Preparation and compressive behavior of porous titanium prepared by space holder sintering process

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Abstract

Porous titanium with the porosity in the range of 44-77% was successfully prepared by space holder sintering process. The size of large pores had been controlled by fractionized the holder. The pore size of the as-prepared samples exhibited bimodal distribution, i.e., the size of large pores was about 200-500μm and the size of small pores was approximate several micrometers. The mechanism for the formation of the pores was explored and the optimal process was determined in this paper. The compressive behavior of the porous titanium was investigated at different processing variables. It was found that the yielding strength and Young’s modulus were strongly depended on the sintering temperature, porosity and pore size. Therefore, the pore structure and properties of the porous titanium could be tailored to satisfy the requirements of biomedical implants.

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Keywords: Porous titanium; Preparation; Compressive behavior; Microstructure

1. Introduction

It is well known that highly porous metals with ch have interesting combination of excellent physical and mechanical properties have been widely used in many fields, such as like industrial filter separator, gas distributor, heat transfer and biomedical implants [1-3]. Especially for biomedical applications, porous titanium structures are of interest due to their prominent mechanical properties, corrosion resistance and good biocompatibility. Recent investigation indicated that for human bone substitute, porous materials with bimodal distributing pore structure, i.e., large pores in the size of 200-500μm and small pores in the...
size of several micrometers, are favorable for the growth of bone tissue and humoral transmission [4-6]. Simultaneously, as humane bone implant, it is very important to have the mechanical properties close to nature bones. As reported, the strength and Young’s modulus of human bone are in the range of 3-20MPa and 10-40GPa[7]. Therefore, lots of research work have focused on the exploitation of porous titanium with bimodal distributing pore size and optimal mechanical properties [8,9].

At present, several methods have been developed to produce porous titanium, such as slip casting, eletro-chemical dissolution, swaging of preform, stacked hollow sphere sintering, selective electron beam melting and space holder method[10-15]. Among these methods, space holder method is a appropriate process for preparing biomedical porous titanium because high porosity, controlled pore size and bimodal distributing pore size can be obtained by changing pore holder[8-10]. However, few work intensively investigated the compressive behaviors of the porous titanium with variable pore size and porosity. In the present work, an attempt has been made to prepare porous titanium by space holder sintering process. The pore size of the sample was controlled by fractionizing the holder.

2. Experimental

In the present experiment, titanium hydride (TiH2) powder of -325 mesh in particle size with irregular shape was used as starting material and ammonium acid carbonate (NH4)HCO3 was employed as space holder material. To achieve a well defined pore size, (NH4)HCO3 was fractionized to -20, -20/+30, -40/+50 and -50/+60 mesh by sieving. Firstly, TiH2 powder added holder material with different content and size was blended in plastic tank for 1 h, and then the mixed powder was compacted to cylinder by cold isostatic compaction under 200 MPa pressure for 30 seconds. Finally, as-prepared greens were sintered in vacuum at different temperature from 850 to 1100°C for 1-3 hrs. In order to make the (NH4)HCO3 decomposed and TiH2 dehydrogenized completely, the temperature was held at 120°C and 650°C for 3 hrs, respectively. The density and porosity of the samples were measured by traditional Archimedes’ method. The pore morphology of the samples was observed by scanning electron microscopy (SEM, JSM-6040, 20kV). Mechanical properties of the porous titanium were characterized by the compressive test employed Instron-1185 universal test machine. The experimental samples with height/diameter ratios of about 2 were compressed at a strain rate of 10-3 S-1.

3. Results and discussion

3.1. Pore structure and porosity

(NH4)HCO3 decomposes at temperature above 60°C to ammonia, carbon dioxide and water, so (NH4)HCO3 was preferred as pore former in the experiment. After held at 120°C for 3 hrs in vacuum, the holder was decomposed completely and the space remained to be pore after sintering at high temperature. The detailed processing parameters and properties of sintering porous titanium were listed in the table 1. From the table, it was clear that real density was gradually increased from 1.76 to 1.97 g/cm3 as the increase of the sintering temperature from 850 to 1100°C when the holder in all the samples was as the same as 50wt%. At the mean time, the porosity of the samples was correspondingly decreased from 60.9 to 56.3%. The effect of holding time on the properties of the porous titanium was also investigated when the sintering temperature was fixed at 950°C. With the holding time was elongated, the real density was increased. But the holding time was elongated from 2 hrs to 3 hrs, the density was only increased from 1.86 to 1.90 g/cm3, which denoted that 2 hrs were enough for the adequate sintering. In the present experiment, TiH2 powder was chosen as raw material. When the temperature was elevated to 650°C, it would dehydrogenize and its sintering activity was very high. The sintering temperature here was lower
as to 950°C, while 1250 or 1300°C was chosen for titanium powder sintering in previous literatures [10]. Therefore, sintering at 950°C for 2 hrs was the optimal process in the present experiment.

Table 1 The real density and porosity of porous titanium prepared at different processing conditions. All the holder materials used here were fractionized to -20 mesh.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Holder (wt%)</th>
<th>Sintering temperature (°C)</th>
<th>Holding time (hrs)</th>
<th>Real density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>850</td>
<td>2</td>
<td>1.76</td>
<td>60.9</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>900</td>
<td>2</td>
<td>1.81</td>
<td>59.9</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>950</td>
<td>2</td>
<td>1.86</td>
<td>58.8</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>1000</td>
<td>2</td>
<td>1.90</td>
<td>57.9</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>1100</td>
<td>2</td>
<td>1.97</td>
<td>56.3</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>950</td>
<td>1</td>
<td>1.60</td>
<td>64.5</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>950</td>
<td>3</td>
<td>1.90</td>
<td>57.9</td>
</tr>
<tr>
<td>8</td>
<td>40</td>
<td>950</td>
<td>2</td>
<td>2.50</td>
<td>44.4</td>
</tr>
<tr>
<td>9</td>
<td>60</td>
<td>950</td>
<td>2</td>
<td>1.58</td>
<td>64.9</td>
</tr>
<tr>
<td>10</td>
<td>70</td>
<td>950</td>
<td>2</td>
<td>1.04</td>
<td>76.9</td>
</tr>
</tbody>
</table>

Fig. 1 SEM images of porous titanium added holder materials with different content (wt%): (a) 40%, (b) 50%, (c) 60% and (d) 70%.
The samples with 40% to 70% former were sintered at 950°C for 2 hrs and the porosity increased as the increase of the former volume. When the value of volume was up to 70%, the porosity was as high as 76.9%.

As a pore former, its homogeneous distribution in matrix directly affected the pore feature of porous titanium. Due to the fine TiH2 particle and damp coarse (NH4)HCO3 particle, the fine TiH2 particle could encapsulate the (NH4)HCO3 particle well and homogeneous mixer was obtained after blending the TiH2 powder and (NH4)HCO3 for 1 h. In fact, two type of pores remained after sintering. One is the small pores with several micrometers which were inherited from the space among TiH2 particles after compaction. The other is the large pores which were leaved after the decomposition of (NH4)HCO3. Fig.1 showed the pore morphology of the as-prepared samples by adding different volume ratio of (NH4)HCO3. As shown in Fig.1, it was clear that the forming open large pores were evenly distributed in the sample. However, the large pores were irregular and had different pore size due to the irregular shape and inconsistent sizes of (NH4)HCO3 particles. With the volume ratio of (NH4)HCO3 increased, the quantity of large pores increased accordingly. Especially, when the volume ratio of holder was up to 70%, amount of large pores were formed and the size of pore wall became thinner, yet the green with above 70% former were collapsed during sintering in our experiment.

![Image of pore morphology](image1)

![Image of pore morphology](image2)

**Fig.2** The pore structural morphology of porous titanium by adding 50wt% holder with different size: (a) -50/+60mesh, (b) -40/+50mesh, (c) -30/+40mesh and (d) -20/+30mesh

Previous investigations indicated that the optimal pores of porous bone substitutes might have bimodal distributing pore size, i.e., the pores with 200-500μm in size were suitable for the growth of osteoblasts
and vasculature and the pores with several micrometer in size were favorable for the humoral transmission[4-6]. Based on the above requirements, in our experiment the former was fractionized to -20/+30, -30/+40, -40/+50 and -50/+60 mesh by sieving to construct pores with different size. Fig. 2 showed the pore structural images of sintered porous titanium. As seen from the figure, it is obvious that the pore size became uniform and the pores were enlarged when relative big and dimension uniform former was added. In Fig. 2 (d), the size of large pores was about 300μm and small pores were about 5μm in size. The porous titanium with this pore structure was the optimal material for applications as biomedical implants.

3.2. Compressive behavior

The compressive properties of the as-prepared porous titanium were investigated in this work. Fig. 3 showed the compressive strength-strain curves depending on the sintering temperature and holder volume ration. From the figure, all the curves exhibited the typical feature of metal foam during compressing, i.e., elastic deformation stage, plateau stage and densification stage. In Fig. 3 (a), the compressive strength gradually increased with the increase of the sintering temperature. The yielding strength of the porous titanium sintered at 850°C was 60MPa and 140MPa of the sample sintered at 1100°C, while the corresponding Young’s moduli were 2.1 to 3.4 GPa which were determined from the slope coefficients of the linear portion of each curves. In Fig. 3 (b), it was evident that the compressive strength was strongly depended on the porosity or the volume ratio of holder. When the volume ratio of holder increased to 70% and its porosity got to 76.9%, the yielding strength was about 40MPa and simultaneously the Young’s modulus was about 1.2 GPa. Compared with the previous work, the yielding strength value here was higher than that of porous titanium with equal porosity[9,10]. It may be due to the pore in different size formed by other holders, such as urea and polymer ball etc. The other reason might be the raw material. TiH2 powder was used here and the stronger sintering neck among particles had formed during dehydrogenization and sintering. But the value of Young’s modulus was relatively lower than that of porous titanium by adding urea as pore former.

Fig. 3 The compressive strength-strain behavior of the porous titanium: (a) added with 50wt% holder that sintered at different temperature for 2 hrs and (b) the holder contents from 40 to 70wt%.

Fig. 4 showed the compressive strength-strain curves of porous titanium by adding holder with different sizes. From the figure, it can be seen that the yielding strength and modulus was sensitively depended on the size of the pore former. When the size of holder was -20/+30 mesh, the strength was about 40MPa. When the size of holder decreased to -40/+50 mesh, the strength increased to about 100MPa. When the
size of holder decreased further, the strength inversely decreased to about 60MPa. For human bones, their strength was in the range of 3-20MPa and the Young’s modulus was in the range of 10-20GPa. Therefore, according to above research results, the mechanical properties of the porous titanium could be tailored by used holder former to meet the requirement of biomedical implants.

![Graph showing compressive strength-strain behavior](image)

**Fig.4** The compressive strength-strain behavior of the porous titanium depending on the holder size. The content of holder was 50wt% in all the samples.

### 4. Conclusions

Porous titanium was fabricated by traditional powder metallurgy technique. The porosity and pore size were controlled by fractionized the holder and the highest porosity might get to 76.9% in the present experiment. Using -30/+40mesh (NH4)HCO3, two types of the pores in size of 200-500μm and several micrometers were obtained after sintering, and this sample with bimodal distributing pore size was suitable for used as biomaterials. The experimental results showed that the compressive strength and Young’s modulus decreased as the increase of the holder content. Increasing the content of holder to 70%, the yielding strength and modulus increased to 40MPa and 1.2GPa, respectively, which were close to the parameter range of human bones.

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### References


