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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 macropores 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-

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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 $(24.4\pm11.4) \mu m$ (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



Fig. 1 SEM image (a) and particle size distribution (b) of Ti powders



Fig. 2 SEM image of PMMA

Table 1 Sintaring propage normators of normality

Table I Sintering process parameters of porous IT					
Test No.	Temperature/°C	Time/h	Vacuum/Pa		
S1	1200	1	7×10 ⁻⁴		
S2	1200	2	7×10 ⁻⁴		
S3	1200	2.5	7×10 ⁻⁴		
S4	1200	3	7×10 ⁻⁴		
S5	1000	2	7×10 ⁻⁴		
S6	1100	2	7×10 ⁻⁴		
S7	1250	2	7×10 ⁻⁴		
S8	1300	2	7×10 ⁻⁴		
S9	1300	2	5×10 ⁻³		

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 K_a 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 \times 8 mm \times 3 mm and the span between the support points was 14 mm. The surfaces of

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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 μ m 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 7×10^{-4} and 5×10^{-3} Pa. The contents of oxygen and carbon determined by chemical analysis are provided in Table 3. As the vacuum changes from 5×10^{-3} to 7×10^{-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. 3 Microstructures of porous Ti sintered at 1100 °C (a), 1200 °C (b) and 1250 °C (c) for 2 h under vacuum of 7×10^{-4} Pa



Fig. 4 Microstructures of porous Ti sintered at 1200 °C for 1 h (a), 2.5 h (b) and 3 h (c) under vacuum of 7×10^{-4} Pa



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

Test No.	Micro-pore size/µm		Macro-pore Size/µm	Grain size/µm	
	Porous Ti	Solid Ti	Porous Ti	Porous Ti	Solid Ti
S 1	8.9±2	13.1±4.1	221±45	54.2±15.0	34.8±12.3
S2	8.5±1.5	11.4±3.8	213±30	57.2±21.7	36.7±19.3
S3	8.2±1.8	11.1±2.2	199±39	82.3±16.6	44±11
S4	6.9±1	10.1±2.7	192±35	99.8±28.9	59.4±15.0
S5	10.3±3.3	12.6±3.6	237±44	23.7±4.8	23.4±6.8
S6	10.1±1.6	12.1±4.5	225±43	40.1±10.1	24.4±6.8
S7	7.6±1.6	10.9±3.7	186±23	72.5±23.2	48.6±9.7
S 8	7.3±2	8.7±2.3	170±40	90.4±27.8	62±10.5

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



Fig. 7 X-ray diffraction patterns of porous Ti under different vacuums: (a) 5×10^{-3} Pa; (b) 7×10^{-4} Pa

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



Fig. 8 SEM image (a) and map scanning images of carbon (b) and oxygen (c) of porous Ti sintered under vacuum of 5×10^{-3} Pa; SEM image (d) and map scanning images of carbon (e) and oxygen (f) of porous Ti sintered under vacuum of 7×10^{-4} Pa

 Table 3 Chemical compositions of Ti powder and porous Ti sintered under different vacuums

Test No.	Oxygen content (mass fraction)/%	Carbon content (mass fraction)/%
S8(7×10 ⁻⁴ Pa)	0.95	0.69-0.86
S2(7×10 ⁻⁴ Pa)	0.95	-
S1(7×10 ⁻⁴ Pa)	0.95	-
S9(5×10 ⁻³ Pa)	1.1	0.78-0.9
Ti powder	0.5	0.01



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,



Fig. 10 Effects of sintering time on tensile strength (a) and tensile elastic modulus (b) of porous Ti under vacuum of 7×10^{-4} Pa and sintering temperature of 1200 °C

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

Table 4 Mechanical properties of porous Ti under different vacuums

Test No.	Compressive strength/MPa	Tensile strength/MPa	Bending strength/ MPa	Compressive elastic modulus/GPa
S8 (7×10 ⁻⁴ Pa)	200±30	149±5.7	434±6.3	4±0.7
S9 (5×10 ⁻³ Pa)	141±15	125±7	264±10	2±0.6

not only due to the escape of gas from the pore wall, which served as channels between connected macropores 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% \pm 3% and average pore size of (7.3 \pm 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

$$n < 2\pi \gamma_{\rm s} / \gamma_{\rm gb} \tag{1}$$

where the specific energy for the free surface (γ_s) is three times of that for the grain-boundary (γ_{gb}). The critical coordination number (n) is about 6π ($n_c \approx 18.84$). 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.



Fig. 11 Pore coordination number of porous Ti under different sintering conditions

It is assumed that, after the evaporation of spherical space holders, the initial shape of large pores remains spherical at low temperature. During sintering, there is always an equilibrium thermodynamic driving force to promote the grain-growth, thus reducing the large pores [38]. When the grain-growth is prohibited, the large pore shrinks by a neighbour switching mechanism, which is similar to the superplastic deformation [37]. Therefore, it is reasonable for the broader distribution of

macro-pore size than that of PMMA particle size used, which is in agreement with the assumption in Ref. [29].

In this study, the pore structure of porous Ti with unchanged fraction of space holder depends on the sintering temperature and time, which is deleterious in terms of the mechanical property. As the sintering temperature and time increase, the pore size and grain size change, as shown in Figs. 5 and 6, thus leading to a changed strength (Figs. 9 and 10). As depicted by the curve proposed, the tensile strength increases with increasing the sintering temperature and time, except for the deviation for Sample S2, which is due to more irregular micro-pores existing because of incomplete densification resulting from the low sintering temperature and time (as shown in Figs. 3(a) and 4(a)). Rising the sintering temperature and time can increase the tensile strength and elastic modulus because the densification increases as well as the pore size decreases. A slight spheroidization in pore shape at high temperature and for long time also contributes to the increase of the mechanical property. However, the reduced strength for samples can be attributed to an increase of non-uniform grain size, which takes an opposite effect on the mechanical property of porous Ti. However, the discrepancy is very large (~ 8 GPa) for Sample S2. This may be due to the wide variation in macro-pore width and the small width of the walls separating the pores, which undergoes micro-plastic deformation in the apparently linear regime of the stress-strain curve [31].

Thus, the initial deformation mode and the final failure mechanism of porous Ti also related to the ductility of the Ti matrix such as the solid Ti, which depend on the grain size, micro-pores and oxygen content in porous Ti ligament. Although, the failure of porous Ti is controlled primarily by the macro-pores [29]. Moreover, the steep increases in strength and elastic modulus of porous Ti with increasing the sintering temperature and time may reflect the fact that micro-porosity is eliminated preferentially to macro-porosity during sintering.

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

- DUBINSKIY S, PROKOSHKIN S, BRAILOVSKI V, INAEKYAN K, KOROTITSKIY A. In situ X-ray diffraction strain-controlled study of Ti-Nb-Zr and Ti-Nb-Ta shape memory alloys: Crystal lattice and transformation features [J]. Materials Characterization, 2014, 88: 127–142.
- [2] THIEME M, WIETERS K, BERGNER F, SCHARNWEBER D, WORCH H, NDOP J, KIM T J, GRILL W. Titanium powder sintering for preparation of a porous functionally graded material destined for orthopaedic implants [J]. Journal of Materials Science: Materials in Medicine, 2001, 12: 225–231.
- [3] ZOU C M, ZHANG E L, LI M W, ZENG S Y. Preparation, microstructure and mechanical properties of porous titanium sintered by Ti fibres [J]. Journal of Materials Science: Materials in Medicine, 2008, 19: 401–405.
- [4] LI J P, LI S H, de GROOT K, LAYROLLE P. Preparation and characterization of porous titanium [J]. Key Engineering Materials, 2001, 218–220: 51–54.
- [5] LI Yan, GUO Zhi-meng, HAO Jun-jie, REN Shu-bin. Porosity and mechanical properties of porous titanium fabricated by gelcasting [J]. Rare Metals, 2008, 27(3): 282–286.
- [6] ERK K A, DUNAND D C, SHULL K R. Titanium with controllable pore fractions by thermoreversible geleasting of TiH₂ [J]. Acta Materialia, 2008, 56: 5147–5157.
- [7] RICCERI R, ARCURI F, MATTEAZZI P. Porous titanium obtained by P/M [J]. Journal de Physique IV, 2001, 11: 51–57.
- [8] YOOK S, YOON B, KIM H, KOH Y, KIM Y. Porous titanium (Ti) scaffolds by freezing TiH2/camphene slurries [J]. Materials Letters, 2008, 62: 4506–4508.
- [9] CHEN Liang-jian, LI Ting, LI Yin-min, HE Hao, HU You-hua. Porous titanium implants fabricated by metal injection molding [J].Transactions of Nonferrous Metals Society of China, 2009, 19(5): 1174–1179.
- [10] LI J, HABIBOVIC P, van den DOEL M, WILSON C, de WIJN J, van BLITTERSWIJK C, de GROOT K. Bone ingrowth in porous titanium implants produced by 3D fiber deposition [J]. Biomaterials, 2007, 28: 2810–2820.
- [11] IBRAHIM A, ZHANG F M, OTTERSTEIN E, BURKEL E. Processing of porous Ti and Ti₅Mn foams by spark plasma sintering [J]. Materials & Design, 2011, 32: 146–153.
- [12] AN Y B, LEE W H. Synthesis of porous titanium implants by environmental-electro-discharge-sintering process [J]. Materials Chemistry and Physics, 2006, 95: 242–247.
- [13] RYAN G E, PANDIT A S, APATSIDIS D P. Porous titanium scaffolds fabricated using a rapid prototyping and powder metallurgy technique [J]. Biomaterials, 2008, 29: 3625–3635.
- [14] LOPEZ-HEREDIA M A, SOHIER J, GAILLARD C, QUILLARD S, DORGET M, LAYROLLE P. Rapid prototyped porous titanium coated with calcium phosphate as a scaffold for bone tissue engineering [J]. Biomaterials, 2008, 29: 2608–2615.
- [15] KRISHNA B V, BOSE S, BANDYOPADHYAY A. Low stiffness

porous Ti structures for load-bearing implants [J]. Acta Biomaterialia, 2007, 3: 997–1006.

- [16] XUE W C, KRISHNA B V, BANDYOPADHYAY A, BOSE S. Processing and biocompatibility evaluation of laser processed porous titanium [J]. Acta Biomaterialia, 2007, 3: 1007–1018.
- [17] LIANG F H, ZHOU L, WANG K G. Apatite formation on porous titanium by alkali and heat-treatment [J]. Surface & Coatings Technology, 2003, 165: 133–139.
- [18] RYAN G, PANDIT A, APATSIDIS D P. Fabrication methods of porous metals for use in orthopaedic applications [J]. Biomaterials, 2006, 27: 2651–2670.
- [19] BANHART J. Manufacture, characterisation and application of cellular metals and metal foams [J]. Progress in Materials Science, 2001, 46: 559–632.
- [20] LI Bo-qiong, LU Xing, WANG De-qing. The effect of processing on microstructures and mechanical properties of porous titanium [J]. Journal of Dalian Railway Institute, 2006, 27: 70–76.
- [21] WEN C E, YAMADA Y, SHIMOJIMA K, CHINO Y, ASAHINA T, MABUCHI M. Processing and mechanical properties of autogenous titanium implant materials [J]. Journal of Materials Science: Materials in Medicine, 2002, 13: 397–401.
- [22] MÜLLER U, IMWINKELRIED T, HORST M, SIEVERS M, GRAF-HAUSNER U. Do human osteoblasts grow into open-porous titanium? [J]. European Cells & Materials, 2006, 11: 8–15.
- [23] LI Bo-qiong, LU Xing. Influence of Ti powder characteristics on the mechanical property of porous Ti using space holder technique [J]. Acta Metallurgica Sinica, 2014, 27: 338–346.
- [24] KARDOKUS J K, MORALES D. Hot pressed and sintered sputtering target assemblies and method for making same: US, 5863398 [P]. 1999.
- [25] ZHU Ke, LI Cheng-feng, ZHU Zhen-gang. Measurement of electrical conductivity of porous titanium and Ti6Al4V prepared by the powder metallurgy method [J]. Chinese Physics Letters, 2007, 24: 187–190.
- [26] WEN C E, MABUCHI M, YAMADA Y, SHIMOJIMA K, CHINO Y,

ASAHINA T. Processing of biocompatible porous Ti and Mg [J]. Scripta Materialia, 2001, 45: 1147–1153.

- [27] LI Z L, WANG Y, ZHANG G Q, XIAO J. 3-D porous Ti manufacture and feature [J]. Orthopaedic Biomechanics Materials and Clinical Study, 2007, 4: 1–4.
- [28] LAPTEV A, VYAL O, BRAM M, BUCHKREMER H P, STÖVER D. Green strength of powder compacts provided for production of highly porous titanium parts [J]. Powder Metallurgy, 2005, 48: 358–364.
- [29] LI B Q, YAN F, LU X. Effect of microstructure on the tensile property of porous Ti produced by powder metallurgy technique [J]. Materials Science and Engineering A, 2012, 534: 43–52.
- [30] GBT 232-1988. Bending test of metal [S]. (in Chinese)
- [31] LI J C, DUNAND D C. Mechanical properties of directionally freeze-cast titanium foams [J]. Acta Materialia, 2011, 59: 146–158.
- [32] JORGENSEN D J, DUNAND D C. Ti-6Al-4V with micro- and macropores produced by powder sintering and electrochemical dissolution of steel wires [J]. Materials Science and Engineering A, 2010, 527: 849–853.
- [33] CHINO Y, DUNAND D C. Titanium foam with aligned elongated pores processed by freeze casting [J]. Acta Materialia, 2008, 56: 105-113.
- [34] SEETHARAMAN V, SEMIATIN S L. Microstructures and tensile properties of Ti-45.5Al-2Nb-2Cr rolled sheets [J]. Materials Science and Engineering A, 2001, 299: 195–209.
- [35] PARHAMI F, MCMEEKING R M, COCKS A C F, SUO Z. A model for the sintering and coarsening of rows of spherical particles [J]. Mechanics of Materials, 1999, 31: 43–61.
- [36] HUANG Pei-yun. The principle of powder metallurgy [M]. Beijing: Metallurgy Industry Press, 1982.
- [37] PAN J, CH'NG H N, COCKS A C F. Sintering kinetics of large pores [J]. Mechanics of Materials, 2005, 37: 705–721.
- [38] COCKS A C F. Constitutive modelling of powder compaction and sintering [J]. Progress in Materials Science, 2001, 46: 201–229.

烧结工艺对添加造孔剂制备多孔钛性能的影响

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摘 要:采用粉末冶金法在不同烧结条件下添加聚甲基丙烯酸甲酯造孔剂制备临床骨科用多孔钛,并研究其形态 特征及力学性能。研究表明:烧结温度的升高及时间的延迟导致多孔钛孔壁晶粒尺寸的增大和孔隙尺寸的减小, 从而提高多孔钛的拉伸强度和弹性模量。与多孔钛相比,未添加造孔剂烧结钛制品的显微组织及力学性能更加依 赖烧结温度及时间。这些机制的相对贡献亦受原始粉末结构及氧含量的影响。 关键词:多孔钛;粉末冶金;显微组织;力学性能

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