Processing and mechanical properties of autogenous titanium implant materials

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Pure titanium and some of its alloys are currently considered as the most attractive metallic materials for biomedical applications due to their excellent mechanical properties, corrosion resistance, and biocompatibility. It has been demonstrated that titanium and titanium alloys are well accepted by human tissues as compared to other metals such as SUS316L stainless steel and Co–Cr–Mo type alloy. In the present study, highly porous titanium foams with porosities $\leq 80\%$ are produced by using a novel powder metallurgical process, which includes the adding of the selected spacers into the starting powders. The optimal process parameters are investigated. The porous titanium foams are characterized by using optical microscopy and scanning electron microscopy. The distribution of the pore size is measured by quantitative image analyses. The mechanical properties are investigated by compressive tests. This open-cellular titanium foams, with the pore size of 200–500 μm are expected to be a very promising biomaterial candidates for bone implants because its porous structure permits the ingrowths of new-bone tissues and the transport of body fluids.

1. Introduction

Pure titanium and some titanium-based alloys are nowadays the most attractive metallic biomaterials for orthopedic and dentistry implants due to their excellent mechanical properties, wonderful biocompatibility, and good corrosion resistance while SUS316L stainless steel and Co–Cr–Mo type alloys are still extensively used [1–3]. Titanium and Ti-6Al-4V have been registered in the ASTM standards and used in the biomedical fields since a long time ago [4, 5]. Recent investigations demonstrated that titanium forms a dense layer of nanometer-scale hydroxy-carbonate apatite (HCA) crystal agglomerates on its surface *in vivo* after subjected to some appropriate surface treatments, and the bonding strength of the apatite layer to the substrates are relatively high [6, 7]. It is believed that bioactive metals such as titanium alloys are useful as bone substitutes, even under load-bearing conditions.

Unfortunately, most bulk metallic implant materials in use today, including titanium and its alloys, continue to suffer from problems of interfacial stability with host tissues, biomechanical mismatch of elastic moduli, production of wear debris and maintenance of a stable blood supply [8, 9]. Therefore, *in vivo* degradations, primarily as a results of the higher wear rates associated with artificial implant materials, and the consequent adverse biological effect of the generated wear debris, results in a shorter lifetime for these artificial implants when compared with natural bones. All present day implants lack two of the most critical characteristics of natural bone tissues: (1) capable of self-repairing and (2) capable of modifying their structure and properties in response to environmental factors such as mechanical load or blood flow. The consequences of the above-cited limitations are profound. To date, all implants have limited lifetimes. Many years of research and development have led to only unessential improvements in the survivability of orthopedic, cardiovascular, and dental or ENT implants at more than 15 years [10, 11]. Yet, as we look forward to the future, we see that we are on the brink of a major breakthrough in health care. Bone is one of the few organs capable of self-regeneration following injury. Hence the emerging of tissue engineering has been motivated by the challenge of producing tissue substitutes that can restore the structural features and physiological functions of natural hard tissues *in vivo*. A major goal of tissue engineering is to synthesize or regenerate tissues and organs. Today, this is done by providing a synthetic porous scaffold, or matrix, which mimics the body's own extracellular matrix, onto which cells attach, multiply, migrate and function. These porous biomaterials rely on their osteoconductive properties to facilitate the migration of osteoblasts from surrounding bone into the implant site and hence assist the healing process. Autogenous bone implant is the best substitute for replacing defect bone at this moment.

The porous matrix must be designed to satisfy several requirements. Firstly, the bulk materials must be

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biocompatible and bioactive. The porous structure must also be designed with high porosity, which provides sufficient space for the attachment and proliferation of the new-bone tissues and the transport of the body fluids. Meanwhile the pore size must be within a critical range usually 200–500 μm: the lower bound is controlled by the size of the cells ($\sim$ 20 μm) while the upper bound is related to the specific surface area through the availability of binding sites. The cellular structure must be interpenetrated to allow the ingrowths of cells, vascularization and diffusion of body fluids [12–17]. And the material must be of appropriate mechanical properties resist handling during implantation and *in vivo* loading. The advantages of cellular metals have been explicitly described in some recent investigations and review [18, 19]. Of particular interest are the mechanical properties and the porous structure that open-cellular foams offer for the adjustable young's moduli, the appropriate mechanical strengths, and the regeneration capability of the new-bone tissues and the transport of body fluids within the pore structure.

The present study was undertaken to develop a matrix that combines the biocompatibility and osteoconductivity of porous titanium foam with controllable pore shape, pore size and porosity. A new fabricated technique, which includes the adding of the selected spacers into the starting powders, for the manufacturing of porous titanium was investigated. The fabricated titanium foam was characterized by optical microscopy, scanning electron microscopy and pore-image analyzes. The compression tests were performed on the titanium foams for studying the mechanical properties.

2. Experimental procedures

2.1. Starting materials

Commercially available titanium powders (purity: $\geq$ 99.9%) and ammonium hydrogen carbonate particles (purity: $\geq$ 99%, powder size: 200–600 μm) were used as starting materials in the present study. Effect of titanium powder size was tested on various sizes from 10 to 150 μm. It was found that titanium powders with a size under 45 μm shown the best effects both in the green-compacting and the sintering processes. The selection of the size of the ammonium hydrogen carbonate particles was decided according to the empirical investigations. These particles have a spherical shape and functioned as spacer material. The choosing of the spacer material was based on its chemical properties, i.e. the capability to hold spaces of pores at the room temperature and to decompose completely at relatively low temperatures so as to avoid the reaction with the titanium powders. The weight ratios of the titanium powders to the spacer particles were calculated to obtain the desired porosities of up to 80% in sintered compact.

2.2. Powder metallurgic process

Fig. 1 shows schematically the processing steps of the powder metallurgic process. This process began by mixing the titanium powders and the spacer particles in an agate mortar thoroughly. After the ingredients homogeneous blended, powders of the mixture were uniaxially pressed at various pressures from 50 to 200 MPa into green compacts. In this study cylindrical compacts and quadrilateral plates were fabricated for examining the macro- and micro-structural characteristics and the mechanical properties, respectively. The green compacts were then heat-treated to burn out the spacer particles, and to sinter into highly porous titanium foams. The heat-treatment process is consisted of two steps as at 200 °C for 5 h and 1200 °C for 2 h.

2.3. Characterization of the autogenous titanium foams

Optical microscopy and scanning electron microscopy were used to characterize the sintered open-cellular titanium foam samples. To determine the porosity, sintered titanium foams were embedded in a cold-mounting acrylic material (dibenenzolperoxide), transversely cut by using a diamond wafering blade and the cut surfaces polished to 1200 grit silicon carbide paper finish. The pore size distributions were measured by quantitative image analyses. Finally, compression tests were carried out on the specimens with a size of $\varnothing 12 \times 15$ mm at room temperature with an initial strain rate of $10^{-3}\,s^{-1}$.

3. Results and discussions

3.1. Microscopical observation

The scanning electron micrograph of the porous titanium is shown in Fig. 2. It can be seen that there are two types

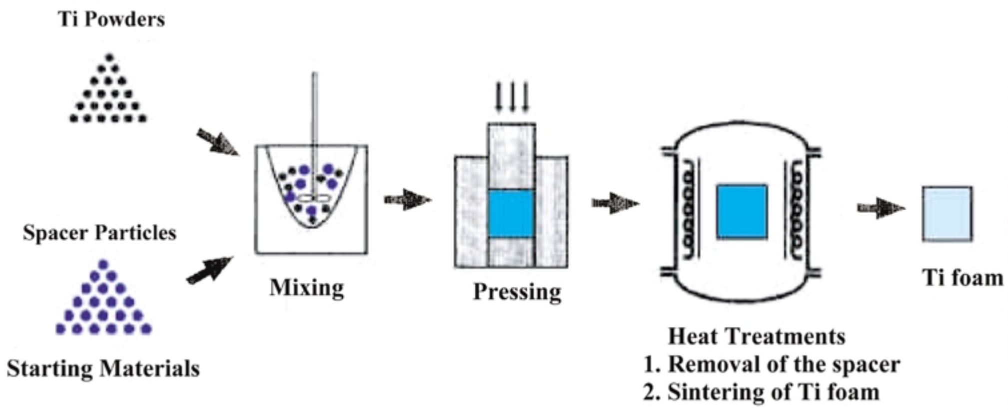

Figure 1 Schematic illustration of the fabrication process for biocompatible porous Ti foams.

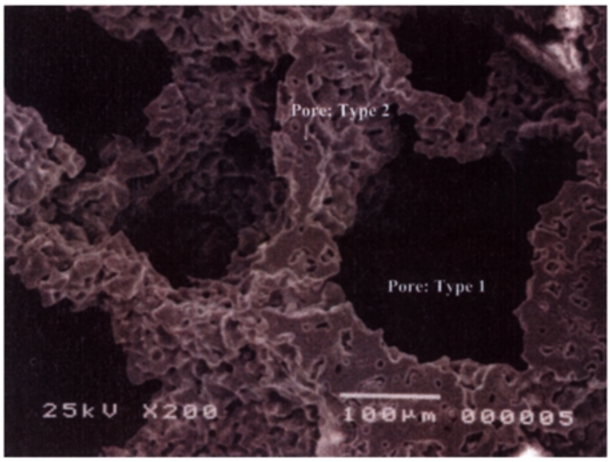

Figure 2 Scanning electron micrograph of the biocompatible porous Ti foam.

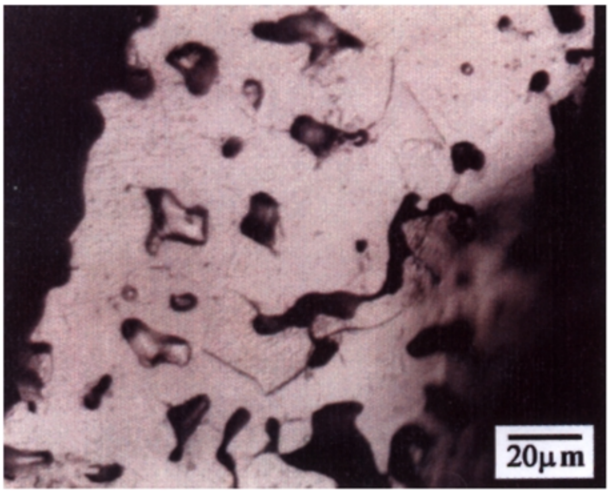

Figure 3 Optical micrograph of a ligament of the porous Ti foam.

of pores in the sample, marked as type 1 and type 2. Type 1 pores is a kind of interpenetrating macro-pores with the size in a range of 200–500 μm, specifically fabricated for its appropriateness for the ingrowths of the new-bone tissues and the transport of the body fluids. Simultaneously, type 2, much finer micro-pores with a size of several micrometers, can be observed in this micrograph. It is presumably resulting from the volume shrinkages that occurred during the sintering process of the titanium powders. The cell walls of the porous titanium foam were rough and honeycomb-like. These features of micro-porous and rough wall-surface are preferable in osteoinductivity [20]. The optical micrograph of a ligament of the porous titanium is shown in Fig. 3. Micro-pores with an average size of 12 μm can be observed obviously in this picture. The porosity of the porous titanium foam is 80% measured by image analyzes. Fig. 4 shows the pore size distribution of the titanium foam sample.

3.2. Compressive properties

3.2.1. Plateau stress

Mechanical properties of the porous titanium foams were studied by compression tests. The nominal stress–nominal strain curves of the porous titanium foams

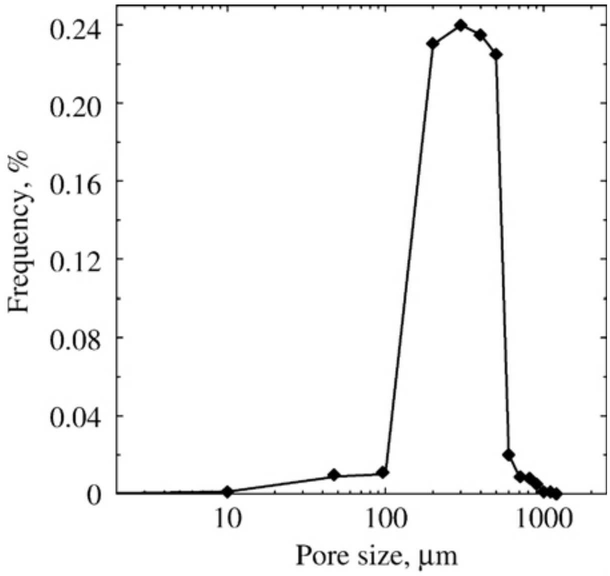

Figure 4 Pore size distribution of the biocompatible porous titanium fabricated by powder metallurgy.

with a porosity of 80% fabricated by powder metallurgical process is shown in Fig. 5. It can be seen that the three curves from three titanium foam samples show the very similar universal characteristics of metallic foam, i.e. an elastic deformation stage at the beginning of deformation, a long plateau stage with a nearly constant flow stress to large strain, about 62% for theses foams, and a densification stage where the flow stress rapidly increases. The deformation occurs in similar manner with three stages in these three foams.

The mechanical properties of the metallic foams have been widely investigated [18, 21–22]. According to Gibson–Ashby model [18], the most important structural characteristic of a foam that influence the plateau stress is its relative density, ρ/ρ_s (the density of the foam ρ, divided by that of the solid material ρ_s). The relationship between the relative stress and the relative density is given by:

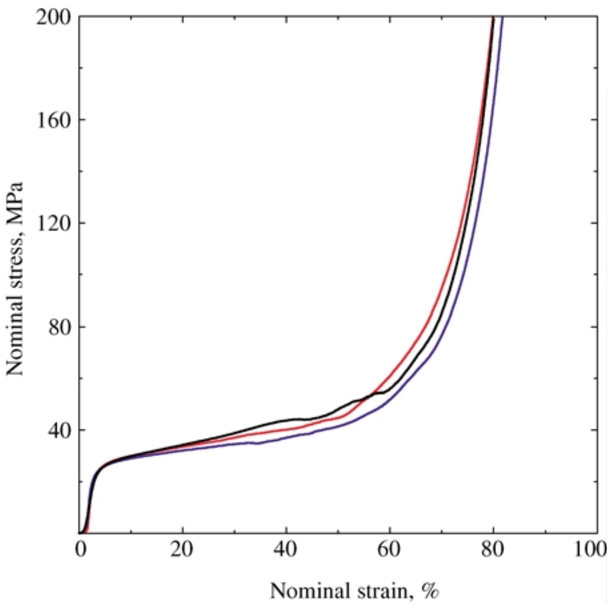

Figure 5 Nominal stress–nominal strain curves of the porous titanium foams with a porosity of 80%.

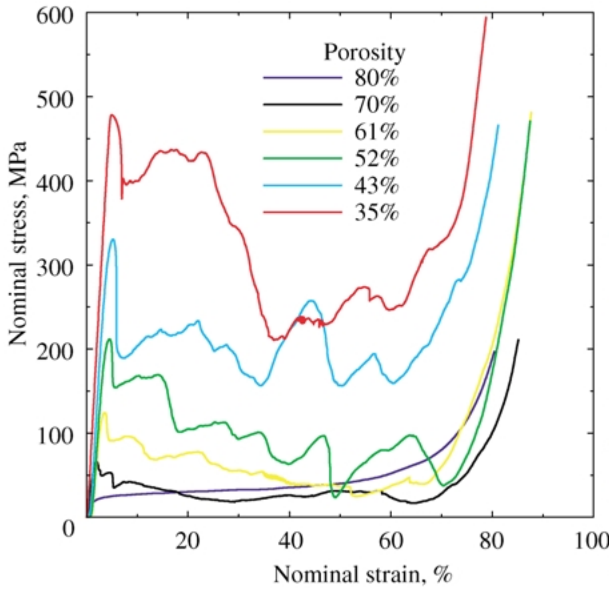

Figure 6 Nominal stress–nominal strain curves of porous titanium foams with various porosities of 35–80%.

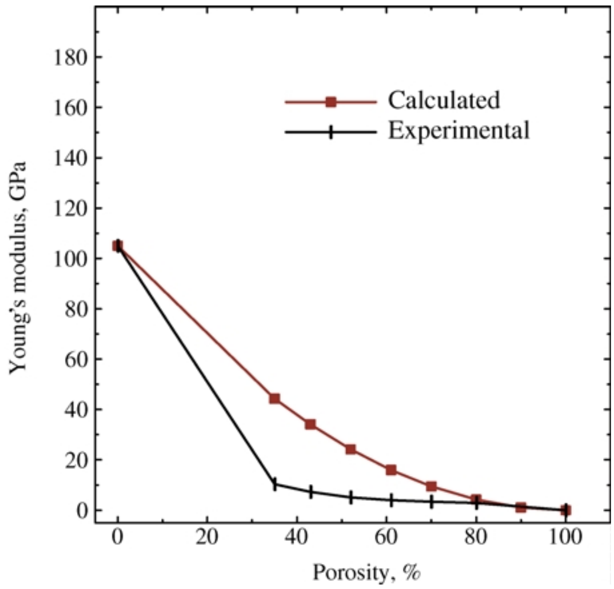

Figure 7 Effect of the porosity on the Young's modulus of the titanium foams.

$$\sigma_{pl}/\sigma_{ys} = C(\rho/\rho_s)^{3/2} \qquad (1)$$

where σ_{pl} is the plateau stress of the foam as mentioned above, σ_{ys} is the yield stress of the cell edge material and C is a constant. Equation 1 indicates that the plateau stress of the foam is proportional to the product of the yield stress of the cell edge solid and the three-seconds power of the relative density. Gibson and Ashby demonstrated that the value of C is 0.3 from the data of cellular metals and polymers. In this study, the plateau stress of the porous titanium foams is approximately 40 MPa, and the density of the foam is 0.90 g/cm^3. The yielding stress of pure titanium is 692 MPa [3]. Substituting these values into Equation 1, it can be seen that the plateau stress of the titanium foams is higher than the theoretical value of 18.57 MPa, predicated by the Gibson–Ashby model (1). Probably this is because the structural difference between the foams fabricated by powder metallurgy and the foams fabricated by casting [22]. Also, the yielding stress of the titanium foams fabricated by powder metallurgical process may be higher than that of the pure titanium due to that the sintering process may enhance the titanium itself.

The plateau stress of the porous titanium foams with a porosity of 80% is approximately 40 MPa, which is presumably strong enough to resist handling during implantation and in vivo loading.

Fig. 6 shows the nominal stress–nominal strain curves of the porous titanium foams with various porosities of 35–80%. It can be seen that the plateau stresses increase with the decreasing of the porosities of the titanium foam.

3.2.2. Young's modulus

A number of micromechanical models have been developed to describe the mechanical behavior of foams. According to Gibson and Ashby [18], the single most important structural characteristic of a cellular solid influencing the Young's modulus E is its relative density, ρ/ρ_s. For an open-cellular foam, the Young's modulus E is proportional to the density raised to the second power, namely,

$$E/E_s = A(\rho/\rho_s)^2 \qquad (2)$$

where A is a constant of 1 including data of rigid polymers, elastomers, metals and glasses. The Young's modulus E of the porous titanium foam is 2.87 GPa in the present study. According to Equation 2, E_s, the Young's modulus of the pure titanium is 105 GPa [3]. Substituting the value of E_s into Equation 2, it can be seen that the theoretical value of the Young's modulus of the porous titanium foam predicated by Gibson–Ashby model (2) is 4.2 GPa. Therefore it can be deduced that the experimental data of the Young's modulus of the porous titanium foam approximately agrees with the Gibson–Ashby model (2) in the present study.

Fig. 7 shows the effect of the porosity on the Young's modulus of the titanium foams fabricated by powder metallurgy. The black points are from the experimental data, and the red points are from the calculations according to Gibson–Ashby Equation 2. It can be seen that the young's modulus decreases with the increasing of the porosity of the titanium foam. Both lines of the calculated and the experimental demonstrated the same tendency. There are small differences between the experimental data and the calculated data when the porosities of the titanium foams are smaller than 70%. But the two lines coincide when the porosities of the titanium foam are 70% and larger, i.e. the experimental data agree with the theoretical data according to Equation 2. According to Gibson and Ashby, the pore walls thicken and the pore space shrinks as the porosity decreases, or the relative density increases; above about 0.3 there is a transition from a cellular structure to one which is better thought of as a solid containing isolated pores [18]. Therefore, Equation 2 is no longer applicable to those titanium foams with porosities below than 70% in the present study.

The properties of titanium foam alloys extend significantly beyond those of dense titanium alloys, opening the door to a broad spectrum of applications that were impossible before. Open-cellular titanium foams with the pore size of 200–500 μm, produced by powder metallurgic process, is an excellent candidate for porous implant because its porous structure permits the ingrowths of new-bone tissues and transport of body fluids. It can be seen that the powder metallurgical process used in the present study can produce titanium foams with controlling porosity, pore size and pore shape, which is ensured by the selecting of the spacer. The strength of the porous titanium foam with the highest porosity of 80% in this study is approximately 40 MPa, which is presumably strong enough to resist handling during implantation and *in vivo* loading. The Young's modulus of the biocompatible porous titanium foam is 2.87 GPa.

4. Conclusions

Open-cellular titanium foams with high porosities up to 80% have been successfully manufactured by a powder metallurgical process. The pore size distribution of the titanium foam is in the range of 200–500 μm. The strength of the porous titanium foam with a porosity of 80% is approximately 40 MPa, which is presumably strong enough to resist handling during implantation and *in vivo* loading; the Young's modulus of the porous titanium foam is 2.87 GPa. To meet practical application needs, the strength and the Young's modulus of the porous titanium foam can be adjusted through the adjustments of the porosity of the foam. The strength and the Young's modulus increase with the decreasing of the porosity. The pore size and the pore shape can also be changed via the choosing of the spacers. These kinds of titanium foams are expected to be used as biocompatible implant materials because its open-cellular structure permits the ingrowths of the new-bone tissues and the transport of the body fluids.

Acknowledgments

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