Additive Manufacturing and Mechanical Properties of Functionally Graded Medical Ti–35Nb–7Zr–5Ta Porous Scaffolds

Huihua Cheng
National Engineering Research Centre of Near-net-shape Forming Technology for Metallic Materials, South China University of Technology, Guangzhou, China
hh.cheng@qq.com

Abstract. Functionally graded porous structure materials produced by additive manufacturing are promising for bone tissue engineering. Uniform and three kinds of gradient porous models (Radial, Axial, and Unidirectional) based on BCC unit were designed and built with selective laser melting. The research results show that: SLMed Uniform porous Ti–35Nb–7Zr–5Ta sample consists of a single β-Ti phase, and microstructure is composed of columnar crystal and cellular structure. The compression test shows that the radial gradient porous structure has higher yield strength (111 MPa), low elastic modulus (4.5 GPa), excellent plasticity, and energy absorption, which is more suitable for the construction of load-bearing orthopedic scaffold.

1. Introduction
With the aging of the population, the rapid development of biomaterials, and tissue engineering, artificial implants are widely used in various clinical operations. Synthetic implants are often used in surgical procedures to replace the damaged and failed parts of the patient to improve the patient's quality of life. The three most used load-bearing implant materials are stainless steel, CoCr alloy, and titanium alloy [1]. Ti-35Nb-7Zr-5Ta (TNTZ) alloy as a new type of alloy β Titanium alloy, due to its extremely low elastic modulus (~ 55 GPa), high biocompatibility, and corrosion resistance, is considered to have great potential to develop as a new generation of medical titanium alloy materials [2].

However, the modulus of TNTZ alloy must be reduced further if it is to match the modulus of human bone (0.022~21.8 GPa) [3]. One standard method to reduce the modulus of a material is to introduce porosity into the structure. At the same time, the interconnected pores of the porous structure are also conducive to cell adhesion, proliferation, and bone tissue regeneration, and other biological cell behaviors, which make the implant and tissue obtain more excellent biological combinations, improve the success rate of implantation [4].

Functionally graded materials (FGMs) have attracted particular attention in orthopedics due to their unique characteristics [5]. In essence, human bone is a typical functionally graded material. The outer area of human bone is dense cortical bone, and the inner space is loose cancellous bone. The gradient distribution of porosity along the radial direction leads to the gradual transformation of bone strength, which is believed to prevent early cracks, leading to destructive bone destruction. In addition, the graded arrangement of pores in the bone can improve mechanical efficiency, overall robustness and meet the behavior guidance requirements of different cells.

Selective laser melting (SLM) technology has a high degree of geometric freedom, can prepare complex internal structures with arbitrary topological layout, flexibly control the pore structure, and
realize the short process and personalized customization of porous structure materials. It is one of the most favorable methods for manufacturing complex porosity structures of artificial bone implants.

In the study, various generating continuous TNTZ FGMs were designed and successfully prepared via SLM to reveal the influence of the gradient design method on mechanical properties and deformation behavior and provide a useful reference for the design and preparation of gradient porous TNTZ alloy for medical implants.

2. methods and Material

2.1. Structural design
Gradient porous structure design is based on Body-Centered Cubic (BCC) unit cell with 60% porosity, the cell size is 1.5 mm, and its pore diameter (d) strut thickness (s) is 600 μm and 500 μm, as shown in Fig.1. The porous structures were designed with Materialise 3-Matic software. The Uniform and three kinds of generating continuous gradient structures (Radial, Axial, and Unidirectional) by changing the strut diameter linearly across cell layers which enables a smooth transition between layers (Fig.2).

![Figure 1 BCC unit cell](image1)

![Figure 2 CAD design model of Uniform and three kinds of gradient structures](image2)

2.2. Material preparation
The raw material used in this experiment is spherical Ti–35Nb–7Zr–5Ta (wt.%) alloy powder prepared by vacuum-consumable arc melting and gas atomization method, and the particle size is 15–90 μm.

EOSINT M280 SLM equipment was used for additive manufacturing. The SLM instrument was operated using an optimum parameter (a laser power of 180 W, a scanning speed v of 1400 mm/s, an 80 μm hatch spacing, a 30 μm layer thickness t, and a scanning direction of 67°) under the protection of a high-purity Ar atmosphere.

2.3. Experimental methods
The phase constitutions of the SLMed porous samples were characterized by X-ray diffraction (XRD; D/MAX-2500/PC, Japan). The microstructures of the samples were examined by scanning electron microscopy (SEM; Philips XL-30 FEG, USA) after polished and followed by etching with Keller's reagent for 20 s. The compression test at room temperature was carried out with the SUNS UTM5105 electronic universal testing machine and the Swiss SYLVAC digital dial indicator extensometer with an accuracy of 0.001 mm. The compression sample size met the ISO 13314 standard, and the compression rate was 0.5 mm/min. The elastic modulus is calculated by the slope of the elastic section of the...
compression curve, and the yield strength is the stress corresponding to 0.2% strain. The energy absorption per unit volume (W) is defined as:

\[ W = \frac{1}{100} \int_0^{\varepsilon_m} \sigma(\varepsilon) d\varepsilon \]

Where \( \sigma \) is the compressive stress; \( \varepsilon \) is the compressive strain; \( \varepsilon_m \) is the upper limit of compression strain (50%).

3. Results and discussion

3.1. Morphology of porous scaffolds

Fig. 3 shows the as-fabricated physical picture and pore morphology of the four porous structures. It can be seen from the figure that the porous sample formed by SLM has high forming accuracy and good surface quality. After measurement, the pore diameter and strut thickness of uniform porous is about 500 \( \mu \)m and 520 \( \mu \)m; compared with the CAD design model, it has less deviation and higher manufacturing accuracy. As-fabricated pore diameter and strut diameters were larger than the original designs, resulting in irregular bumps and unmelted powder on the surface. This difference is characteristic of the SLM process and is caused by effects such as staircase stepping due to layered manufacturing.

![Figure 3](image)

Figure 3 (a1-d1) The as-fabricated physical picture and (a2-d2) pore morphology of the four porous structures: (a) Uniform; (b) Radial; (c) Axial; (d) Unidirectional

3.2. Phase and microstructure

Fig. 4 and Fig. 5 are the XRD pattern and the microstructure of the building direction (BD) of the Uniform porous sample, respectively. It can be seen from XRD that the porous sample formed by SLM is composed of a single \( \beta \) phase. From the microstructure map, it is found that the structure is mainly composed of columnar crystals in the inner area of the molten pool and the cell structure of the molten pool boundary. The growth direction of columnar crystals is perpendicular to the boundary of the molten pool and parallel to the direction of the SLM building. It is mainly formed by the local temperature gradient caused by the layer-by-layer stacking manufacturing process. Under the high-speed laser scanning, the melt has a very fast solidification speed and a large degree of undercooling during the solidification process and the upper layer serves as a non-uniform nucleation substrate, generating a large number of crystal nuclei at the interface and free along with all directions for growth, due to a large number of crystal grains, adjacent crystal grains are mutually restricted during the growth process and cannot continue to grow, resulting in the formation of a metastable cell structure [6].
3.3. Mechanical Properties

Fig. 6 shows the compressive stress-strain curves of uniform porous and three kinds of gradient porous specimens; mechanical property data are listed in Table 1. Compression test results show that the compression curve of BCC uniform porous TNTZ material can be divided into three deformation stages: (I) Elastic deformation stage, in which the compression stress and compression strain become linear, and elastic deformation occurs in the inner element strut of porous structure; (II) Plastic deformation stage, the material is plastically deformed, and the element strut is bent, showing a long stress yield platform. During this stage, the element structure enters the energy absorption process. The longer the yield platform is, the higher the energy absorption efficiency; (III) Densification stage, as the deformation continues, due to the good plasticity and toughness of TNTZ alloy, the unit pillar will not have a brittle fracture and lamellar fracture but will produce bending deformation until the two pillars contact each other and densify, resulting in a sharp increase in stress. According to the characteristics of the compression curve, the Uniform porous structure is a typical bending-dominated structure.
Table 1  Mechanical properties of four kinds of porous structures

| Mechanical property       | Pore type | Uniform | Radial | Axial | Unidirectional |
|--------------------------|-----------|---------|--------|-------|----------------|
| Yield strength (MPa)     |           | 101     | 111    | 27    | 38             |
| Elastic modulus (GPa)    |           | 3.6     | 4.5    | 1.4   | 2.1            |
| Energy absorption (MJ/m³)|           | 132     | 128    | 101   | 127            |

In contrast, the radial gradient porous structure has higher yield strength and elastic modulus, which are 111 MPa and 4.5 GPa, respectively, significantly higher than the axial and unidirectional gradient structure. It can be seen from the compression curve that the radial gradient and uniform porosity will enter the stage of stress plateau after yielding, while the stress value will continue to rise after the unidirectional gradient yielding. This deformation behavior leads to the energy absorption of these three kinds of porosity at 50% strain, which is about 130 MJ/mm³. To sum up, radial gradient porous has excellent comprehensive mechanical properties. Compared with long human bone (yield strength 104-121 MPa, the elastic modulus 10-30 GPa) [7], it has an excellent combination of high strength and low modulus, and better toughness and energy absorption, which is more suitable for the construction of load-bearing orthopedic scaffold.

Fig. 7 shows the deformation behavior of uniform porous and three kinds of gradient porous specimens during compression. It can be seen from the figure that the deformation of uniform porous is uniform during the whole compression process, the radial gradient porous is drum-shaped deformation, and the axial porous is the first to bend and deform in the middle region due to the smaller diameter of the rod in the middle part. Similarly, the single-phase gradient porosity starts at the top. There is no obvious fracture and breakage phenomenon in the compression process of all samples, so they have high toughness.

Figure 7  Deformation modes of porous structures: (a) Uniform; (b) Radial; (c) Axial; (d) Unidirectional
4. conclusion
In this study, Uniform and three kinds of gradient porous models (Radial, Axial, and Unidirectional) based on BCC unit were designed and successfully manufactured by SLM technology. By comparing the mechanical properties of each porous structure, it can provide relevant reference and theoretical basis for the design and clinical application of gradient porous titanium alloy implants. The main conclusions are as follows:

(1) The SLMed Uniform porous sample consists of a single β-Ti phase, and microstructure is composed of columnar crystal in the inner region of the molten pool and cellular structure at the boundary;

(2) Uniform and gradient porous TNTZ scaffolds have low elastic modulus and good plasticity. Among them, the radial gradient porous structure has higher yield strength (111 MPa), low elastic modulus (4.5 GPa), and excellent energy absorption, which is more suitable for the construction of load-bearing orthopedic scaffold.

Acknowledgment
This work was financially supported by the Joint Funds of the National Natural Science Foundation of China (No. U19A2085), the Key Basic and Applied Research Program of Guangdong Province (No. 2019B030302010), and the Optical Valley Science Research Project, WEHDZ (No. 2019001).

References
[1] J. Qazi, B. Marquardt and H. Rack, "High-strength metastable beta-titanium alloys for biomedical applications," JOM, vol. 56, pp. 49-51, November 2004.
[2] X. Luo, L. Liu, C. Yang, H. Lu and Y. Li, "Overcoming the strength–ductility trade-off by tailoring grain-boundary metastable Si-containing phase in β-type titanium alloy," J. Mater. Sci. Technol., vol. 68, pp. 112-123, March 2021.
[3] D. Barba, E. Alabort and R. Reed, "Synthetic bone: design by additive manufacturing," Acta Biomater., vol. 97, pp. 637-656, October 2019.
[4] X. Tan, Y. Tan, C. Chow, S. Tor and W. Yeong, "Metallic powder-bed based 3D printing of cellular scaffolds for orthopaedic implants: A state-of-the-art review on manufacturing, topological design, mechanical properties and biocompatibility," Mater. Sci. Eng. C, vol. 76, pp. 1328-1343, July 2017.
[5] S. Choy, C. Sun, K. Leong and J. Wei, "Compressive Properties of Ti-6Al-4V Lattice Structures Fabricated by Selective Laser Melting: Design, Orientation and Density," Addit. Manuf., vol. 16, pp. 213-224, August 2017.
[6] K. Prashanth and J. Eckert, "Formation of metastable cellular microstructures in selective laser melted alloys," J. Alloys Compd., vol. 707, pp. 27-34, June 2017.
[7] C. Stewart, B. Akhavan, S. Wise and M. Marcela, "A review of biomimetic surface functionalization for bone-integrating orthopedic implants: Mechanisms, current approaches, and future directions," Prog. Mater. Sci., vol. 106, 100588, December 2019.