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Original Article

Synthesis and characterization of *Porous titanium*

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Abstract

Porous titanium with good strength and three-dimension pore structure was fabricated by using TiH_2 as vesicant foaming titanium powder. This kind of porous titanium with good bio-mechanical compatibility may have the potential to alleviate the problems caused by the mismatch of the strength and Young's modulus between implant (110 GPa for titanium) and bone. Moreover, the pores (mainly in 100-700 μm) are all interconnected. This porous structure would endow the materials with better activity between bone and porous implant matrix. Furthermore, biocompatible porous titanium with a porosity of 33.51-49.09 vol.%, a compressive strength of 156.19-173.34 MPa and a hardness of 438.51-461.40 is known to be a good candidate material for use as bone implants. In the present study, porous titanium was fabricated by using a powder metallurgical process. The effects of process variables, such as the size of the foaming agent and the sintering temperature, on the pore structure and the mechanical properties were investigated. The relationships between the pore structure and the mechanical properties were also studied.

Keywords: Porous titanium, sintering, biomechanical compatibility, bioactivity

1. introduction

Ideal bone substitute materials should be biocompatible to ensure the safety of the implants in the human body, to fulfill required load bearing functions during the implantation period, and to encourage bioactivity, such as, bonding between materials and bone and rapid new bone formation.

Pure titanium (Ti) is a silvery-white, lustrous metal with low mass density (4.51 g/cm^3) and good flexural strength (above 400MPa) (ASM Handbook, 1990). Titanium and its alloys are widely used in both aerospace and non-aerospace applications. Aerospace applications include their use in gas turbine engines for both military and commercial aircrafts, airframes, and for various applications in missiles and space vehicles. Non-aerospace applications include the use of Ti in specialty chemical, pulp and paper, oil and gas, marine, biomedical, and consumer goods industries (Zbigniew *et al.*, 2005).

Porous titanium has been developing recently for biomedical applications. Biocompatible porous titanium with a porosity of 33% and a compressive strength of a compact human bone can reach 170-193 MPa. It is difficult, however, to make various shapes, since they are sintered and shaped in a mold. As reviewed recently, porous titanium can be produced by various sintering methods, including partial sintering of powders (Ik-Hyun *et al.*, 2003) or by sintering of powders around a temporary space-holding phase (D.J. Blackwooda *et al.*, 2000). An alternative foaming method for Ti alloys was developed by pressurizing an argon gas into titanium matrix during hot isostatic pressing (Huanlong *et al.*, 2004).

In this study, porous titanium was produced by mixing the space holder particles with Ti powders. TiH_2 was used as the space holders. The mixed powders were sintered at

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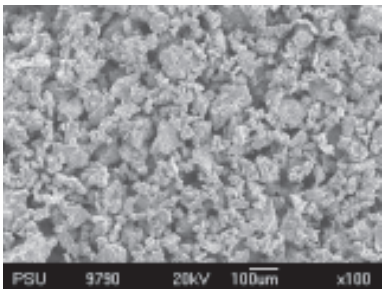
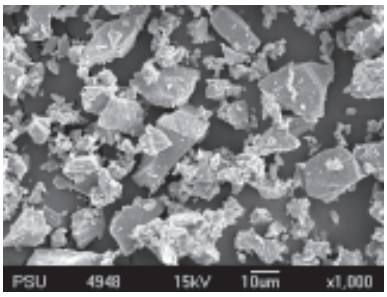


(a)



(b)

Figure 1. SEM micrographs of precursor: (a) Ti and (b) TiH_2

various sintering temperatures. The porous titanium specimens were then characterized by scanning electron microscopy (SEM). Mechanical properties were investigated by compressive tests and hardness tests.

2. Materials and method

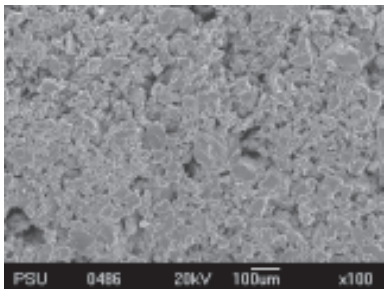
2.1 Starting materials and powder metallurgical processing

Figure 1 (a) shows the irregular shape of starting material, titanium powder, with a mean particle size of 150 µm. TiH_2 with mean particle sizes of 45-53 µm and 53-75 µm, respectively, were used as the space holder. It is observed from Figure 1(b) that the TiH_2 powder also has an irregular shape.

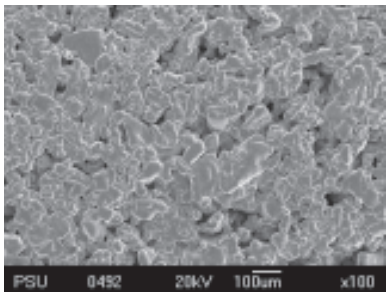
The powders were poured into a stainless steel die with a 5 mm inner diameter. Ti powder was mechanically mixed with the space holder powder. The amount of space holder powder was in the range 0-20 % by weight. After mixing, the mixed powders were then compacted in the die by using uniaxial pressures of 77 MPa and 102 MPa at ambient temperature. The compacted specimens were then sintered at temperatures of 1173, 1373 and 1573 K for 2 hrs under an argon gas atmosphere. A heating/cooling rate used in the sintering process was 5°C/min.

2.2 Assessment of the morphology of the porous titanium

The macroporous structure of the titanium was characterized by Scanning Electron Microscopy (SEM) (JSM-5800 LV, JEOL). The effects of foaming agent, compaction



(a)



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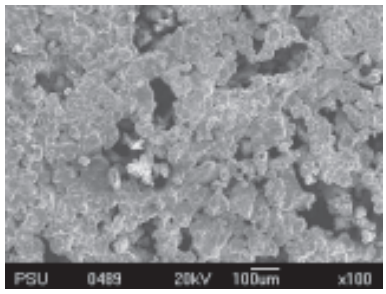

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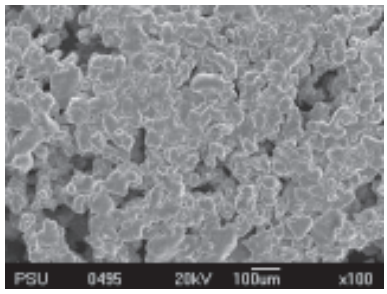

(d)

Figure 2. SEM micrographs of porous Ti compact sintered at 1373K, compaction pressure at 77 MPa: (a) 10% TiH_2 45-53 µm (b) 10% TiH_2 53-75 µm (c) 20% TiH_2 45-53 µm and (d) 20% TiH_2 53-75 µm.

pressure and sintering temperature were also analyzed by using SEM to observe the fractured surfaces of the samples. The open porosity was evaluated by a Multipycnometer. The pore structure of the porous titanium was examined using an Optical Microscope (OM). The distribution of the interpore connections was measured from an Image Analyzer by using the UTHSCSA Image Tool program. The phase structure analysis of the sintered samples was conducted with X-ray

diffraction (XRD) (PHILIPS with Cu Kα radiation).

2.3 Mechanical evaluations

To demonstrate the mechanical properties of the implant material, we evaluated hardness and compression strength. The hardness of the sample was measured by a Rockwell hardness instrument (Model HV-5 Low Load Vickers). Compression tests were performed using a Universal testing machine (HOUNSFIELD, 100KS). Compression tests were performed according to JIS R 1608. Cylindrical-shape samples 5 mm in diameter and 10mm long were tested with a loading rate of 0.6 mm/min.

3. Results and discussion

Figure 2 illustrates the SEM micrographs of sintered porous Ti with varying amounts of TiH_2. It is noted that the porosity of the metal is a function of the foaming agent. X-ray diffraction patterns of the specimens sintered at 1173, 1373 and 1573K are shown in Figure 3. It appears from this figure that the only crystalline phase present in all specimens is titanium.

Table 1 summarizes the total porosity of porous Ti for various sintering conditions. In the study, the porosity of porous Ti is in the range of 33.51-49.09 vol.%, and the open porosity is greater than 16.62 vol.%, suggesting that most pores are three-dimensionally interconnected. It is also noted from table 1 that compaction pressure, sintering temperature, size and amount of foaming agent influence the densification behavior of porous Ti in the temperature range from 1173 to 1573 K. Increasing compaction pressure provides better packing density and contact size of mixed powders which leads to a decrease in porosity. Additionally, the density of sintered specimens could be improved by increasing the sintering temperature as the atomic mobility is better at higher temperatures. Despite slight effect, the increase in the size and amount of the foaming agent give rise to the increase

Table 1. The total porosity of porous Ti sintered compacts for various sintering conditions.

Sintering temperature (K)	Compaction pressure (MPa)	Type of foaming agent	% Foaming agent	Size of foaming agent(μm)	Total porosity (%)	Open porosity (%)
1173	77	Pure Ti			42.88	24.78
		TiH_2	10	45	46.76	34.89
				53	45.08	32.04
			20	45	49.09	42.96
				53	48.22	40.57
	102	Pure Ti			40.40	23.31
		TiH_2	10	45	44.79	32.23
				53	42.73	29.74
			20	45	46.27	39.79
				53	45.63	38.11
1373	77	Pure Ti			39.00	22.19
		TiH_2	10	45	43.08	31.91
				53	41.52	28.32
			20	45	44.08	38.66
				53	42.95	35.81
	102	Pure Ti			37.87	21.84
		TiH_2	10	45	42.94	30.47
				53	39.16	25.80
			20	45	43.05	37.56
				53	40.92	33.78
1573	77	Pure Ti			36.76	20.06
		TiH_2	10	45	39.88	29.04
				53	38.75	24.47
			20	45	42.67	35.31
				53	40.24	32.66
	102	Pure Ti			33.51	16.62
		TiH_2	10	45	38.26	27.03
				53	36.41	22.26
			20	45	40.00	32.72
				53	37.57	28.38

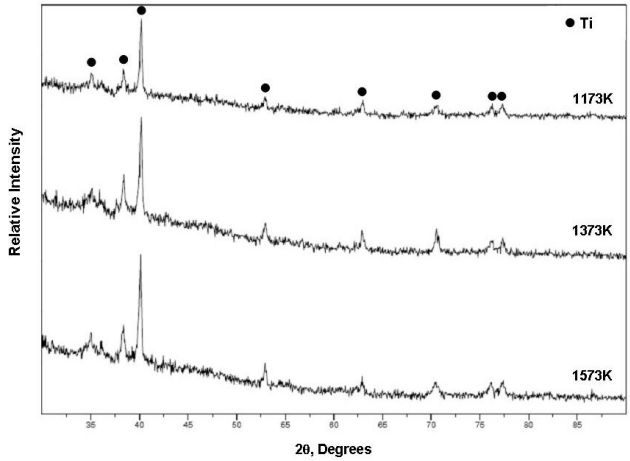

Figure 3. X-ray diffraction patterns of the metal sintered at 1173, 1373 and 1573K

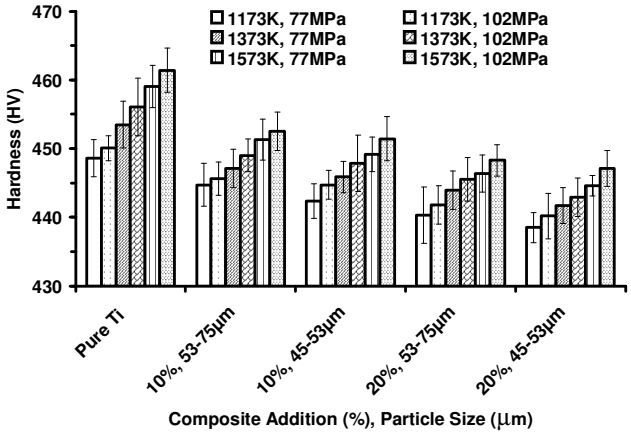

Figure 4. Hardness as a function of porosity of sintered porous Ti compacts.

in porosity of sintered specimens due to the decrease in packing density of green specimens and sintered specimens, respectively.

Figure 4 represents the hardness of the metal as a function of sintering temperature. It is obvious that the hardness increases with increasing sintering temperature. Note that the lowest sintering temperature for which the Rockwell hardness can be measured is 1173 K; the sample is too brittle to resist the deformation induced by the indenter of the hardness experiment if the sintering temperature is lowered.

The compressive strength of porous Ti specimens at various sintering conditions is shown in Figure 5. It is obvious that compressive strength increases with increasing the compaction pressure and sintering temperature. On the other hand, a decrease in compressive strength is detected when the amount of foaming agent increases. However, there is no clear relationship between the compressive strength and the size of the foaming agent.

In this study, the compressive strength of porous Ti specimens is in the range of 156.19-173.34 MPa, which is lower than the compressive strength for bone (295 MPa). This low yield strength for the compact may be due to low yield strength of the commercial pure bulk Ti which is used as a starting material. Since compressive yield strength is more relevant than the bending strength for biomedical applications, an increase in yield strength of porous Ti specimens is desirable. Moreover, high fatigue strength is indispensable for implants. It is assumed that an increase in yield and fatigue strengths can be achieved by lowering the porosity of Ti alloy powder compacts. Porous Ti alloy compacts having low Young's modulus and high yield and fatigue strengths will be fabricated for human bone implants when a b-Ti alloy powder with low Young's modulus is employed as a starting material. Further studies on the optimization of alloy compositions, alloy powder sizes, and sintering conditions are needed for biomedical applications of porous Ti implants.

We have developed a porous bioactive titanium implant material with an interconnected complex porous structure and a porosity of 33.51-49.09%. This titanium implant material has an ultimate compressive strength of around 156.19-173.34 MPa, which is close to that of cortical bone (80-295MPa). Several other attempts to develop porous bioactive titanium implant materials have been reported. C.E. Wen et al. reported porous titanium with high porosity, up to 80%, and these open-cellular foams (pores: 200-500 ìm) have exceptional characteristics (e.g., Ti foam porosity 78%, compressive strength 35 MPa, Young's modulus 5.3 GPa). (C.E. Wen *et al.*, 2001). Li *et al.* reported a porous titanium alloy (Ti6Al4 V) with a porosity of 80% and compression strength of 10MPa (Li J *et al.*, 2002). Producing porous metal implants with sufficient mechanical properties is generally difficult. This porous titanium alloy can be successfully coated with calcium phosphate by the biomimetic method to enhance osteoconductivity and osteoinductivity in vivo (Habibovic P *et al.*, 2005). In this paper, we report a powder sintering method of producing porous titanium implants that possess a unique interconnected porous structure with the superior mechanical property of an ultimate compression strength of 156.19-173.34 MPa. Moreover, the

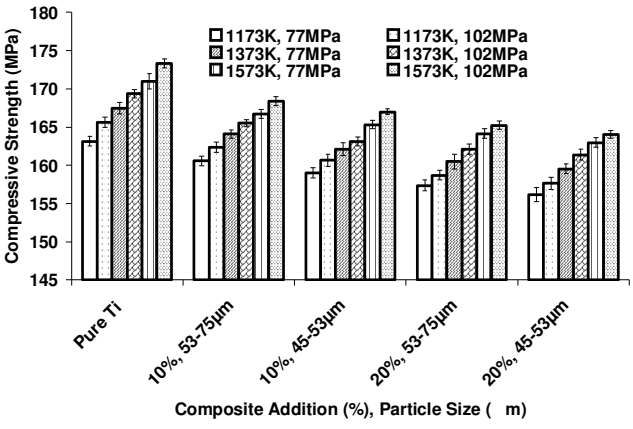

Figure 5. Compressive strength as a function of porosity of sintered porous Ti compacts.

low compressive modulus (4.7 GPa) of our porous bioactive titanium may be beneficial to reducing stress shielding under load-bearing conditions, compared to other load-bearing implants made of solid titanium (110GPa) or other metals (Ik-Hyun *et al.*, 2003).

4. Conclusions

This study has demonstrated that porous Ti compacts having porosities ranging from 33.51 to 49.09 vol.% are successfully fabricated by powder sintering. The porous Ti has rough surfaces depending on the size of the foaming agent. It is found that the porosities and mechanical properties of porous Ti can be controlled by the size and amount of the foaming agent, compaction pressure and sintering temperature. Compressive strengths of porous Ti having the porosity around 33 vol.% are close to those of human cortical bone.

Acknowledgement

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