Effect of sintering processing on property of porous Ti using space holder technique

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Abstract: Porous Ti for the application in clinic orthopaedics field was manufactured by powder metallurgy technique using polymethyl methacrylate as the space holder under different sintering conditions. The final morphological features and mechanical properties were described. The results show that the increase of sintering temperature and time leads to improved grain size of porous Ti ligament and decreased pore size, with a concomitant increase of tensile strength and elastic modulus. The microstructure and mechanical properties of solid Ti depend more on the sintering temperature and time than those of porous Ti. The relative contributions of these mechanisms of porous Ti vary with the initial microstructure and oxygen content.

Key words: porous Ti; powder metallurgy; microstructure; mechanical property

1 Introduction

Porous Ti and its alloys are potential materials for orthopaedic and dental applications due to their biological and mechanical compatibilities with the host bone tissue [1]. The processing of porous Ti can be carried out in different ways, such as furnace sintering [2,3], sponge replication [4], gelcasting [5,6], mixed sintering [7], freeze casting [8], metal injection molding [9], fiber deposition [10], spark plasma sintering [11], environmental-electro-discharge-sintering [12], rapid prototyping [13,14], laser engineered net shaping [15,16] and surface modification [17].

Among the methods, powder metallurgy is a very simple and cost-efficient method to obtain porous Ti with appropriate pore structure and excellent properties, such as loose powder sintering [2] and space holder technique [18,19]. LI et al [20] previously reported porous Ti (with porosity of 5%~50%, micro-pore size of <50 µm and elastic modulus of 10~40 GPa) sintered by Ti powder compacts. To achieve functional parts with a well defined open porosity, sintering has to be stopped at an early stage. The micro-pore structure of porous Ti depends mainly on the particle size of the initial powder, the densification of material before sintering and the sintering conditions. The residual micro-porosity can be controlled by adjusting these parameters. However, this possibility is subject to limitations when large macro-pores are required. In this case, the space holder method could provide a foamed Ti structure with a close to homogenous macro-pore structure (100~700 µm in pore size) and high levels of porosity (33%~80%) [21~23]. Moreover, the mechanical properties of porous Ti can be adjusted by choosing the size, shape and content of the space holder used. Normally, stearin [24], carbamide [25], ammonium hydrogen carbonate [26] and polyurethane foam [27] are considered to be good space holder materials. However, LAPTEV et al [28] reported that the strength of green compact using ammonium bicarbonate as the space holder decreased by storing them in air at room temperature because of the slow decomposition, which already started at room temperature.

In the present study, the porous Ti samples with porosity of 50% and macro-pore size of 170~221 µm were fabricated by powder metallurgy technique using polymethyl methacrylate (PMMA) as the space holders, which had regular spherical shape and compact stability and were beneficial to controlling the macro-
pore morphology. The relationships between fabrication processing (sintering temperature, sintering time, and vacuum conditions), microstructures and mechanical properties of porous Ti were investigated. For comparative purpose, similar measurements were carried on the solid Ti prepared by the same processing but without the space holders in green body of Ti powders.

2 Experimental

2.1 Materials

The mixtures containing irregularly shaped commercial pure Ti (CP-Ti) powders with the size of (24.4±11.4) µm (Fig. 1) and 50% (volume fraction) spherical PMMA with the size of 200–315 µm (Fig. 2) were compacted under the uniaxial pressure of 500 MPa to form green bodies, which is the same as the method reported in Ref. [29]. The green compacts were heated up to 250–450 °C for 5 h in a vacuum furnace to remove the space holders, then sintered at high temperatures, as described in Table 1. The solid Ti was prepared by the same processing but without the space holders in green body of Ti powders for comparison.

2.2 Microstructure examination

The morphology of the porous Ti was observed using scanning electron microscopy (JEOL Japan, JSM−6360LV and JSM−7100F) and optical microscopy (ZEISS Germany, Neophoto−32). The porosity was evaluated from the mass and apparent volume of the specimen. The distribution of pore and grain size was measured by quantitative image analysis. The mean diameters were measured through pore’s centroid at 2° intervals. The phase of porous Ti was identified using X-ray diffraction (Rigaku Corporation D/MAX−Ultima+, Japan) with Cu Kα radiation at 40 kV and 40 mA. The oxygen content was determined by a nitrogen and oxygen determinator (LECO USA, TC−436), while the carbon content was determined by a carbon determinator (LECO USA, CS−444LS). The experiment condition for the measurement of chemical composition was at 25 °C with the humidity of 40%. In addition, the distribution of oxygen and carbon was tested by an electro-probe microanalyzer (EPMA−1600, Japan).

2.3 Mechanical testing

The longitudinal three-point bending test was performed on a compression testing machine (Logo Japan, AG5000−A) [30]. The curvature radius of the bending head was 4 mm. The dimensions of bending specimens were 20 mm × 8 mm × 3 mm and the span between the support points was 14 mm. The surfaces of
all the specimens were polished using waterproof sandpaper with increasing the abrasiveness from 200 to 1500 grit until there were no scores on the surface. The strain was increased at intervals of 0.1%.

The compression test and tensile test were detailed in Refs. [20,29]. The elastic modulus was calculated from the stress increment and the corresponding strain increment. At least three measurements were carried out under the same conditions, and the mean values were calculated.

3 Results

3.1 Microstructures of porous Ti

3.1.1 Effects of sintering temperature and time on microstructures of porous Ti

The structure of porous Ti varies with the sintering temperature and time, as shown in Figs. 3 and 4, respectively. There are two types of pores in the samples: the interconnected macro-pores obtained by the decomposition of space holder and the micro-pores obtained by partially sintering of Ti powders on the pore walls, which are the same as the micro-pores measured on solid Ti [29] under the same cold compress and sintering condition. As the sintering temperature and time increase, the pore shape becomes round and the micro-pores decrease in size and number. The macro-porosity of porous Ti is only slightly affected by the sintering parameters, due to the unchanged fraction of space holders (50%).

Figures 5 and 6 show the distribution of the pore size and grain size in terms of mean diameter based on the SEM images. 90% of the macro-pores have the size in the range of 200–300 µm which is reported to be the optimum pore size for the attachment and proliferation of new-bone tissues and the transport of body fluids [21]. Combined with Table 2, the grain size increases with increasing the sintering temperature and time, while the pore size takes an opposite change. In addition, the grain size in solid Ti is smaller than that in porous Ti, but this occurs only in the regions where the walls between macro-pores are small. Also, the micro-pore size in solid Ti is greater than that in porous Ti, which should indicate that much of this microporosity is just on the surface of the macro-pores so that the final effect observed shows this reduced microporosity.

3.1.2 Effect of vacuum on microstructures of porous Ti

The X-ray diffraction patterns shown in Fig. 7 reveal only the existence of α-Ti phase in porous Ti sintered under the vacuum of $7 \times 10^{-4}$ and $5 \times 10^{-3}$ Pa. The contents of oxygen and carbon determined by chemical analysis are provided in Table 3. As the vacuum changes from $5 \times 10^{-3}$ to $7 \times 10^{-4}$ Pa, the contents of oxygen and carbon in porous Ti decrease, which are much higher than those in original Ti powder (0.5% for oxygen and 0.01% for carbon). Based on the element distribution map of porous Ti by EPMA, as shown in Fig. 8, the carbon and oxygen mainly exist in the edge of macro-pore, and the adsorption of oxygen in the Ti matrix is homogeneous. However, the oxygen content is very high even in the initial powders so it is normal to appear very high oxygen content and homogeneous distribution. The oxygen contamination due to the densification process is on the order of 0.95%(1.1%−0.05%=0.9%(1.05%), which is larger than 0.8% oxygen reducing the tensile ductility of CP-Ti [31]. But it is less
Fig. 5 Effects of sintering temperature on grain size distribution (a), mean grain size (b), macro-pore size distribution (c), mean macro-pore size (d), micro-pore size distribution (e) and mean micro-pore size (f) of porous Ti

Fig. 6 Effects of sintering time on grain size distribution (a), mean grain size (b), macro-pore size distribution (c), mean macro-pore size (d), micro-pore size distribution (e) and mean micro-pore size (f) of porous Ti

than the oxygen values (1.2%–1.8%) that detrimentally affected the ductility of the sintered Ti–6Al–4V forms in Ref. [32], and much lower than the value of 3.8% reported by CHINO and DUNAND [33] in foam using powders with much higher initial oxygen content. This contamination could be further reduced by using high vacuum, and by insuring that the initial powders are completely devoid of air and/or water. Also, increasing the sintering temperature and time for porous Ti results in near-zero changes in oxygen content (Table 3), indicating that most of the oxygen increase occurs during the initial sintering step, when the foams have high surface area and may contain small amounts of adsorbed air and/or water. The carbon in this part may come from PMMA and concentrate on the edge of the macro-pores, but also may be due to the metallographic preparation because it is difficult to completely remove the remains from polished interior micro- and macro-pores. The
Table 2 Microstructure characteristic of Ti samples

<table>
<thead>
<tr>
<th>Test No</th>
<th>Micro-pore size/μm</th>
<th>Macro-pore Size/μm</th>
<th>Grain size/μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Porous Ti</td>
<td>Solid Ti</td>
<td>Porous Ti</td>
</tr>
<tr>
<td>S1</td>
<td>8.9±2</td>
<td>13.1±4.1</td>
<td>221±45</td>
</tr>
<tr>
<td>S2</td>
<td>8.5±1.5</td>
<td>11.4±3.8</td>
<td>213±30</td>
</tr>
<tr>
<td>S3</td>
<td>8.2±1.8</td>
<td>11.1±2.2</td>
<td>199±39</td>
</tr>
<tr>
<td>S4</td>
<td>6.9±1</td>
<td>10.1±2.7</td>
<td>192±35</td>
</tr>
<tr>
<td>S5</td>
<td>10.3±3.3</td>
<td>12.6±3.6</td>
<td>237±44</td>
</tr>
<tr>
<td>S6</td>
<td>10.1±1.6</td>
<td>12.1±4.5</td>
<td>225±43</td>
</tr>
<tr>
<td>S7</td>
<td>7.6±1.6</td>
<td>10.9±3.7</td>
<td>186±23</td>
</tr>
<tr>
<td>S8</td>
<td>7.3±2</td>
<td>8.7±2.3</td>
<td>170±40</td>
</tr>
</tbody>
</table>

diffraction peaks in Fig. 7 are corresponding to Ti but the small unidentified 42° and 58° angles would be confirmed further.

3.2 Mechanical properties of porous Ti

The correlations between tensile properties and sintering parameters are shown in Figs. 9 and 10. The tensile strength for porous Ti sintered at 1000–1300 °C for 2 h and under the vacuum of 7×10⁻⁴ Pa is between (73±1.4) and (149±5.7) MPa. The tensile elastic modulus is between (2±1.2) and (6±0.1) GPa. For a given sintering temperature (1200 °C), as the sintering time increases from 0.5 to 3 h, the tensile strength and elastic modulus of the porous Ti increase from (105±0.3) to (125±9.4) MPa and (3±2.4) to (6±2.4) GPa, respectively. However, the tensile strength and elastic modulus of the porous Ti sintered for 2.5 h decrease anomaly. The
### Table 3 Chemical compositions of Ti powder and porous Ti sintered under different vacuums

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Oxygen content (mass fraction)/%</th>
<th>Carbon content (mass fraction)/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S8(7×10^{-4} Pa)</td>
<td>0.95</td>
<td>0.69−0.86</td>
</tr>
<tr>
<td>S2(7×10^{-4} Pa)</td>
<td>0.95</td>
<td>−</td>
</tr>
<tr>
<td>S1(7×10^{-4} Pa)</td>
<td>0.95</td>
<td>−</td>
</tr>
<tr>
<td>S9(5×10^{-3} Pa)</td>
<td>1.1</td>
<td>0.78−0.9</td>
</tr>
<tr>
<td>Ti powder</td>
<td>0.5</td>
<td>0.01</td>
</tr>
</tbody>
</table>

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### Table 4 Mechanical properties of porous Ti under different vacuums

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Compressive strength/MPa</th>
<th>Tensile strength/MPa</th>
<th>Bending strength/MPa</th>
<th>Compressive elastic modulus/GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>S8(7×10^{-4} Pa)</td>
<td>200±30</td>
<td>149±5.7</td>
<td>434±6.3</td>
<td>4±0.7</td>
</tr>
<tr>
<td>S9(5×10^{-3} Pa)</td>
<td>141±15</td>
<td>125±7</td>
<td>264±10</td>
<td>2±0.6</td>
</tr>
</tbody>
</table>

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#### Fig. 9 Effects of sintering temperature on tensile strength (a) and tensile elastic modulus (b) of porous Ti under sintering time of 2 h and vacuum of 7×10^{-4} Pa

Maximum deviations from the proposed curves are noted at 1200 and 1250 °C for 2 h. Based on the results in Ref. [20], the tensile elastic modulus porous Ti is less than 82% that of the solid Ti.

The mechanical properties of the porous Ti sintered under different vacuum conditions are illustrated in Table 4. As the vacuum changes from 5×10^{-3} to 7×10^{-4} Pa, the compressive strength increases from (141±15) to (200±30) MPa (close to 125−150 MPa for the Ti foam with 52%−54% porosity and 0.84% (mass fraction) oxygen content [31]), and the compressive elastic modulus increases from (2±0.6) to (4±0.7) GPa. The tensile strength and bending strength of the porous Ti take the similar changes. This is likely that the main effect is the decreased ductility of Ti walls from the high oxygen content (0.95%−1.1%).

### 4 Discussion

From the above experimental results and analyses, the macro-pores are originated from the removal of spherical PMMA particles and then the diffusion of Ti atom. Simultaneously, the formation of micro-pores is
not only due to the escape of gas from the pore wall, which served as channels between connected macro-pores of porous Ti, but also from the volume shrinkages during the sintering process of the Ti powders. For bone implants, the irregular micro-pore is undesirable, as it weakens the material without being accessible to bone ingrowth because of its small size. For this reason, increasing the sintering temperature to 1200–1300 °C is necessary to reduce the volume of micro-pore (porosity of 8%±3% and average pore size of (7.3±2) µm for the porous Ti sintered at 1300 °C). In addition to the equiaxed microstructure in the majority of the sample, Widmanstatten structure is observed too. Such morphologies of the transformed α microstructure in specimens should be formed during cooling at a moderately high rate (about 25 °C/s in the temperature interval of 1300–1000 °C) from the supertransus temperature, which are in agreement with the results reported by SEETHARAMAN and SEMIATIN [34].

Combined with the previous work [20], the influence of sintering temperature and time on the grain size and micro-pore size in solid Ti and porous Ti can be expressed by parabola relationship. At low sintering temperature, more pores at the grain boundary impede the grain boundary moving and decrease the grain growth coefficient, thus the grains grow slowly. At high sintering temperature, the density increases, and the impeded force of grain boundary moving decreases, hence the grains grow quickly. Moreover, grain coarsening is observed for those samples sintered at high temperatures or for long time. As the internal energy is the sum of surface and grain boundary energies [35], the migration mechanism is the mass transport on the actual free surface and grain boundary of the row of particles. The vacancy transfers from concave neck to protruding surface of particles through surface diffusion, which can not only cause the neck growth but also make the micro-pores rounding and shrinkage. During the final sintering stage, the whole body shrinks slowly by small micro-pores disappearing [36]. Densification is limited by the evolution of contacting particles into equilibrium shape, thus much more micro-pores are approach to sphere and isolated, as shown in Figs. 3 and 4. In addition to the surface diffusion mechanism, the evaporation condensation mechanism is probably important except for the porous Ti sintered at 1300 °C under the vacuum of 7×10^{-4} Pa [29].

By contrast, the grain size and micro-pore size of solid Ti depend more on the sintering temperature and time than those of porous Ti. For solid Ti only existing micro-pore, the formation and growth of grain are in strict accordance with the sintering theory for unary system. For porous Ti with two kinds of pores, the evolution of micro-pore takes different changes to some extent. According to the simplest sintering kinetics of large pores in a dense polycrystalline solid [37], the condition for the pore to shrink is

\[ n < 2\pi \gamma_s / \gamma_{gb} \]  

where the specific energy for the free surface (\(\gamma_s\)) is three times of that for the grain-boundary (\(\gamma_{gb}\)). The critical coordination number (\(n\)) is about 6\(\pi\) (\(n_c=18.84\)). If the pore surrounded by too many grains, the free energy gains due to the extension of the grain-boundaries into the pore outbalances, and the free energy loses due to the elimination of the pore surface. So, the pore should grow instead of shrink [37]. Figure 11 illustrates the coordination number for porous Ti under different sintering conditions. The coordination number of micro-pore in porous Ti is always lower than the critical value, while that of macro-pore in porous Ti is almost lower than the critical value except for the porous Ti sintered at 1000 °C for 2 h. Moreover, the increase of sintering temperature and time leads to a decrease of coordination number. Therefore, the shrink of macro-pore during sintering process is associated with the growth of surrounding grains, which gives the driving force for the elimination of macro- and micro-pores in porous Ti. That could result in some differences of micro-pore size and grain size in solid Ti and porous Ti.
5 Conclusions

1) With increasing the sintering temperature from 1000 to 1300 °C and the sintering time from 0.5 to 3 h, the pore shape becomes round and the micro-pore decreases in number. The grain size of porous Ti ligament increases with increasing the sintering temperature and time, while the pore size takes an opposite change.

2) The tensile strength and elastic modulus of porous Ti increase with increasing the sintering temperature, time and vacuum degree. At proper sintering parameters (sintered at 1300 °C for 2 h and under the vacuum of 7×10⁻⁴ Pa), the tensile strength and elastic modulus of porous Ti reach (149±5.7) MPa and (6±0.1) GPa, respectively.

3) The grain size in solid Ti is smaller than that in porous Ti, while the micro-pore size in solid Ti is larger than that in porous Ti. The microstructure and mechanical property of solid Ti depend more on the sintering temperature and time than those of porous Ti.

References


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