Fabrication of porous titanium implants by three-dimensional printing and sintering at different temperatures

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INTRODUCTION

Titanium (Ti) is used in a myriad of medical prosthetic devices, running the gamut from artificial joints and dental implants to heart valves and fixture screws. It is a widely used implant material because of its irresistible benefits: excellent mechanical properties, superior corrosion resistance, and unsurpassed biocompatibility. However, Ti has a higher elastic modulus than the human bone. Bone-implant modulus mismatch then causes stress shielding, which in turn causes poor osseointegration and bone formation. One way to reduce the elastic modulus of pure bulk Ti so that it more closely matches that of the human bone is by introducing pores. Porous Ti reportedly had bone-implant modulus near-net-shape fabrication of porous 3D implants composed of β-tricalcium phosphate (β-TCP) and a bioactive glass were manufactured via the 3DP process in a bid to remodel maxillofacial or craniofacial defects in an esthetical way and in significantly reduced operation times. In response to the increasing interest of using porous Ti for tissue-engineering scaffolds, Ryan et al. successfully fabricated porous Ti scaffolds using a 3DP and powder metallurgy technique and reported that the fabricated porous Ti scaffolds had the properties to be employed in orthopedic applications.

In this study, a porous Ti implant was fabricated using 3DP. The CAD model design was converted into

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an STL (Surface Tessellation Language) file, which was sliced into thin cross-sectional layers with 80% of Ti powder bonded on each slice. After the fabricated Ti implant prototypes were sintered at 1,200, 1,300, or 1,400°C, their microstructures and mechanical properties were evaluated to investigate the feasibility and potential of using 3DP to fabricate customized porous Ti implants.

MATERIALS AND METHODS

Fabrication of porous Ti implant prototypes
1. Production of green porous Ti implants
Dimensions of porous Ti implant prototype were 25 mm in diameter and 20 mm in height. Bonding area in each layer was capped at 80%. The finished implant design was exported to an STL file for 3DP processing.

Materials used were 200 mesh Ti powder (purity 98.5%; Shanghai CNPC Powder Material Co.) for the implants and an aqueous solution of 10% aqueous polyvinyl alcohol (PVA; 120 mesh) as the binder. Powder and binder were mixed at a ratio of 10:1 (mass), and the blended mixture was carefully filled into the supply chamber of a 3D rapid prototype printer (LTY 3D printer, Fochif Mechatronics Technology Co., Ltd., Shanghai, China). Polyvinylpyrrolidone (PVP), as the penetration enhancer, was dissolved in distilled water at a concentration of 0.05% and then poured into the supply chamber.

The 3D printer comprised three sensors for X, Y and Z axes, a print head, and a powder dispenser. The print head and powder dispenser moved along the Y-axis from left to right to spread a layer of powder on the Z-axis platform. Once a layer was completed, the Z-axis platform moved down by the thickness of the layer. While the print head moved back along the Y-axis, it printed the binder according to the design of the implant’s cross-section. This process was repeated layer after layer until the whole 3D-structured prototype was completed. Maximum travel distance of the print head was 200 mm in both X and Z directions, and 250 mm in the Y direction.

Scan rate in X direction was 0.4 m/s, while that in Y direction was 0.2 m/s. Spin speed of powder dispenser was about 250 rpm. Thickness of each printed layer was 0.1 mm after two cycles of printing. In this study, a total of 16 green porous Ti implant prototypes were produced, de-powdered, air-dried at room temperature for 24 h, and then stored on the shelf for 5–7 days before sintering.

2. Sintering of green porous Ti implants
To ensure complete decomposition and removal of the binder from the green Ti implant prototypes before sintering, one prototype was randomly selected to have the range of unbinding temperatures determined and confirmed by thermogravimetry and differential thermal analysis (TG-DTA) (Fig. 1) with a thermal analyzer (STA-429C, Netzsch, Bavaria, Germany). In Fig. 1, the red line shows that the primary PVA binder decomposed at 200–300°C, while the remaining PVP binder completely decomposed at 300–500°C.

The remaining 15 prototypes were equally divided into three groups according to the different sintering temperatures: 1200, 1300, or 1400°C. The green Ti implant prototypes were placed in alumina crucibles for sintering under protective argon atmosphere. Figure 2 shows the sintering temperature curve for the 1,300°C group.

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis
SEM was used for the microstructural evaluation of the porous Ti implants sintered at different temperatures. EDX analysis was used to obtain qualitative information on the full elemental composition of sintered porous Ti implant. This combined SEM/EDX analysis was carried out using a field-emission scanning electron microscope and EDX elemental analyzer (Sirion 200, FEI, USA; INCA, Oxford Instruments, UK).
Porosity measurement
Apparent porosities of porous Ti implants sintered at different temperatures were determined by Archimedes principle. For each sintered Ti implant prototype, dry weight (W1) was measured using a precision balance (XB-124, Shanghai Precision Instruments Co., Ltd., Shanghai, China). The prototype was then submerged in water to be boiled for 3 h, before soaking for another 24 h. Weight of Ti implant prototype suspended in water (W2) was measured. After the prototype was retrieved out of water and blotted dry using a tissue paper to remove excess water, it was immediately re-weighed (W3). Porosity was calculated using the formula below:

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\text{Apparent porosity (\%)} = \frac{W_3 - W_1}{W_3 - W_2} \times 100\%
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Vickers hardness test
Surface hardness of the sintered Ti implant prototypes was measured using a microhardness tester (HV-1000, Hengxin Technology Co., Ltd., China) with a load of 100 g for 15 s. The mean value of five readings of each sintered Ti implant prototype was then calculated and recorded.

Compressive strength and modulus of elasticity measurements
Compressive strength and elastic modulus of each sintered Ti implant were measured using a universal testing machine (Z100, Zwick GmbH, Ulm, Germany) with 100 kN load cell. Applied load was directed parallel to the long axis of the prototype at an increasing strain rate of 5 mm/min.

Statistical analysis
Porosity, hardness, elastic modulus, and compressive strength data of porous Ti implants sintered at different temperatures were subjected to one-way analysis of variance (ANOVA) followed by post-hoc Student-Newman-Keuls (SNK) test. Level of significance was set at \( p < 0.01 \).

RESULTS

Green porous Ti implants
A total of 16 porous Ti implant prototypes (25 mm diameter, 20 mm height) were produced by 3DP in this...
study. Before sintering, details on the surface of green porous Ti implant could be clearly seen and there were neither obvious cracks nor distortion (Fig. 3).

**Sintered porous Ti implants**

After sintering, all the three groups of sintered porous Ti implants had visible orderly rows of micropores in clear details. Surface of the sintered Ti implant was also free of cracks, shimmering in metallic luster (Fig. 4).

**SEM and EDX analysis**

Figure 5 shows the SEM images of the porous Ti implants before and after sintering. Before sintering, all green porous Ti implants had visible macropores (Fig. 5a). After sintering, all the three groups of porous Ti implants sintered at different temperatures exhibited coral-like microstructures (Figs. 5b–5d). Pore size ranged between 50 and 150 μm, with pore interconnectivity present throughout the 3D structure of the Ti implants. Number of pores larger than 100 μm decreased as the sintering temperature increased.

According to EDX elemental analysis, Ti accounted for more than 98% of the chemical composition of sintered Ti implants (Fig. 6).
Porosity
Porosity of sintered Ti implants decreased from 65.01% to 41.06% as the sintering temperature increased from 1200°C to 1400°C (Table 1).

Surface hardness
Surface hardness of sintered Ti implants increased from 115.2±0.6 VHN to 182.8±2.1 VHN with increase of sintering temperature (Table 2).

Compressive strength and modulus of elasticity
Table 3 presents the compressive strengths and elastic moduli of porous Ti implants sintered at different temperatures. Elastic modulus increased from 5.9±0.5 GPa to 34.8±1.5 GPa with increase of sintering temperature, and compressive strength increased from 81.3±4.3 MPa to 218.6±7.1 MPa.

Statistical analysis
There were statistically significant differences in porosity, surface hardness, elastic modulus, and compressive strength data among the different sintering temperatures (p<0.01). SNK comparison test revealed that there were significant differences among the three groups. Surface hardness, elastic modulus, and compressive strength of sintered Ti implants increased significantly with the increase of sintering temperature. On the other hand, porosity decreased significantly with the increase of sintering temperature.

DISCUSSION
In 3DP fabrication, layer thickness affects the bonding between the powder-deposited cross-sectional layers. With thick multi-layered structures, one of the common causes of failure stems from shearing in the core layers and sliding at the interfaces between the layers. In the present study, the small particle sizes of Ti, PVA, and PVP powders allowed for reduction in the minimum thickness of each printed layer, hence keeping to a minimum the risk of sliding between the powder layers during or after the 3DP process.

Water-soluble PVP binder not only increased particle-to-particle contact adhesion, but also powder flowability —which in turn enabled a more rapid dissolution of the blended mixture of Ti powder and PVA aqueous solution. Interparticle spacing between adjacent Ti particles was reduced, leading to better initial mechanical properties for the green porous Ti implants. The uniform spherical shape and large surface area of these powder particles were also a large driving force for sintering. A combination of these factors thus culminated in sintered products with good mechanical properties. Therefore, the materials used in this study, namely, 98.5% purity Ti, PVA powder, and water-soluble PVP binder, exhibited promising applicability for 3DP fabrication of porous Ti implants.

EDX elemental analysis revealed that both PVA and PVP binders were completely decomposed and removed from the Ti powder after the debinding process. This meant that there was minimum influence of the binders on the dimensional shrinkage of sintered Ti implants. Shrinkage was largely due to interparticle diffusion bonding and surface fusion of the Ti powder particles (10).

When sintered at 1,200, 1,300 and 1,400°C, the porosities of Ti implants were 65.01%, 46.73%, and 41.06% respectively. Across the cross-sections of porous Ti implants, SEM micrographs showed well-defined porous structures with uniformly distributed pores of 50–70 μm as well as sparsely scattered large pores of 120–150 μm. It has been shown that sintered density increased, but porosity decreased, with increase of sintering temperature (10). Results of this study showed that porosity indeed decreased significantly with increase of sintering temperature. Sintering at a lower temperature gave rise to a porous network with more large pores and a higher degree of interconnectivity.

In the present study, CAD model of the porous Ti implant was designed such that only 80% of Ti powder was bonded on each slice/layer. Before sintering, orderly rows of small pores were clearly seen on the surface of the green part. After sintering, relatively large pores

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| Table 1 Porosities of porous Ti sintered at different temperatures. |
|-----------------------------|------------------|
| Sintering temperature (°C) | Porosity (%)     |
| 1,200                       | 65.01±1.03       |
| 1,300                       | 46.73±0.73       |
| 1,400                       | 41.06±0.31       |

| Table 2 Hardness values (VHN) of porous Ti sintered at different temperatures. |
|-----------------------------|------------------|
| Sintering temperature (°C) | Hardness (VHN)  |
| 1,200                       | 115.2±0.6        |
| 1,300                       | 148.6±1.1        |
| 1,400                       | 182.8±2.1        |

| Table 3 Elastic moduli and compressive strengths of porous Ti sintered at different temperatures. |
|-----------------------------|------------------|
| Sintering temperature (°C) | Elastic modulus (GPa) | Compressive strength (MPa) |
| 1,200                       | 5.9±0.5          | 81.3±4.3 |
| 1,300                       | 16.2±0.9         | 135.4±8.5 |
| 1,400                       | 34.8±1.5         | 218.6±7.1 |
 (>100 μm) were found. According to published literature, the ideal porosity of bone implant materials was in the range of 30–90%, while pore size larger than 100 μm was conducive to bone cell ingrowth for implant stabilization. Further research should be done to investigate how the parameters of 3DP fabrication process could be adjusted to obtain porous Ti implants with porosity and pore size which are propitious to cell growth.

The compressive strength and elastic modulus of the natural bone are 130–180 MPa and 2–30 GPa respectively. A 3DP-fabricated, porous Ti implant by Wiria et al. had compressive strength of 167–455 MPa and elastic modulus of 4.8–13.2 GPa — which was compatible with the elastic modulus of the natural bone. In the present study, the mechanical properties of sintered porous Ti implant increased significantly with increase of sintering temperature. This was due to significant decrease in porosity and concomitant increase in sintered density as sintering temperature increased. Although only 80% of Ti powder was bonded on each cross-sectional slice/layer in this study, the compressive strength and elastic modulus of the porous Ti implant fabricated in this study were 81.3–218.6 MPa and 5.9–34.8 GPa respectively, which closely matched those of the natural bone. Hardness ranged between 115.2 and 182.8 VHN, which was slightly lower than that of commercially pure titanium at 204±7 VHN.

The porous Ti implant fabricated by 3DP process in this study reduced the elastic modulus of pure bulk Ti to closely match that of natural bone. This thus prevents bone resorption due to modulus mismatch, which would cause implant loosening.

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REFERENCES