Fabrication and Mechanical Properties of Porous Ti-24Nb-4Zr-8Sn Alloy Developed for Biomedical Application

Xuying Cheng, Shujun Li, Yulin Hao, Rui Yang

Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China

Metal-based porous materials are currently the preferred choice as bone/cartilage implants due to their idiosyncratic porosity improving the biocompatibility of implants. Ti-24Nb-4Zr-8Sn (in weight percent and abbreviated as Ti2448) is a new beta-type titanium alloy developed for biomedical application. The alloy possesses low modulus, high strength, good corrosion resistance in the physiological environment and non-toxicity. This study focuses on the fabrication and mechanical properties of porous Ti2448 alloy aimed for use as load-bearing implants. A bulk porous biomedical Ti2448 alloy was prepared by powder-metallurgy technique including cold-roll forming and vacuum sintering. The effects of processing parameters, such as rolling reduction, size and volume percentage of space-holder on porosity, average pore size, compressive strength and Young's modulus of porous Ti2448 alloy were investigated. The results showed that porous Ti2448 alloys of 17.5%~46.8% in porosity, 168~509 µm in average pore diameter, 30~325 MPa in compressive strength and 2.3~27.2 GPa in dynamic modulus can be fabricated by controlling process parameters. Compared with porous CP Ti fabricated by the same method, porous Ti2448 alloy has much higher strength-to-modulus ratio and better mechanical compatibility, which may greatly reduce stiffness mismatch between implant and bone after implantation.

Keywords: Biomedical titanium alloys, porous Ti-2448 alloy, elastic modulus, rolling forming, mechanical properties

1. Introduction

Metal-based biomaterials have been extensively used to produce orthopedic implants due to their better balance between strength and toughness than ceramics and polymeric materials. Since titanium and its alloys possess good mechanical properties and corrosion resistance, they have been used widely to produce the "load-bearing" implants for biomedical applications. However, several studies have demonstrated that one of the major drawbacks of implants made of bulk metallic materials is the elastic mismatch between the implant and its surrounding bone tissue, which leads to the stress shielding phenomena. Together with the bio-inert nature of their surface, it is difficult to get strong bonding between implant and bone tissue, which might result in the loosening of implant-bone interface. The introduction of the porous structure would be a valid way to reduce elastic modulus and provide necessary space to facilitate cell vascularization and new bone in-growth. The porous materials can be fabricated with many techniques such as solid-state foaming by superplastic expansion of argon-filled pores, rapid prototyping, self-propagating high-temperature synthesis, polymeric foam replication, selective electron/laser beam melting and powder metallurgical process.

Ti-24Nb-4Zr-8Sn (Ti2448) is a new beta-type titanium alloy developed for biomedical application with the desired biomechanical properties such as high strength, low elastic modulus, large recoverable strain and good corrosion resistance. In this study, the porous Ti2448 alloy with a controllable interconnected pore was fabricated by the powder metallurgy technique including the cold rolling of the capsule powder and vacuum sintering. The effect of processing parameters including rolling reduction in thickness, size and volume percent of space-holder on porosity, average pore size, compressive properties and Young's modulus was investigated.

2. Materials and Methods

2.1 Starting Materials

The powders were prepared by the electrode induction melting gas atomization (EIGA) equipment. They were sieved in an Ar protection atmosphere to get powders with two diameter ranges of 180~300 µm and 50~80 µm. The particles of polymethyl methacrylate (PMMA) were used as the space-holder material which is entirely spherical in shape with the diameters of 150~500 µm. The PMMA was selected as the space-holder material due to its good mechanical strength and hardness to avoid falling to pieces during the cold rolling forming, and favorable chemical property to decompose completely at relatively low temperature so as to avoid the reaction with the host powders.

2.2 Preparation of Porous Ti2448 Alloy

The capsules filled with Ti2448 alloy powders (180~300 µm) were cold rolled with the rolling reduction of 20%, 30%, and 40% in thickness respectively and then sintered in a vacuum of 1 × 10⁻⁶ Pa without the applied external pressure at a temperature of 1423 K for 4 h. To increase the porosity, the PMMA particles were added in some samples. Since the previous studies have shown that the size of the metal powder should be smaller than that of the space-holder, Ti2448 alloy powders with smaller particle size (50~80 µm) were mixed with the PMMA particles of 30%, 40% and 50% in volume fractions and the binding admixture. The rolling reduction was controlled to 40%.
These capsules containing space-holder were first heated at temperature 673K for 4 h to remove the PMMA and then sintered at 1423 K for 4 h.

## 2.3 Sample Characterization

The density of the porous materials was estimated from the weight and the apparent volume of the specimen. The porosity was calculated using the following equation:

\[ P = \left(1 - \frac{\rho}{\rho_0}\right) \times 100\% \]

where \( \rho \) and \( \rho_0 \) are density of porous materials and dense materials, respectively. Microstructures of Ti2448 powders and the porous Ti2448 samples were observed by scanning electron microscope (SEM). Optical microscopy (OM) was used to determine the pore size distribution and mean pore size measured by quantitative image analyses using the commercially available software Scis-Ias8. The compression test of porous Ti2448 samples was carried out using cylindrical shaped samples with the diameter of 3 mm and length of 6 mm at room temperature under a strain rate of \( 10^{-4} \text{s}^{-1} \). Young's modulus of porous samples was measured by the resonance method at ambient temperature using a rectangular shaped sample with the dimensions of \( 60 \times 15 \times 3 \text{ mm}^3 \). The formula to calculate the modulus of a rectangular shaped sample is:

\[ f_R = 1.028 \times 10^6 \times \left( \frac{T}{L^2} \right) \left( \frac{E}{\rho} \right)^{1/2} \]

in which \( f_R \) is the resonant frequency (Hz), \( T \) the thickness of the sample (mm), \( L \) the length of the sample (mm), \( E \) the modulus of the material (GPa) and \( \rho \) the density of the material (g/cm³).

## 3. Results and Discussions

Figure 1 shows SEM micrographs of Ti2448 alloy powders produced by the EIGA process with the diameter ranges of 180~300 µm (Figure 1(a)) and 50~80 µm (Figure 1(b)). Powder particles produced by the gas atomization are almost spheroid, with a small fraction of ellipsoid, only occasionally with adhered satellites.

The characteristic parameters of pores of sintered porous Ti2448 alloys were summarized in Table 1. For the porous alloys free of the space-holder, both porosity and average pore size decrease with the increase of the rolling reduction. Under the conditions of 30 vol. % PMMA particles and 40% thickness reduction, the PMMA particle sizes have positive contribution on the average pore sizes but slight effect on the porosities. Under the conditions of similar PMMA particle size range and rolling reduction, the increase of PMMA particle volume results in higher porosities but a little effect on the average pore sizes. In summary, the porous alloys free of the space-holder have the total porosity and the average pore size in the ranges of 17.6%~32.4% and 166~271 µm respectively while the addition of the space-holder increases them to 33.6%~46.8% and 345~509 µm. It is clear that the addition of space-holder favors the increase of porosity and the governing of average pore size.

### Table 1. The porosity and average pore size of porous Ti2448 alloys fabricated by various processing

<table>
<thead>
<tr>
<th>Order</th>
<th>Volume percent of PMMA (Vol. %)</th>
<th>Particle size of PMMA (µm)</th>
<th>Rolling reduction (%)</th>
<th>Sintering condition</th>
<th>Porosity of porous Ti2448 (%)</th>
<th>Average pore size of porous Ti2448 (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>20</td>
<td>1150°C for 4h</td>
<td>32.4</td>
<td>271</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>40</td>
<td>1150°C for 4h</td>
<td>26.8</td>
<td>191</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>40</td>
<td>1150°C for 4h</td>
<td>17.6</td>
<td>166</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>150-225</td>
<td>1150°C for 4h</td>
<td>36.8</td>
<td>345</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>225-300</td>
<td>1150°C for 4h</td>
<td>34.2</td>
<td>407</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>300-500</td>
<td>1150°C for 4h</td>
<td>33.6</td>
<td>475</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>40</td>
<td>300-500</td>
<td>1150°C for 4h</td>
<td>41.7</td>
<td>503</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>300-500</td>
<td>1150°C for 4h</td>
<td>46.8</td>
<td>509</td>
<td></td>
</tr>
</tbody>
</table>

Mechanical properties of the porous alloys were measured by compression test and the nominal stress-strain curves of porous Ti2448 alloys prepared without space-holder were shown in Figure 2. It can be
seen that there is an almost linear increase in stress in
the first stage and then a plateau region with a nearly
constant flow stress before the collapse of the tested
specimens. The reason for this behavior is probably
cells collapse as a result of cell walls yielding. The
compressive fracture surface of the porous alloy was
observed by SEM. For example, Figure 3 shows that
the porous materials sintered with 50 ~ 80 µm alloy
powders and 30 vol. % space-holder have different
particle sizes. It is clear that the fracture surfaces are
rough due to the porous structure of the materials.
There exist two kinds of pores. The larger pores have
sizes being similar to those of the decomposed space-
holder while the smaller pores relate with the sizes of
the alloy powders. The variations of the compressive
strength with porosity and average pore size are plotted
in Figure 4 and 5, respectively. It can be seen that the
compressive strength has negative dependence on the
porosity and the average pore size. The porous Ti2448
alloys of 30 ~ 325 MPa in compressive strength were
successfully fabricated in this work, which is higher
than the human cortical bone (20 ~ 200 MPa). Addition-
ally, the porosities of the fabricated porous Ti2448
alloys are in the range of 17.6% ~ 46.8%, which is
close to the optimal porosity of implant materials for
ingrowths of new-bone tissues (20% ~ 50%).

4. Conclusions

In this study, the porous structures of the Ti2448
alloy with porosities ranging from 17.6% to 46.8%
were fabricated successfully by the powder metallurgy
technique. The pore characteristics can be adjusted by
the control of processing parameters including the roll-
ing reduction in thickness, size of space-holder and its
volume percentage. The compressive strength decrea-
ses with the increase of the porosities and the average pore size while Young’s modulus has a strong dependence on the porosities but a weak relation to the average pore sizes. The fabricated porous structures of Ti2448 alloy have compressive strengths in the ranges of 30 ~ 325 MPa and Young’s moduli of 2.3 ~ 27.2 GPa, which is in good matches with the biomechanical properties of the cortical bone.

![Graph showing compressive strength and dynamic Young’s modulus as a function of average pore size.]

**Figure 5.** Compressive strength and dynamic Young’s modulus as a function of average pore size

**REFERENCES**


7) G. Ryan, A. Pandis, D.P. Apatitidis, Biomaterials. 2006;27;2651.


9) J. P. Li, R.W. Joost, A.B. Clemens, G. Kraas, Biomaterials. 2006;27;1223.


12) P. Heiirl, L. Muller, C. Koner, R.F. Singer, F.A. Muller, Acta Biomater. 2008;4;1536.


