

3D Printed Titanium Alloy in Bone Repair

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Abstract:

Today, with more and more cases of bone injury around the world, people are now in need of efficient bone care. The 3D printing technique has found wide application in the field of bone restoration. Metallic materials are widely used in clinic, and Ti alloy is a good medical material for its outstanding properties. The advantages and disadvantages of 3 main 3D-printing techniques for metals are discussed, including selective laser melting (SLM), electronic beam melting (EBM) and binder jetting (BJG). Therefore, 3 kinds of powder technology suitable for Ti alloy are presented, including plasma rotating electrode process (PREP), gas atomization (GA) and plasma atomization (PA). In addition, the presentation and optimal application of 3D printed Ti alloys in the treatment of bone diseases are also discussed. Through a review of the latest advances in relevant areas, this article will offer valuable data and instruction to apply 3D printing to bone treatment.

Keywords: Titanium alloy; bone repair;3D printing.

1. Introduction

Bone is critical for the survival of human body. Studies indicate that there are four million patients worldwide who require a bone transplant or a bone-replacing operation each year. In the US, the prevalence of age-related bone disorders is rising. In Europe, since 2010, the number of fracture cases has increased by around 28% as the population grows [1]. Human beings are in urgent need of efficient bone treatment.

In recent years, 3D printing, also called additive manufacturing, has been widely applied in the field of bone healing, since it enables personalised therapy based on the circumstances in which the patient is injured, making it easier to treat, less uncomfortable for patients, and preventing the risk of conventional bone graft failure [2].

Traditional metal-based implants have been widely used in clinic because of their outstanding mechanical performance. Since the 1960's, pure titanium has been used as a human implant in clinical oral research [3]. Along with the progression of excellent Ti alloy,extensive applications have been seen in the field of medical implantation. Ti and its alloys possess the merits of high intensity, low density, corrosion-resistance and biocompatibility [4, 5].

This paper reviews the research progress of 3D printed Ti alloys in bone reconstruction. Based on the analysis of the requirement of Ti alloy in bone restoration, this paper presents the relevant techniques of 3D printing in the restoration of bone. Moreover, it will be helpful to apply 3D

printing techniques to the restoration of bone and custom bone restoration materials.

2. Demand for Titanium Alloy Material in Bone Repair

If a person suffers from bone defect, he or she may recover to some degree, but sometimes he is unable to recover under certain circumstances, for example major defects, since the cells are unable to grow or divide under these conditions [6]. A common approach is to transplant a bone from another part of the patient's body into the part to be repaired. However, the number of transplantable bones in a person's body is limited. In addition, there can be complications in the donor area following the transplant. What's more, donations from other people may be denied from non-specific immunity [6, 7]. To overcome the severe restrictions of traditional bone repair, the use of artificial implants has attracted increasing interest.

Titanium and its alloys are the most widely used metal for clinical use. Pure titanium has a elastic modulus of 110GPa, which is much greater than that of bone, but less than that of similar metals such as stainless steel [7-10]. Because of the stress shielding effect, this difference in elastic module may lead to osteoporosis, fracture, skeletal atrophy, and early implantation failure. Researchers have created a porous Ti framework that can lower the module and emulate the strength of natural bone so that it can be more securely attached to the surrounding tissues. Furthermore, the inter-connected holes in the scaffold can reduce

the time for healing, enhance angiogenesis and nutrition transfer [9]. Titanium implants have a high compression strength, a skeletal elasticity module, and a long-term bone ingrowth is enhanced. Thus, the porous titanium matrix is a good candidate for the restoration of the bone defect. Shi et al. used 3D printing technology to print out porous artificial titanium bone with Ti6Al4V powder as the basic material, and it has a uniform honeycomb structure [11]. It had a micropore size which was less than 10 μm , with porosity of 70.56%, compressive strength of 194 MPa and bending strength of 105 MPa, and its structure and performance could meet the requirements of human bones.

3. 3D Printing Technology suitable for Titanium Alloy Implants

Several few typical 3D printing technologies are described below, such as selective laser melting (SLM), electron beam melting (EBM) and binder jetting (BJG).

3.1 SLM

SLM is a newly developed fast prototype technique, which has been regarded as a promising technique in recent years. As SLM develops, 3D printing can be applied in practice instead of just modeling [12]. SLM has found wide application in titanium-based biomaterials. It is capable of producing complicated construction components and fine machining of the alloy in a highly precise and highly flexible manner [13]. The SLM procedure consists of three-dimensional modeling, hierarchical data treatment, powder-bed fabrication and laser-fusing [12]. Firstly, a high energy laser beam was used for selective melting of the metallic powder layer based on the geometrical data model of 3-D software. Then, the formed molten pool is quickly solidified at approximately 103 ~ 106 K/s. Eventually, the desired shape is achieved [14]. The complete process happens in a closed chamber which is filled with inert gas, usually nitrogen. The main technological parameters are the beam power, the velocity of the laser beam, the length of the hatch, the overlap of the hatch and the type of the hatch. Such technological parameters are essential to the manufacture of components without defects [15].

SLM has the merits of a wide variety of available materials, a capability for optimizing performance in machining of the parts, enhanced functionality, comparatively low cost, and a nearly net-shape assembly that can be put into service. But there are drawbacks as well. It is characterized by a comparatively slow technology, large dimension limitation, high energy cost, high start-up cost, long time to optimize technological parameters, difficulty in handling dust and roughness of manufactured components

[15].

Titanium alloy is very suitable for 3D printing using SLM due to its cleanliness and high utilization rate in the process. With 3D printing, the potential of titanium can be fully utilized. Because of its low Young's Modulus (~ 62 Gpa) and high cooling rate, a type of titanium alloy named Ti-45nb has been widely used in implants [16].

3.2 EBM

EBM resembles SLM, which uses layer-by-layer technology [15]. In this procedure, an electron beam is employed to selectively melt and fuse the metallic powder layer under vacuum conditions [17].

A strong electronic beam (maximum 3 kW [15]) is employed to merge the given metallic power level (from 50-150 μm thick [15]) until the complete geometrical shape of the required part is achieved. Firstly, the electrons are emitted from a heated tungsten filament or a cathode of lanthanum hexaboride (LaB6). Next, through electromagnetic lens, the electrons are sped up, concentrated, and deflected. The desired geometric shapes are manufactured on the pre-heated starter board [17]. During the heating, a few electric rays are used to heat the powder layer for a few times so that the powder grains are agglomerated and the temperature remains within the construction volume [15, 18]. The pre-heating method and the application temperature are decided by the material and powder performance of the material. The temperature of the powder grains was reduced by the electron beam when they were pre-heated. The material is solidified, the construction stage is lowered, and a new coating of dust is laid. This cycle continues until the complete geometry of the part is obtained. Lastly, the components are chilled on the machine [17].

The main technological parameters of EBM include beam power, the scanning rate, the focal point, the diameter of the beam, the distance between the beam, the surface temperature, the pre-heat temperature (including the repetition, the rate and the intensity of the ray), the outline policy and the scanning strategy [15].

Preheating-Up the printer and the material prior to the electron beam attack may result in a reduction in the residual stress of the manufactured components, thus eliminating the requirement for post-manufacture thermal treatment. Consequently, the components manufactured are superior to those of wrought or cast products. Meanwhile, EBM allows for the production of non-stress and martensite free structures [19].

Ti-6Al-4V has good corrosion resistance due to high strength-to-weight ratio [19]. Recently relevant papers on EBM processing for Ti-6Al-4V focus on the use of manufactured components in prostheses [20, 21]. Harrysson

et al produced a hip stem with Ti- 6Al-4V, and EBM was also applied to the lower jaw implant by Derand et al [21, 22].

3.3 BJJ

BJJ has received increasing concern in the field as well as in academic circles. Two materials are normally employed in this method: a metallic/ceramic-based material that forms a component and a binding material that binds the material between layers [15]. In this method, a CAD model is used for selective deposition of a liquid binder on a powder bed to create a cross-section for every layer. Then, the printed components are solidified and depowdered. Then there is the stripping and sintering process, in which the printed components are placed in a uniform heat environment to improve the mechanical integrity. The whole process doesn't need a vacuum enclosed environment or inert protective atmosphere [23]. There are a number of post processes for manufacturing components, such as solidification, depowdering, sintering, penetration, anneal and finishing [15]. Such post operations can require a longer period of time than a real press (in particular, a firing of components) and lead to higher costs [15]. The key factors are the grain diameter and the distribution of the grain, the shape of the grain, the binding material, the binding agent and the saturation degree of the adhesive. [23].

Printing is usually quicker on its own compared to SLM or EBM. The process does not require heating, so there are no remaining stresses in the components. Nevertheless, it is possible that porosity exists since the bulk of the solidification occurs during sintering, and the size, dimension and form of the pores can vary across the various components manufactured in the same lot. In addition, the structure of manufacturing parts can be coarse as a result of lengthy post-treatment [15].

Regarding the treatment of Ti Alloy Powder in BJJ, the variation of particle diameter and the degree of compacting have significant effect on the porosity. Moreover, as compared with the irregularly shaped powder, the ball powder has a higher green density and a higher density and thus a more robust structure. Not as described above, the hot treatment (e.g. sintering) of Ti alloys is difficult because of their reactivity and has to take place under an inert atmosphere [24].

4. Preparation Method of Titanium Alloy Powder

The properties of 3D-printed implants depend much on the quality of the powder of titanium alloy [25]. Then we will describe the manufacturing technology of Ti alloy powder, including plasma rotating electrode process

(PREP), gas atomization (GA) and plasma atomization (PA).

4.1 PREP

The PREP procedure takes place in a helium-filled stainless-steel enclosure (25). The high-speed spinning metal bar is heated at one side by high temperature, and the liquid is dissolved into drops, which are then broken up and tossed out by the centrifugal force. Small drops of water become solid in the air, and they become spherical under the pressure of the surface, resulting in a fine powder [26]. More circular particles can be generated by PREP. The price, on the other hand, is higher [27]. Furthermore, it is possible that this approach will result in a solidification segregation in the course of preparing the powder, which will result in the deposition of an impurity grain consisting of an oxide on the border as a result of the diffusion in the densifying process [26].

4.2 GA

GA is used to compress and atomise the liquid metal using a high-speed flow of gas [28]. Normally, air is used as an atomizer. The gas shall be applied at a pressure between 350kPa and 4 MPa [27]. The GA technology consists of three major stages: melting, atomizing and solidifying [29]. Firstly, high-speed atomizer is discharged from a high-pressure storage tank into an atomizer which is maintained at low atmosphere. The rapid expansion of the compression atomizer is then introduced into the low-pressure chamber from the high-pressure vessel. The kinetic shock of a high speed gas jet results in the flow of liquid metal being deformed and decomposed into tiny fused grains [28].

GA has many merits such as spherical powder shape, the cleanliness, the rapid solidifying of the granules and the high productivity [28]. But in this process, the formation of satellite particles is common which is smaller particles attaching to the larger primary particles created from atomization. Satellite particulates occur as a result of the impact of particulate matter on atomisation, which can interfere with the free movement of particulate matter [29]. The GA is divided into 3 kinds of technologies: free-fall gas atomization (FFGA), close-coupled gas atomization (CCGA) and electrode induction gas atomization (EIGA). The major differences in the operating principles of the GA technology lie in the distance from the nozzle to the gas atomizer and the process of making the liquid melt [29].

4.3 PA

PA uses pre-alloyed steel wire as input, which is fused with high-speed plasma torches and then split into drops at the same time [30]. Since the liquid metal is free from

contamination by other solid metals, there is no interaction between them and no satellite grains formed. Nevertheless, attention should be paid to the gas holes created by the trapped gas in the plasma atomization powder. A further drawback of PA is that it only receives the feed input as a wire, which adds to the cost, since wire forms are often costly, and also restricts experiments with non-conducting materials like Ti3Al [25, 30].

Factors which may be modified in order to change the size and volume of particulates are as follows: wire diameter, wire feed velocity, gas pressure, and the angle and distance from the conductor to the plasma outlet [25].

5 Clinical Application and Optimization

Implants of Ti and Ti Alloys include artificial hip joints, artificial knee joints and bone plates [26]. The largest single titanium alloy utilized in the production of biomedical devices is Ti-6Al-4V [27]. But in the case of permanent implantation, the release of vanadium and aluminium can be poisonous. Consequently, the introduction of vanadium-without and aluminum alloys for implantation is based on Ti-6Al-4V implants. Examples of such novel alloys are Ti6Al-7Nb (ASTM F1295), ASTM F1713 (ASTM F1713), Ti-12Mo6Zr (ASTM F1813) [26]. The present tendency is that the combination of the recombinant BMP 9 (rhBMP9) and the 3D printing porous titanium is obtained to acquire the compound scaffold [28]. Zhu et al combined rhBMP9 and Ti6Al4V scaffolds made using EBM technique to produce a complex structure with excellent mechanical performance and biological activity for the restoration of bone [29].

Titanium alloys have been shown to have the best biocompatibility in biomedical applications. But its biological compatibility is inferior to that of the biological active substances such as CaP or HAP, which is classified as a bioactive material. In order to enhance the biocompatibility, the phosphor - calcium - based ceramics are often applied to the surface of the titanium alloy.

6. Conclusion

There are many factors that prevent the human skeleton from repairing itself when it is damaged. 3D printing technology plays an important role in personalized bone therapy. Titanium alloy has become the mainstream of metallic medical implants with its excellent performance, and with the assistance of 3D printing technology, its potential can be better utilized. The three mainstream 3D printing technologies for metallic materials, SLM, EBM, and BJG, and the three-titanium alloy powder production technologies, PREP, GA, and PA, presented in this paper,

each have their own advantages and disadvantages in terms of cost, precision, quality, and speed. The choice of 3D printing technology for metal and the quality of titanium alloy powder has an important impact on the quality of the finished product. In the future, there is a need for a high-precision, high-quality, high-output, and low-cost machining process in the field of metal 3D printing technology as well as titanium alloy powder molding technology. Meanwhile, when talking about the mechanical properties of titanium alloy implants, there is a lot of room for optimization by changing the macro and micro structure of titanium alloy implants. The biocompatibility of titanium alloys can also be improved by combining titanium and titanium alloys with different inorganic and organic materials and using different manufacturing processes. In the future, titanium alloys can become more ideal metal medical implants for bone therapy with the help of 3D printing technology.

References

- [1]Xue N, Ding X, Huang R, et al. Bone Tissue Engineering in the Treatment of Bone Defects. *Pharmaceuticals*, 2022, 15: 879.
- [2]Chen Jiatian, Zhou Huaijuan, Fan Yingwei, et al.3D printing for bone repair: Coupling infection therapy and defect regeneration. *Chemical Engineering Journal*, 2023, 471: 144537.
- [3]Niu Jingzhe, Sun Zhonggang, Chang Hui ,et al. Review on 3D Printing of Biomedical Titanium Alloy. *Rare Metal Materials and Engineering*, 2019, 48(5): 1697-1706.
- [4]Gu Y, Sun Y, Shujaat S, et al. 3D-printed porous Ti6Al4V scaffolds for long bone repair in animal models: a systematic review. *J Orthop Surg Res*, 2022, 17: 68.
- [5]Wu Y, Zhou H, Zeng Y, et al. Recent Advances in Copper-Doped Titanium Implants. *Materials*, 2022, 15: 2342.
- [6]Xu Y, Zhang F, Zhai W, et al. Unraveling of Advances in 3D-Printed Polymer-Based Bone Scaffolds. *Polymers*, 2022, 14: 566.
- [7]Li Z, Wang Q, Liu G. A Review of 3D Printed Bone Implants. *Micromachines*, 2022, 13: 528.
- [8]Parthasarathy J, Starly B, Raman S et al. Mechanical evaluation of porous titanium (Ti6Al4V) structures with electron beam melting (EBM). *J Mech Behav Biomed Mater*, 2010, 3: 249–259.
- [9]Gu Y, Sun Y, Shujaat S et al. 3D-printed porous Ti6Al4V scaffolds for long bone repair in animal models: a systematic review. *J Orthop Surg Res*, 2022, 17: 68.
- [10]Rodriguez-Contreras A, Punset M, Calero JA, et al. Powder metallurgy with space holder for porous titanium implants: a review. *J Mater Sci Technol*, 2021, 76: 129–149.
- [11]Shi YL, Guo ZM, Li XM, et al. Study on Preparation of Cellular Ti6Al4V Porous Titanium Skeleton by 3D Printing-Gel Casting. *Powder Metall Ind*, 2018, 28: 34–39.
- [12]Zhang C, Ren Y, Chen X.The Development Situation of

- Selective Laser Melting Metal Powder Based on 3D Printing. Proceedings of 2014 International Conference on Experimental and Applied Mechanics, 2014: 7.
- [13]Yan X, Yin S, Chen C, et al. Effect of heat treatment on the phase transformation and mechanical properties of Ti6Al4V fabricated by selective laser melting. *J Alloys Compd*, 2018, 764: 1056–1071.
- [14]Zhou Y, Zhang K, Liang Y, et al. Selective Laser Melted Magnesium Alloys: Fabrication, Microstructure and Property. *Materials*, 2022, 15: 7049.
- [15]Gokuldoss PK, Kolla S, Eckert J. Additive Manufacturing Processes: Selective Laser Melting, Electron Beam Melting and Binder Jetting—Selection Guidelines. *Materials*, 2017, 10: 672.
- [16]Gao B, Zhao H, Peng L, et al. A Review of Research Progress in Selective Laser Melting (SLM). *Micromachines*, 2023, 14: 57.
- [17]Necati U, Adem C, Kubilay A. Machinability of 3D printed metallic materials fabricated by selective laser melting and electron beam melting: A review. *Journal of Manufacturing Processes*, 2022, 80: 414-457.
- [18]Milberg J, Sigl M. Electron beam sintering of metal powder. *Prod Eng Res Devel*, 2008, 2: 117–122.
- [19]Kolamroudi MK, Asmael M, Ilkan M, et al. Developments on Electron Beam Melting (EBM) of Ti–6Al–4V: A Review. *Trans Indian Inst Met*, 2021, 74: 783–790.
- [20]Murr LE, Amato KN, Li SJ, et al. Microstructure and mechanical properties of open-cellular biomaterials prototypes for total knee replacement implants fabricated by electron beam melting. *J Mech Behav Biomed Mater*, 2011, 4(7): 1396.
- [21]Harrysson OL, Cansizoglu O, Marcellin-Little DJ, et al. Direct metal fabrication of titanium implants with tailored materials and mechanical properties using electron beam melting technology. *Mater Sci Eng C*, 2008, 28(3): 366.
- [22]Dérand P, Rännar LE, Hirsch JM, et al. Imaging, Virtual Planning, Design, and Production of Patient-Specific Implants and Clinical Validation in Craniomaxillofacial Surgery. *Craniomaxillofacial Trauma Reconstr*, 2012, 5(3): 137.
- [23]Li M, Du W, Elwany A, et al. Metal Binder Jetting Additive Manufacturing: A Literature Review. *ASME J Manuf Sci Eng*, 2020, 142(9): 090801.
- [24]Amir M, Amy M, John E, et al. Binder jet 3D printing—Process parameters, materials, properties, modeling, and challenges. *Progress in Materials Science*, 2021, 119: 100707.
- [25]Jang TS, Kim D, Han G, et al. Powder based additive manufacturing for biomedical application of titanium and its alloys: a review. *Biomed Eng Lett*, 2020, 10, 505–516.
- [26]Yu S, Zhao Y, Zhao G, et al. Review on preparation technology and properties of spherical powders. *Int J Adv Manuf Technol*, 2024, 132: 053–1069.
- [27]Mathias LE, Pinotti VE, Batistão BF, et al. Metal powder as feedstock for laser-based additive manufacturing: From production to powder modification. *Journal of Materials Research*, 2024, 39: 19–47.
- [28]Somjit M, Ali S, Wang C. Experimental and numerical investigations on molten metal atomization techniques – A critical review, *Advanced Powder Technology*, 2022, 33(11): 103809.
- [29]Shaun Z, Wing L, Andrew N. Atomization of metal and alloy powders: Processes, parameters, and properties. *AIChE J*, 2023, 69(11): e18217.
- [30]Sun P, Fang ZZ, Zhang Y, et al. Review of the methods for production of spherical Ti and Ti alloy powder. *JOM*, 2017, 69(10): 1853–1860.