Influences of sintering temperature on pore morphology, porosity, and mechanical behavior of porous Ti

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Abstract

The purpose of this study was to determine the influences of the sintering temperature on the pore morphology, porosity, and mechanical behavior of titanium foams. Porous Ti samples were successfully manufactured using the metal powder metallurgy method in conjunction with sintering at the four temperatures (900, 1000, 1100, and 1200 °C). The sintering temperature significantly influenced the pore morphology, porosity, and mechanical behavior of the titanium foams. The titanium foams were characterized using an optical microscope in conjunction with scanning electron microscopy. A fracture showed the appearance and growth of a sintering neck between adjacent particles. As the sintering temperature increased, the sintering necks gradually became clearer. The porosity decreased from 56.48% to 46.83% as the sintering temperature increased from 900 °C to 1200 °C, while the initial yield strength of the porous titanium increased from 101.81 to 208.01 MPa. The porous titanium foams produced by the metal powder metallurgy method have a significant utilization potential in hard-tissue engineering.

1. Introduction

Over the past few years, foamed metals have become outstanding novel structural and functional materials. The two primary characteristics of metal matrices and pores provide them with the structural characteristics and excellent performances of both metal and porous materials [1–4]. Compared to conventional bulk metals, these incomparably lightweight foam metals have not only good conductivities, impact toughnesses, thermal shock resistances, and weldabilities as metal properties, but also characteristics of porous materials with small bulk densities, small relative masses, large specific surface areas, high specific mechanical values, good sound absorption, good transmission, and good damping [5]. Nowadays, the remarkable mechanical properties, excellent biological compatibility, and good resistance to corrosion of porous titanium materials make them the most promising biomedical metal materials, which have been applied in various industries [6–8]. For example, the good resistance to corrosion in numerous environments is attributed to the capacity of titanium to produce a steady oxidation protective coating. Thus, Ti and Ti alloys are ideal materials for biological implants [9]. The strength and Young modulus of a titanium foam material can be adjusted by controlling its porosity to match those of the human bone. Thus, stress shielding can be effectively avoided in titanium implantation [10]. Although porous titanium materials have been used in numerous industries in recent years, various problems need to be overcome in the research and popularization of porous titanium. To improve the performance index of porous titanium to address practical needs and expand its application field, the pore
morphology, porosity and mechanical behavior of porous Ti have been investigated using different methods. Ahmad et al. [9] successfully produced porous titanium using the slurry foaming method combined with vacuum sintering and reported that the density of porous titanium is proportional to the compression strength but inversely proportional to the porosity as the sintering temperature increases. Ibrahim et al. [11] fabricated porous Ti and Ti5Mn alloys using powder metallurgy by adding 2-wt.% TiH₂ as a foamer and 15-wt.% NH₄HCO₃ as a pore-forming material. The powders were consolidated by spark plasma sintering under 16 MPa and under pressureless conditions. Under pressureless conditions, the porosity of the porous material decreased with the increase in the sintering temperature. The elastic modulus increased from 35 to 51.83 GPa with the sintering temperature in the range of 950 to 1100 °C. Zou et al. [12] used the fiber sintering method to prepare porous titanium with three-dimensional (3D) through-through pore characteristics, where the porosity was between 29% and 84%. When the porosity was between 55% and 60%, the compressive yield strength was between 150 and 230 MPa, while the elastic modulus was between 4.0 and 4.2 GPa, similar to those of the human bone tissue. 3D printing and sintering methods can also be used to prepare porous titanium. Ghassemieh et al. [13] showed that the porosity varied from a maximum of approximately 65% at the surface to the range of 30% in the interior below the final sintering temperature of 1100 °C. Between 97% and 99%, the internal porosity was interconnected. In addition, Esen et al. [14] used a Mg powder as a space holder to mix the Mg powder with a Ti–6Al–4V alloy powder and pressed it into a shape. The mixed powder was sintered under the protection of Ar to volatilize the Mg powder and the porous Ti–6Al–4V alloy was prepared with an elastic modulus of 1.42–14.7 GPa and strength of 28.2–150 MPa. The manufacturing techniques and experimental parameters significantly affected the pore characteristics of the porous Ti. Thus, the corresponding mechanical properties and uses were also considerably different. Although experimental studies have elucidated the required properties of porous titanium, the quantitative results are not satisfactory, and systematic research is lacking.

In this study, the porous Ti samples are fabricated by the metal powder metallurgy method [15]. To obtain a porous sample, urea with a small particle size was used as a space holder. The microstructures of the samples were characterized using an optical microscope and scanning electron microscopy (SEM). This research aims to investigate the effects of sintering temperature on the relevant morphological and mechanical properties, namely porosity, pore interconnectivity, pore size distribution, yield strength and Young’s (elastic) modulus of porous Ti samples in order to determine the suitable sintering temperature for the manufacture of titanium dental implants using space-holder technique. It provides guidelines for the future utilization of porous Ti in hard-tissue engineering.

2. Experimental methods

2.1. Powder preparation and consolidation
A commercially pure Ti powder (purity: 99.99%), supplied by Xingrongyuan Technology Co., Ltd (China), with an average particle size of 30 μm, was used in this experiment. The powders had irregular shapes. X-ray diffraction (XRD) was employed to analyze the phase composition of the Ti powder in a scanning range of
5°–90° with a scanning step of 0.0217° s⁻¹. The microstructures and XRD patterns are shown in figure 1. Urea was selected as the pore former because of its superior spherical form and chemical characteristics [16]. The morphology of urea is shown in figure 2. The urea particles were filtered to a size range of 60–80 μm. The volume fraction of urea was 60%. The compositions and specifications of the raw materials are listed in table 1. The auxiliary lubricant material zinc stearate (its main function is to lubricate the punch and concave die walls of the grinding tool to ensure smooth extrusion and stripping to obtain a good-quality raw compaction) and argon gas with a purity of 99.999% and flow velocity of 1 l·min⁻¹ used in the washing furnace before powder mixing and heat treatment were also employed.

The mixture was prepared by mixing urea and titanium powder for 10–15 min to obtain a more uniform distribution of urea and titanium powder to prepare a porous titanium with a stable structure. The final powder mixture was compacted in a cylindrical steel mold. In our previous work [17], the initial yield strength of porous titanium prepared at 150 MPa reached 222.69 MPa and excessive pressing pressure will bring negative influence to the pressing of powder and the demoulding of raw billet. The best pore characteristics and mechanical behavior were obtained for a porous Ti prepared at 150 MPa. During the sintering, the compaction pressure was 150 MPa, while the heating rate was 10 °C min⁻¹ in the whole cycle. When the pressure gauge was stabilized at 150 MPa, the pressure was maintained at 60 S, so that the pressure could be effectively transmitted in the mixed materials; the arch bridge effect was avoided. Finally, the prepared green compacts were placed in a vacuum induction furnace to avoid oxidization. Based on the differential thermal analysis of the urea and sintering of Ti powders, the heat treatment included three steps, at 200 °C for 3 h to remove moisture, at 400 °C for 1 h to decompose urea, and at 900, 1000, 1100, and 1200 °C for 3 h to proceed with the high-temperature sintering, followed by furnace cooling. Only the sintering temperature was varied in this study.

### 2.2. Material characterization

The pore morphological characteristics of the samples were analyzed using SEM and metallographic analysis. The porosity (p) of the titanium foam, i.e., the ratio of the pore volume to the total volume, was calculated as:

| Material       | Purity (%) | Particle size (μm) |
|----------------|------------|--------------------|
| Titanium powder| 99.99%     | 50                 |
| Urea           | 99.5%      | 60–80              |
| Zinc stearate  | 99.5%      | 1–2                |

Figure 2. Morphology of urea.
\[ P = \left(1 - \frac{\rho}{\rho_s}\right) \times 100\% \]  

where \( P \) is the total porosity percentage, \( \rho \) and \( \rho_s \) are the densities of the specimen and theoretical density of titanium (\( \rho_s = 4.51 \text{ g cm}^{-3} \)), respectively, and \( \rho/\rho_s \) is the relative density. The densities of the produced specimens were determined using the Archimedes method [18]. The apparent density of the porous titanium was determined by weight and dimension measurements. Using a ruler, the length, depth, and width of the sample (expressed in centimeters) can be measured [19].

A compression testing machine (MT-5150) was used to evaluate the compression performances of the samples. The movement rate of the pressure head was 1.5 mm min\(^{-1}\). The mechanical properties, such as the yield strength, of the porous titanium were investigated. The yield strength was defined as the stress producing a 0.2% residual deformation.

### 3. Results and discussion

Figure 3 shows metallography images of the titanium foams produced at the four sintering temperatures. According to the observation by optical microscope, the pores of the porous titanium were densely distributed without obvious defects and the overall distribution of the pores was uniform, indicating that the urea and titanium powder were fully mixed and evenly distributed in the raw billet during the mixing and pressing stages. At sintering temperatures of 900 and 1000 °C, the change in pore size was not obvious, but the number of pores was significantly larger than that at sintering temperatures of 1100 and 1200 °C. When the sintering temperature was 1100 °C, the pore size, connected structure, and local pore wall thickness increased. When the sintering temperature was further increased to 1200 °C, the pore size was decreased, while the pore wall thickness was further increased.
The microstructures, porosities and pore structures of the porous titanium samples were evaluated by SEM, with a working distance of 23.29 mm and high voltage of 20.0 kV. Figure 4 shows SEM images (at magnifications of 30, 200, and 1000×) of the titanium foam samples obtained at the four sintering temperatures (a) 900 °C; (b) 1000 °C; (c) 1100 °C; (d) 1200 °C.

**Figure 4.** SEM morphologies (at magnifications of 30, 200, and 1000×) of the porous Ti samples obtained at the four sintering temperatures (a) 900 °C; (b) 1000 °C; (c) 1100 °C; (d) 1200 °C.

The microstructures, porosities and pore structures of the porous titanium samples were evaluated by SEM, with a working distance of 23.29 mm and high voltage of 20.0 kV. Figure 4 shows SEM images (at magnifications of 30, 200, and 1000×) of the titanium foam samples obtained at the four sintering temperatures. In the sintering, with the increase in the sintering temperature, owing to the diffusion of atoms outside the particle and pressure triggered by the interfacial tension, the Ti atoms flow toward the contact point of the particles [9]. Thus,
the point contact gradually expands to face contact, produces the sintering neck, which continues to grow, and finally changes the pore shape, size, and number.

Figure 4 shows that the specimens sintered at the four temperatures have good qualities. The low-magnification SEM morphology shows numerous pores with a uniform distribution, irregular shape, and large difference in size; most of them are open holes. With the increase in temperature, the high-magnification SEM morphologies show that the bonding surface and sintering neck gradually formed and expanded, the growth platform gradually became obvious, the number of micropores decreased, and the size of macropores initially increased, and then decreased, indicating that higher temperatures facilitated the continuous diffusion and migration of atoms and continuous densification of the substrate during the entire sintering.

When the sintering temperature was 900 °C, the titanium particles were concentrated together, the sintering neck between the particles was small, the pore edge was sharp and rough, the junction of the pore wall was small, and there were numerous micropores without closure on the pore wall. At 1000 °C, the number of macropores tended to be smaller, the pore size was slightly increased, the pore edge became smooth, and the roughness of the pore edge was further decreased. When the sintering temperature was increased to 1100 °C, the number of micropores on the pore wall was largely reduced and the micropores were almost round. The size of the macropores was increased, whereas the number of macropores was increased significantly. The sintering neck was thickened and layered growth steps appeared. This indicates that the sintering conditions were good at this temperature. At 1200 °C, the sintering neck was thicker and the growth steps were more obvious. The number of micropores in the pore wall was significantly reduced compared to that before and the size of the micropores on the pore wall was smaller, which tended to be closed.
Figure 5 shows the influence of the sintering temperature on the porosity ($\varepsilon$) of the porous titanium. It demonstrates that the porosity has a strong dependence on the sintering temperature. The increase in the sintering temperature from 900 to 1200 °C decreases the sample porosity to 56.48%, 50.72%, 47.82%, and 46.83%. This was expected as at higher sintering temperatures metal powder particles become soft and ductile, which increases the contact areas and slightly decreases the void size [20]. As the temperature increases, the porosity difference of the porous titanium gradually decreases and tends to slowly change. When the sintering temperature increases from 1100 to 1200 °C, the change in the porosity is only 0.99%. At this moment, the change in the porosity is reflected mainly in the closure of micropores in hole walls and further shrinkage of macropores. When the sintering temperature increases from 1100 to 1200 °C, the change in porosity is smaller than 1.00%, which also indicates that the sintering power brought by the increase in the sintering temperature is not obvious. When the temperature reaches 1100 °C, the sintering of the porous titanium reaches a relatively ideal state with a good pore structure.

The yield strength and Young modulus are crucial mechanical properties of metal foams [21, 22]. The stress–strain curves and initial yield strengths at different sintering temperatures obtained by the mechanical tests are shown in figures 6 and 7. The initial yield strength of the titanium foam increased with the sintering temperature. At the different sintering temperature (900 to 1200 °C), the corresponding initial yield strengths of the porous titanium were 101.81, 130.58, 199.33, and 208.01 MPa, respectively. With the increase in sintering temperature, the sintering neck between the Ti powder particles grows and coarsens and the binding force between the titanium powders is further improved. The final mechanical properties of the sintered products were also better. The maximum increase in the yield strength was 67.85 MPa obtained with the increase in the sintering temperature from 1000 to 1100 °C. When the sintering temperature continued to increase to 1200 °C, the yield strength curve rose slightly and the increment in yield strength was only 8.28 MPa. The increase in strength is the result of the closure of some micropores and further shrinkage of macropores in the pore wall, which also indicates that the influence of the increase in the sintering temperature on the initial yield strength was limited in the range of 1100 to 1200 °C.

On the other hand, the variation trend of the stress–strain curves of the titanium foams at the four sintering temperatures was reflected mainly by the stress platform region of the stress–strain curve in the state of horizontal stable fluctuations at temperatures of 900 and 1000 °C. The stress–strain curve shows a slow upward trend in the stress platform region at temperature of 1100 and 1200 °C. When the sintering temperature is low, the sintering neck is relatively thin and the binding force between the particles is relatively small. Thus, the sintering neck was easily broken and destroyed during compression. When the temperature was higher, the sintering neck was further coarsened and the pore wall was densified, which improved the bearing capacity of the titanium matrix. Thus, the porous titanium can bear a higher pressure in the pore wall collapse stage under stress.

4. Conclusions

Titanium foams were fabricated using the metal powder metallurgy method with urea as a space holder. The effects of the sintering temperature on the pore characteristics and mechanical behaviors of the titanium foams were studied. The following conclusions were obtained by this study.
1. The sintering temperature is a key parameter in the preparation of porous titanium, which is a significant element in determining the atomic diffusion coefficient of the system. With the increase in sintering temperature, the atoms diffused fully and the shrinkage of the hole and tendency of the edge of the hole to become smooth were more obvious. The increase in the sintering temperature also reduced the porosity of the titanium foam.

2. The mechanical tests revealed that the initial yield strength of the titanium foam increased with the sintering temperature in the range of 101.81 to 208.81 MPa. The increase in the sintering temperature might enhance the mechanical properties of titanium foams.

3. According to the effect of the sintering temperature on the mechanical properties of titanium foams and energy consumptions considerations, 1100 °C was a suitable sintering temperature for the preparation of titanium foams.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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