, (iv) top plate, (v) ‘O’ ring and (vi) ceramic tube.
5.2.3 μCT-based quantification of pore and interconnect

The three dimensional structure of both the sintered precursor and reduced samples was characterised using micro-computed tomography (μCT, Phoenix, X-ray Systems and Services GmbH). The reconstructed 3D raw data was analysed to determine the pore and interconnect size using ImageJ [154] and Amira 4.0 (TGS series, Mercury Computer Systems). The procedure for the quantification of pore and interconnect is summarised in Figure 5.4. The major steps involved were the application of a 3x3x3 median and diffusion filter to remove noise (Figure 5.4(a)), pore / interconnect segmentation and labelling in ImageJ and subsequent analysis of 2D data, described below, to derive 3D results. These steps were applied on 2D slices.

After filtering, the image stack was binarized (Figure 5.4(b)) and segmented using watershed algorithm slice by slice (Figure 5.4(c)). The watershed segmentation is required to separate overlapping pores. The segmented slices with isolated pores were labelled and analysed for 2D areal distribution of pores (Figure 5.4(d)). The pores

![Figure 5.4. Procedure to derive 3D pore and interconnect sizes from 2D slice: (a) a filtered slice, (b) after thresholding (a) to label solid and void space, (c) showing the result of watershed segmentation to isolate overlapping pores, (d) isolated pores were labelled to extract quantitative data, (e) subtracting (b) from (c) to isolate individual interconnect and, (f) labelling of the interconnect for further quantification. The procedure was carried out on a number of slices to get a representative number of 2D pores for the analysis.](image-url)
touching the slice edges were not analysed. The radius of each pore was taken as radius of an equivalent circle with the same area. The maximum radius across all the pores, \( R_{\text{max}} \), was calculated. At this step, the pores whose centroid was within an outer shell of thickness \( R_{\text{max}} \) of analysed volume were also excluded from the analysis.

A plane through a 3D random distribution of mono-sized spheres would have a range of circular cross sections, with their maximum diameter equal to the diameter of the sphere. The in-plane areal distribution of circular cross sections is a known function of sphere diameter. Conversely, the analysis is extendible to derive the 3D size distribution of poly-dispersed spheres from their 2D areal distribution in slice [155], summarised below.

First divide the maximum 2D pore size, characterised by its radius \( R_{\text{max}} \), into 12 “classic” intervals, each 10\(^{-0.1}\) smaller than its predecessor. This is equivalent to the maximum radius of the poly-dispersed spheres in 3D. The number density of the pores in 3D in interval \( i \) \((N_{Vi})\), is related to the 2D areal number densities \((N_{Ai})\) as:

\[
N_{Vi} = \alpha_i N_{Ai} - \sum_{j=1}^{i-2} \alpha_{j+1} N_{Ai(i-j)}
\]

where,

\[
\alpha_i = \frac{1}{P_i} \left( \alpha_i P_i - \sum_{j=1}^{i-2} \alpha_{j+1} P_{i-j} \right)
\]

is a conversion coefficient. \( P_i \) is intersection probability of circular cross sections in a 2D slice to fall in the \( i_{th} \) interval (from volume of a 3D mono-dispersed sphere).

The size distribution of interconnects is obtained in a similar manner. The thresholded image (Figure 5.4(b)) is subtracted from the watershed-segmented image (Figure 5.4(c)). The inverse of the resulting image (Figure 5.4(e)) had the interconnects isolated as lines. These line interconnects were labelled like pores and, their Feret diameter (the longest distance between any two points in a line interconnect) recorded (Figure 5.4(f)). Physically interconnects are 2D circular entity. However, if each of the interconnects is represented by an exscribed sphere, each would leave a circular trace in the 2D slice with its diameter equal to its Feret diameter. Now that the areal distribution of the interconnects is known, their 3D size distribution is obtained following the procedure for the pores.

5.2.4 Further characterisation of material

Scanning electron microscopy (SEM) using a JSM840 was used to characterise the microstructure. X-ray diffraction (XRD, using a Phillips PW1710) and Eltra ON900
machine (Eltra, Germany) were employed for phase and post-reduction oxygen analysis, respectively. The ON900 oxygen analyser heats a predetermined weight of a sample in a graphite crucible up to 3000 °C. The oxygen in the sample reacts with the carbon in the crucible and concentration of the CO/CO₂ in the resulting gas is calculated and related the oxygen in the test sample.

Compression testing (ϕ = 5.7 mm, h = 4.7 mm) was performed using a 10 kN load cell universal testing machine (Z010, Zwick, GmbH, Ulm, Germany). PTFE tape was used to minimise contact stresses. The cross head displacement was corrected for machine compliance using standard procedure [117]. To measure Young’s modulus the specimen were unloaded prior to yielding and Young’s modulus was obtained during unloading prior to yielding. This procedure has been shown to yield more accurate modulus than those derived from loading curves in the case of foam [133]. It is pointed out that due to limited production and the difficulties in specimen preparation no tensile/fatigue test was carried out.

The permeability of the foam was characterised using the experimental methods described in Chapter 3 [134].

5.3 Results and discussion
The reduction of an oxide precursor foam made with the standard composition and sintered at 1150 °C (S_1150) is presented first. The influence of processing conditions upon the precursor properties and their subsequent impact on the final reduced metallic foam, are then discussed. The processing variables studied were sintering temperature; ceramic loading in the slurry and reduced atmospheric pressure foaming. The effect of reduction temperature on the physical and mechanical properties of the resulting foam was also investigated. Finally, the mechanical and fluid flow properties are characterised.

5.3.1 Reduction and characterisation of a standard foam
Optical macrographs of the as-sintered (1150 °C) ceramic precursor and the resulting reduced metallic foam are shown in Figure 5.5. A homogeneous distribution of sub-millimetre size pores is evident in both foams, with ~80% of porosity. As in the case of standing liquid metal foams [156], high porosity and very fast gelation of the foam led to the homogeneous foam structure in the precursor, which was retained after the reduction as well. There is significant linear shrinkage (~17%) due to the volume change upon conversion of the TiO₂ to Ti (~6%) and densification of the resulting metallic wall-struts.
The XRD patterns of the oxide powder, sintered oxide precursor and the reduced metal foam are shown in Figure 5.6. The crystal structure of the as received oxide powder was confirmed as anatase. Sintering at above 950°C transformed this into the denser rutile form. Note, in all but the 950°C sintered case (where the anatase form was retained), transformation to rutile occurred. However, prior work by Ma et al. [78] found that the crystal structure of the precursor does not affect the reduction kinetics. After reduction, the XRD patterns confirm that the precursor has transformed into metallic titanium with trace amounts of TiC (Figure 5.6(c)); however, no oxide phases could be identified. TiC is known to form at the cathode as a result of $\text{CO}_2^-$ ion reduction at the cathode [150]. It has been reported that carbonate ions form at the carbon anode by reaction with $\text{CO}_2$ and are reduced at the cathode in the latter stages of reduction. The presence of trace levels of TiC is not considered a problem for scaffold applications as a prior study has shown that TiC coatings cause no adverse affects on cells in culture [157].
Oxygen analysis of the reduced foam sintered at 1150°C showed it was equivalent to a grade 4 CP-Ti, with a level of 0.44 wt.%. Three specimens at different sintering temperatures (1050, 1150, 1250°C) in total were analysed for oxygen content, giving a mean value of 0.34 wt.% with standard deviation of 0.14. The purpose of the current work was to establish proof of principle and no attempt was made to control oxygen content. It is therefore all the more remarkable that the lowest oxygen level obtained was 1650 ± 50 ppm. Given the very high specific surface area of these foams, this is a relatively low level. An oxide coating of 10 nm thickness (a typical thickness for the oxide formed at room temperature [158]) on a 5 μm Ti particle (the length scale of dumbbell foam strut structure) would give 4100 ppm. The current foams have an oxygen level equal or better to results obtained using the space-holder method [117].

Figure 5.6 shows μCT scans of the precursor, the reduced foam, a commercially available titanium implant foam (processed via the space-holder technique, [117]) and human trabecular bone. The gel cast FFC Ti foam has a highly interconnected porous structure, which in combination with its thinner walls, appears to have the closest match in morphology to the human bone. However, the pore and interconnect size in the trabecular bone are larger than either titanium foam.
The pore- and interconnect-size distributions derived from 2D μCT slices are given in Figure 5.8(a-b). The pore size $d_{50}$ was 360 and 340 μm in the precursor and reduced foam, respectively. Figure 5.8(c-d) shows the tomographic slices with pre- and post-reduction spherical morphology of the pores. The interconnect size $d_{50}$ values were 145 and 180 μm in the precursor and in the reduced foam, respectively. Both the pore and the interconnect sizes are compatible for biomedical applications, where the minimum interconnect size of 100 μm is thought to be required for vascularised bone ingrowth [159]. Note that both the pore and interconnect size can be further tailored by altering the foaming conditions, as demonstrated below.
The precursor and the reduced foams exhibited two scales of porosity: primary pores formed by the foaming which have a diameter of approximately 350 μm, and ‘secondary’ intra-strut pores that are micron scaled (Figure 5.9). Analysis of the standard processing conditions has illustrated that the gel cast FFC foams have at least as good properties for implant applications as existing commercial foams.

Figure 5.8. (a) Cumulative pore size distribution of the precursor and the reduced foams (S_1150) and (b) cumulative interconnect size distribution. Typical tomographic slices of the (c) precursor and (d) the reduced foam illustrating the pores’ spherical nature or the pores.
**Figure 5.9.** Secondary electron image of S_1150 showing the two scales of porosity: (a) precursor; and (b) reduced Ti. Primary pores are in the range of 350 µm, contributing to almost all of the porosity and, the secondary pores, 1-10 µm were within foam wall.

It is proposed that this hierarchically structured porosity may offer many unique benefits for biomedical bone implant applications. For example the modulus of the structure will be controlled by both levels of porosity, allowing a range of moduli whilst retaining the large macropore size required for cell in growth and vascularisation [160]. Further, the micron sized porosity within the struts could allow the scaffold to be impregnated with various coatings such as hydroxyapatite [161-162], bioactive glasses [163], or growth stimulating proteins retained within a polymer matrix. There is growing evidence of the
effect of scaffold topography on osteoblastic progenitor cell morphology. In general, rough surfaces have been found to have a favourable influence on cell attachment and growth. Dalby et al. [164] studied the effect of three kinds of surface topography on primary human osteoblast-like cell model. The three different kind of topography on HAPEX™ (hydroxyapatite-reinforced polyethylene composite) substrate studied were: (i) as machined (M), (ii) polished (P) and (iii) roughened (R). They found that the R topography (achieved by placing it in an ultrasonic bath containing 4 $\mu$m Al$_2$O$_3$ particles) was most suitable for osteoblast phenotype expression and subsequent mineralisation and hence closer to an optimal surface for implant application. Gray et al. [165], employing in vitro studies with rat calvarial osteoblastic cells, found increased evidence of bone formation at grooved locations in the scaffold. The surface roughness in these studies varied over two orders of magnitude. In the former it was less than ±2 $\mu$m whereas in the latter study the grooves were 350 $\mu$m wide and of variable depth. Whilst these studies established the superiority of rough surface over a polished one, uncertainty remains as to the optimal degree, shape and extent of surface topographical features.

5.3.2 Effect of processing parameters
Figure 5.10 shows the pore structure of a typical porous ceramic precursor fabricated with the standard composition (S_950). Figure 5.10(b) shows the pore size when the precursor was cast under a reduced atmospheric pressure (~30 kPa applied using a rotary vacuum pump). The pore size distributions of these foams were analysed. The S_950 foam had a $d_{50}$ pore diameter of 373 $\mu$m (Figure 5.10(d)), while the application of a reduced atmospheric pressure increased the mode to 688 $\mu$m, an 84% increase in diameter (or over 6 fold increase in pore volume). The macroscopic pore size can be important for tissue scaffold applications [5]; controlling the pressure allows a simple method for tailoring the pore size to match requirements.
Figure 5.10. (a-c) typical slice of sintered precursors processed under three different conditions: (a) slurry with standard composition and pressure (S_950); (b) the same as (a) but the foam was set under reduced atmospheric pressure of ~30 kPa (S_950 Vac); (c) slurry with low ceramic loading and foam setting standard conditions (1 atm, S_1000_LL); (d) cumulative pore size distribution of the precursors in (a-c); and (e) secondary electron image of the pore wall of S_950.

Figure 5.10(c) shows the result of reducing the ceramic loading of the slurry. Comparing this structure with the S_950 (Figure 5.10(a)), the macroscopic pore sizes were smaller. Figure 5.10(d) shows that the $d_{50}$ diameter decreased to 270 μm (S_1000_LL) from
367 ± 8 μm (S_950 and S_1150). The wall thickness also changed significantly. Within the struts the scale of the sintered ceramic particle network became significantly finer with an increase in the percentage of intra-strut porosity, and hence a reduced overall relative density (see sample S_1000_LL in Table 5.2). Further, the low ceramic loading changed the morphology of the foam walls, leading to highly porous foam strut in the reduced foams (Figure 5.10(c)).

For the range of sintering temperatures tested with standard composition (950 – 1450 °C, see Table 5.2), the precursor percentage porosity was consistently 81 ± 2% and the average macroscopic pore size had a $d_{50}$ diameter of 367 ± 8 μm (calculated on two of the samples S_950 and S_1150). The interconnect $d_{50}$ was 154 ± 14 μm (calculated on two of the samples S_950 and S_1150). Although the percentage porosity remained approximately constant, the sintering temperature had a significant influence on the as-sintered oxide particle size (see Figure 5.11(a-c)). At the lower sintering temperature the walls are highly-interconnected porous structures (Figure 5.11(a)), while at the highest sintering temperature, the walls are solid (Figure 5.11(c)). There was over an order of magnitude increase in the oxide particle size (and spacing between them) as the sintering temperature was raised from 950 °C to 1450 °C, i.e. from submicron size (Figure 5.11(a)) to well over 10 μm (Figure 5.11(c)). The driving force for the increase in particle size is the minimisation of surface area. During sintering, the rate of particle coalescence increases exponentially with increasing temperature due to increased diffusion.

The resulting influence of sintering temperature on the reduced foams is shown in Figure 5.11(d-f). Although there is no effect on the macroporosity, there is a very significant effect on the secondary intra-strut porosity. The morphology of foam walls appears to be very dependent upon the TiO$_2$ grain size in the sintered precursor. For the reduced Ti foam sintered at 950 °C, a fine structure of interconnected Ti nodules and pores (each ~5-10 μm) is formed within the walls, which is termed a dumbbell structure. At a sintering temperature of 1150 °C (Figure 5.9(b)), the nodule size increased as did the pore size (although the pore number density appears to decrease). At the highest sintering temperature, 1450 °C, the intra-strut porosity completely disappeared, forming a solid wall. The sample S_1250_HT was reduced at 1000 °C unlike rest of the samples which were reduced at 910 °C. High temperature reduction resulted in increased consolidation of Ti and a smoother surface as compared to S_1150 (Figure 5.9(b) sintered at a temperature 100 °C less than S_1250_HT). It is worth noting that ceramic loading in the precursor foam had an effect on the intra-strut porosity in the reduced
foam. For example, the sample S_1000_LL (Figure 5.10(e)) exhibited far more porous foam walls as compared to the S_950 (Figure 5.11(d)). The ceramic loading is expected to affect the intra-strut porosity of samples sintered at other temperatures as well. Thus, the factors controlling the intra-strut pore size are much more complex.

5.3.3 Mechanical properties and permeability

The mechanical properties of the reduced foam (S_1150) were measured in compression and compared with a low density commercial titanium foam (78% porosity). The stress-strain response of the two foams is shown in Figure 5.12. The higher porosity (81%) of the gel cast FFC foam, together with its high level of intra-strut porosity leads to a reduction in the modulus and yield stress as compared to the space-holder foam. Under compression, the current foam which had a bulk density less than water (0.85 g cm$^{-3}$) has a yield strength of $\sim$7 MPa and a Young’s modulus of 0.75 GPa. This modulus is
comparable to that for the trabecular structure within a human vertebrae (0.30 GPa [166]).

Another important characteristic of porous implants influencing their biological performance is permeability [124]. The permeability of the standard condition Ti foam was measured as described in the methods, and found to have a value of 158x10^{-12} m^2 (or ~158 Darcy), comparing reasonably to the measured permeability of human trabecular bone (400-11000 Darcy) [167]. The permeability of the current material was slightly lower than those measured in a similar percentage porosity commercial space-holder foams [134]. This is due to the smaller pore and interconnect size (~25%) of the current foam, as well as the higher specific surface area due to the intra-wall porosity.

One of the samples (S_1250_HT) was reduced at 1000 °C. Interestingly, upon reduction this foam shrunk by ~40% as compared to ~17% for those reduced at 910 °C. The yield strength of this foam was 10% higher (7.6 MPa) than the standard foam (S_1150). S_1250_HT also had a high porosity (82%) and permeability (344 Darcys). The high permeability of this foam is probably a result of the smoother surface of the foam (Figure 5.11(e)), since permeability can be approximated as being inversely proportional to the square of the interfacial area [120].

In summary, the combination of gel casting of a ceramic precursor together with FFC reduction has produced a novel hierarchically structured Ti foam, which is capable of achieving a range of pore microstructures and mechanical and physical properties, of particular relevance to biomedical applications. The ability of the current process to

![Graph showing stress-strain behavior](image)

Figure 5.12. Comparison of the stress-strain behaviour in the current Ti foam (S_1150) to one produced via a commercial space-holder technique (78% porosity).
tailor the inter- as well as intra-strut pore morphology independently of each other makes this process unique among the existing methods of titanium foam production. Moreover, the morphology of intra-strut porosity, if optimised, offers the potential to allow controlled drug delivery through embedded coatings.

5.4 Conclusions
A novel methodology for producing hierarchical structure titanium alloy foams has been developed combining gel casting of a TiO$_2$ precursor followed by electrolytic reduction via the FFC Cambridge process. The resulting Ti foam was found to have the following properties:

- A highly interconnected open foam structure with macroscopic pores ($d_{50}$ diameter of $371 \pm 44 \, \mu m$ with large interconnects with $d_{50}$ diameter $204 \pm 29 \, \mu m$ (calculated on S$_{950}$ and S$_{1150}$) appropriate for cell ingress and vascularisation. The porosity of the reduced samples ranged from 72 to 88%. The macropore size was easily altered by varying the gel casting conditions.

- Microporosity (~1-5 $\mu m$) was produced within the strut walls which can be tailored by altering the gel casting conditions. Further, these open cell micron sized pores could allow the scaffold to be impregnated with coatings such as hydroxyapatite, bioactive glasses, or drug release agents.

- The mechanical properties of the resulting hierarchically structured foam are appropriate for tissue scaffold applications, with a very low specific modulus (~1 GPa) and good compressive strength (7 MPa).

- The new Ti foam has a permeability of 29 to 344 Darcys, appropriate for tissue scaffold applications. The bio-inert nature of titanium surfaces (TiO$_2$ and TiC) are non-toxic, though TiO$_2$ has been reported to show bioactive characteristics [70, 168-170].
6 Conclusions

In the first part of this thesis a number of methodologies for characterising the flow and mechanical properties of Ti foams were investigated. Their applicability was determined using a commercially available space-holder foam. In the second part a novel processing route was developed to produce hierarchically structured Ti foam and the techniques developed in the first part were used to characterise it. The conclusions obtained are divided into these two sections.

6.1 Characterisation technique

The \( \mu \)CT-based novel image analysis routines, developed in-house as well as developed under this project, were used for the non-destructive quantification of several key structural characteristics influencing the biological performance of scaffold materials. These included pore size distribution; interconnect size distribution and flow permeability. This was demonstrated on three different titanium foams with porosity levels of 51, 65 and 78%. The modal values of pore (and interconnect) size are 589 (288), 438 (254) and 488 (263) \( \mu \)m for samples with 51, 65, and 78% porosity, respectively; exceeding the minimum requirement for interconnectivity for biocompatibility (100 \( \mu \)m).

To select the foam best matched to cancellous bone, the \( \mu \)CT data was used to perform computational fluid dynamics simulations of nutrient flow. The 65% porous foam was found to closely match the permeability values possessed by healthy cancellous bone. Hence, of the three commercial space holder foams tested, the P65 foam is the most suitable for bone implant applications based on the two criteria used in this study.

A number of techniques for predicting the mechanical properties of the Ti foams were investigated: analytic, micromechanics and direct FEM. The direct FEM approach provided the most accurate predictions for Young’s modulus, yield strength (modulus within 8% of experimental values for P51 and P65) and post yield behaviour. The Gibson-Ashby analytic model gave a reliable prediction for yield strength and its anisotropy by extending it to the more general case of an orthorhombic unit cell. However, this model is only applicable to high porosity foams (>70%). Although the procedure is applicable to most foams and composite materials it was demonstrated here for commercial titanium foam used for biomedical implants.

The post yield behaviour of the 65% porosity foam was characterised using interrupted compression testing in combination with \( \mu \)CT. These results illustrated that the localised collapse of large and unfavourably orientated pores occurs at dispersed points
throughout the volume, which is critical in understanding the failure mechanisms in metallic foams.

### 6.2 Novel hierarchically structured Ti foam

A novel method for producing hierarchically structured titanium alloy foams has been developed combining gel casting of a TiO$_2$ precursor followed by electrolytic reduction via the FFC Cambridge process. The resulting Ti foam was found to have the following properties:

- A highly interconnected open foam structure with macroscopic pores (modal diameter 402 μm for S$_{1150}$) with large interconnects (modal diameter ~208 μm). The porosity of the reduced samples ranged from 72 to 88%. The macropore size was easily altered by varying the gel casting conditions.
- Microporosity (~2-10 μm) was produced within the struts, and its size may be tailored by altering the gel casting conditions. Further, these open cell micron sized pores could allow the scaffold to be impregnated with coatings such as hydroxyapatite, bioactive glasses, or drug release agents.
- The mechanical properties of the resulting hierarchically structured foam are appropriate for tissue scaffold applications, with a very low specific modulus (~1 GPa) and good compressive strength (7 MPa) and compressive ductility.
- The new Ti foam has a permeability of 29 to 344 Darcys, appropriate for tissue scaffold applications. The bio-inert nature of titanium surfaces (TiO$_2$ and TiC) are non-toxic, though TiO$_2$ has been reported to have osteoconductive characteristics [70, 168-170].

The major achievement of this work has been the production of a new Ti foam with a macroporous structure which is more than adequate for cell ingress and vascularisation. Without doubt, these materials show great promise for use as a biomedical implant material of the future. Furthermore, the new process offers a unique opportunity to obtain a structure in metallic foams in general, that might not be achievable otherwise. It has been demonstrated that it is possible to tailor the primary inter-strut pores and the intra-strut porosities independent of one another by a variety of means. Both types of porosity play crucial roles in biomedical applications. The foams are mechanically strong and highly permeable, reinforcing further their suitability as biomedical implant material. It is the author’s belief that, if used to its maximum potential, the new titanium
foam produced in a single step from TiO₂, will replace the conventional and costly space-holder foams entirely.
7 Further work

The objectives of this project were:

(i) To use, and develop as necessary, non-destructive modelling tools to characterise porous scaffolds. These scaffolds were evaluated against their ability to achieve properties deemed crucial for their efficient functioning, and were compared to commercially available titanium scaffolds commonly used in spinal fusion applications;

(ii) To establish the feasibility of producing titanium foam from a novel ceramic (TiO$_2$) precursor route; and

(iii) To characterise the new foam and to optimise the processing conditions to improve upon the existing property portfolio for its intended applications as a biomedical implant.

The characterisation study on the commercial titanium foams performed according to the first set of objectives provided a reference point for the basic properties to be achieved in the new titanium foam under the remaining set of objectives. Although significant progress has been made, further actions are required to realise the full potential of the new material and to push it into real applications. A non-exhaustive list would include: more accurate methodology to determine the cell wall properties, leading to non-destructive determination of the foam properties; further optimisation of precursor making; and optimisation of the FFC process.

Porous medium, though microscopically heterogeneous, is treated as homogeneous for its macroscopic properties such as yield stress and Young’s modulus. Obviously, these properties of the foam would be a function of the cell wall material characteristics and porous architecture. However, exact determination of the cell wall properties presents a difficult set of challenges. For example, the commercial foam made by the space holder technique exhibited a cell wall structure far removed from monolithic titanium. To determine the cell wall properties of this foam, virtual monolithic titanium blocks (processed in a similar fashion to the titanium foam in all respects but for the absence of space holder) were made and tested. However, the titanium blocks exhibited a microstructure that differed slightly from the microstructure of the cell wall in the foam. Since properties are a function of the microstructure, any simulation of foam behaviour based on the properties of the titanium blocks would carry forward the error in input cell wall material behaviour. In the case of titanium, for which the mechanical properties are strongly influenced by the interstitials such as oxygen, extra care is needed to match
these elements in the Ti blocks to that of foam. With regard to the new titanium foam, an attempt to produce a Ti block reflecting the properties of the cell wall of the new titanium foam was unsuccessful due to an inability to dry and sinter a crack-free unfoamed precursor simulating the cell wall material in porous precursor. Thus there is a need to derive cell wall material behaviour directly from Ti foam. Nanoindentation may prove to be a vital tool. Although it is still under development, it has shown great promise.

A major strength of the new process emanates from its ability to tailor the metal foam structure at the precursor making step. The standard gel casting composition studied in the thesis has been reached by maximising TiO$_2$ loading for a given amount of the remaining reagents. This has resulted in a characteristic pore size and morphology which, although very promising for biomedical applications, is not necessarily the optimum microstructure. The effects of altering the quantity of other reagents in the slurry should be investigated. It is thought that the type and amount of the surfactant/s would possibly have the maximum influence on pore size and cell wall characteristics. Other process variables of interest are the application of vacuum just after casting, different means of mechanical foaming, etc. Novel methods of rapid prototyping techniques, such as 3D printing, for making the precursor offer the possibility to produce a structure employing computational topology design to optimise the porous structure.

The overall process would certainly benefit from any progress in the FFC Cambridge process. Notably the effect of double melt electrolysis, use of calcium titanate or lower oxides of titanium in the precursor, the control of oxide ion activity in the molten salt and the reduction temperature are some of the parameters that would have influence on final foam properties. Beta Ti alloys are attractive for biomedical applications due to their lower Young’s modulus. These alloys, if processed via this route, will have the added benefit of increased deoxidation kinetics during the final stage of reduction. This is because oxygen diffusion in the bcc β phase is significantly faster when compared to α Ti alloys. Note that the last stage of deionisation of the Ti-O solid solution is the slowest step of all. Also, the results presented in this thesis, especially the mechanical and transport property (i.e. permeability), are not from a statistically significant quantity of experiments. A greater number of reductions and subsequent characterisation is required to derive a representative value of the aforementioned properties.

Titanium has a very high affinity for interstitial elements such as O, C, and N. Although it was possible to achieve as low oxygen as 0.16 wt% in this project, effort to further
reduce the oxygen and other impurities should improve the ductility of these foams significantly. Ideally, these foams will be coated with other bioactive / osteoconductive surface layer to enhance its \textit{in vitro} and \textit{in vivo} performance. Various surface modification techniques (mechanical, physical and chemical) for biomedical Ti alloy implants, reviewed recently [66, 171], could be evaluated. To conclude, the method of producing titanium foam described in this thesis is quite versatile. Both of the intra-and inter-strut porosities can be tailored independently of each other. However, for biomedical applications, though there are numerous reports of relative importance of pore size and morphology, an optimum structure for a given application and, its dependency on patient specific variables (age, sex, health etc) is elusive. Overall, the process developed here is awaiting input from orthopaedic surgeons and other researchers in biomedical field to allow it to offer its full potential.
References


88. Ho ST, Hutmacher DW. A comparison of micro CT with other techniques used in the characterization of scaffolds. Biomaterials. 2006;27(8):1362-76.


Appendix A: Ultrasound characterisation

The equipment for performing ultrasonic measurements consisted of a pulser-receiver PR 5077 (Panametrics Inc., Waltham, MA USA), an oscilloscope WaveRunner 62Xi (Lecroy Corporation, Chestnut Ridge, NY, USA), and several ultrasonic transducers, which cover the following frequencies $f = 0.05, 0.1, 0.25, 0.5, 1.0, 2.25, 5.0, 10$ and $20$ MHz. The oscilloscope gives access to the time of flight of the ultrasonic wave through the specimen, $t_s$, which together with the travel distance through the specimen, $\ell_s$, gives the phase velocity of the longitudinal or transversal wave, $v_L$ or $v_T$, through the relation $v_i = \ell_s/t_s$. Frequency, $f$, and wave velocity, $v$, of an ultrasonic wave give access to the wavelength, $\lambda$, through $\lambda = v/f$. The apparent mass density, $\rho_{\text{app}}$, of each specimen was determined by dividing its mass, $M$, by its volume, $V$, i.e. $\rho_{\text{app}} = M/V$. The sample-specific porosity, $\phi$ [%], was obtained as:

$$\phi = \frac{\rho_s - \rho_{\text{app}}}{\rho_s} \cdot 100$$ (7.1)

where $\rho_s$ is the density of monolithic titanium.

Combining the conservation of linear momentum law, with the generalised Hooke’s law for the linearised strain tensor, together with the general plane wave solution for the displacements inside an infinite solid medium, the expressions for the elasticity tensor components for an isotropic material as a function of the material mass density and the wave propagation velocity is [15]:

$$C_{1111} = \rho v_L^2 \quad \text{and} \quad C_{1212} = G = \rho v_T^2$$ (7.2)

where $C_{1111}$ and $C_{1212}$ are the elastic stiffness tensor components related to normal and shear deformation; and $G$ is the shear modulus. Young’s modulus, $E$, and Poisson’s ratio, $\nu$, are then defined in terms of these stiffness tensor components by:

$$E = \frac{C_{1212} \left( 3C_{1111} - 4C_{1212} \right)}{C_{1111} - C_{1212}} = \rho \frac{v_L^2 (3v_L^2 - 4v_T^2)}{v_L^2 - v_T^2}$$ (7.3)

and,
The inhomogeneities within a representative volume element (REV, see also Section 2.7.2 and Figure 2.8) of ‘porous titanium’ are the voids with an average diameter of \( d = 350\text{–}400 \, \mu m \). Thus, a longitudinal ultrasonic wave with frequency of 0.5 MHz and velocities of \( \sim 2\text{–}4 \, \text{km/s} \), and a transversal wave with frequency 0.25 MHz and velocities of \( \sim 1\text{–}2 \, \text{km/s} \) (see Table 4.1), implying wavelengths of \( \sim 4\text{–}8 \, \text{mm} \), characterise an REV of ‘porous titanium’ with \( \ell_{\text{REV}} \geq 1.1 \, \text{mm} \).

Because of the practical absence of inhomogeneities in CP-Ti (\( d \ll 0.01 \, \mu m \)) it can be characterised over the full frequency range of 0.05 – 20 MHz, employing wavelength of 0.3 - 120 mm for longitudinal waves (Table 4.1).
Appendix B: Measurement and modelling of permeability

The experimental procedure to measure the permeability, as described in Section 3.2.4, involved taking at least four sets of measurements of the steady state flow rate as a function of pressure gradient. Table B1 lists all such measurements of pressure gradient and the steady state flow rate for foams P51, P65 and P78. A plot of applied pressure difference vs. steady state flow rate would result in a linear curve if the flow were

Table B1. Measured steady state flow rate as a function of pressure gradient.

<table>
<thead>
<tr>
<th>Direction</th>
<th>Reading No.</th>
<th>P51</th>
<th>P65</th>
<th>P78</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Delta P/L$, Pa/m</td>
<td>$v_o$, m/s</td>
<td>$\Delta P/L$, Pa/m</td>
</tr>
<tr>
<td>x</td>
<td>1</td>
<td>219275</td>
<td>0.00149</td>
<td>75574</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>333200</td>
<td>0.00221</td>
<td>141709</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>640675</td>
<td>0.00412</td>
<td>311255</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1316875</td>
<td>0.00722</td>
<td>528899</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>723697</td>
<td>0.0401</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td></td>
<td></td>
<td>218659</td>
</tr>
<tr>
<td>y</td>
<td>1</td>
<td>73399</td>
<td>0.0006</td>
<td>61250</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>191160</td>
<td>0.0014</td>
<td>159250</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>354897</td>
<td>0.0026</td>
<td>379750</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>601712</td>
<td>0.0042</td>
<td>595350</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>795025</td>
<td>0.0503</td>
</tr>
<tr>
<td>z</td>
<td>1</td>
<td>65678</td>
<td>0.0003</td>
<td>71050</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>163070</td>
<td>0.0008</td>
<td>161700</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>310374</td>
<td>0.0014</td>
<td>382200</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>473504</td>
<td>0.0020</td>
<td>673750</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>658548</td>
<td>0.0027</td>
<td>1033900</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>799765</td>
<td>0.0030</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1046896</td>
<td>0.0038</td>
<td></td>
</tr>
</tbody>
</table>
Darcian. However, Figure 3.2 (as was the case with P51 and P78) shows that the range of experimental pressure difference applied resulted in non-Darcian - i.e. non-linear-flow. It is for this reason that the Dupuit-Forchheimer equation (Eq. 3.1) was employed

![Figure B1. Linear variation of ($\Delta P/(L\nu)$) as a function of seepage velocity ($\nu$).](image-url)
to account for the non-linearity. The experimental data were plotted as \( \frac{\Delta P}{\Delta L v_0} \) as a function of \( v_0 \) in Figure B1 (a-c); the symbols used are as defined in Eq. 3.1. From Eq. 3.1, a linear interpolation of the data in Figure B1 (a-c) would have a \( y \)-intercept equal to the ratio between fluid viscosity and the permeability. The permeability was thus obtained from the values of \( y \)-intercept and the known fluid viscosity.

**Simulation of permeability**

Simulation of permeability was performed under boundary conditions (see Section 3.2.5) such that the flow remained in the laminar region. Prior study has indicated that if the Reynolds number is <0.1, then the flow remains laminar for flow through a porous medium as used in this study [110]. During this simulation, the Reynolds number remained relatively low (approx 0.001), thus ensuring Darcian flow. It is noteworthy that a very high Reynolds number (as high as >2000) is required to deviate from laminar (i.e. pure viscous, Darcian flow) in a tube.

The slight non-linearity at the inlet and outlet (Figure 3.4) is due to the end effect [172]. At the outlet, an all-fluid buffer layer is required to counter the reverse flow. In the close vicinity to the inlet, the flow is turbulent. However, in only a short distance past the inlet, flow becomes stable. In the middle region the pressure varied in a linear fashion. The minor deviations from linearity may be attributed to localised structural changes in the simulated volume. The apparent random deviation from linearity (noise) will be eliminated if sufficient numbers of data are sampled. Ideally, these simulations should have been validated with results which are closer to the experimental non-Darcian flow regime. However, due to computational instability, no simulation was performed in the regime where the flow becomes turbulent/non-Darcian.