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Preparation of Bone Implantation of Porous Titanium Alloy Materials Research Progress

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Abstract

In view of the problems of bioinertia and mechanical properties of bone implants made of titanium alloy materials, which are quite different from human bone tissue, this paper mainly reviews four methods to improve the performance of titanium alloy, namely powder metallurgy, additive manufacturing, gel injection molding and discharge plasma sintering. The biocompatibility and mechanical properties (elastic constant and elastic modulus) of the bone are more matched with those of human bone, and the application prospect of the four methods was prospected.

Keywords

Porous Titanium Alloy; Preparation Method; Biocompatibility; Mechanical Properties; Application Prospect.

1. Introduction

The elastic modulus of bone implant materials should be similar to that of human bone for carrying and transmitting loads; At the same time, it should have certain biological activity to facilitate cell adhesion and growth. In bone implantation surgery, the difference between the elastic modulus of the implant material and the elastic modulus of human bone (0.1~30GPa) is often too large [3-5], and the biological inertia of the implant material leads to surgical risks and even failures. Compared with medical materials such as stainless steel and aluminum alloy, titanium alloy has good biocompatibility, mechanical properties, and corrosion resistance [1,2], making it more suitable for bone tissue repair as a bone implant material. Titanium alloys used as bone implant materials have undergone three generations of development, as shown in Figure 1. The elastic modulus of the first generation of titanium alloys is 50 to 120 GPa [6,7]; The elastic modulus of the second generation titanium alloy is 100~110GPa [8]; The third generation titanium alloy has a lower elastic modulus (40-100 GPa) and better biocompatibility, but has lower strength and poor wear resistance, and its relative elastic modulus is still high [9].

In order to solve the above problems, scholars at home and abroad have conducted a lot of research, and found that porous materials can effectively reduce the elastic modulus; Human bones also have a porous structure, and porous bone implant materials are more suitable for the growth and adhesion of bone tissue cells. Therefore, the use of different preparation methods has made porous titanium alloy bone implant materials a hot topic in current research. At present, the commonly used preparation methods include powder metallurgy, additive manufacturing, gel casting, selective laser melting and other methods. In this paper, four preparation methods are reviewed, and the application prospects of different methods are summarized.

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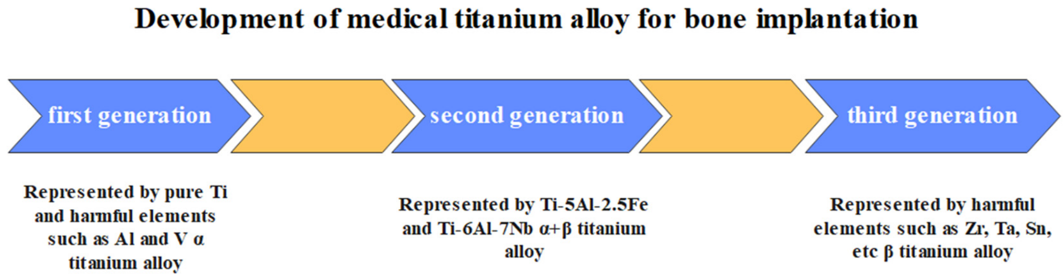
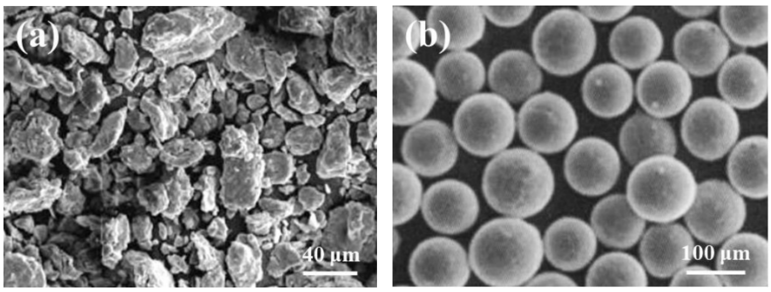


Figure 1. Development History of Medical Titanium Alloys for Bone Implantation [9]

2. Preparation Method and Performance Characteristics of Porous Titanium Alloy for Bone Implantation

2.1 Powder Metallurgy Method

Powder metallurgy is a process technology that uses powder as raw material and undergoes the steps of forming and sintering to form products with specific shapes. Titanium alloys prepared by powder metallurgy can be nearly net shaped, have low manufacturing costs, and have good mechanical properties [10,11]. According to the different original shapes of powders, powder metallurgy can be divided into pre alloying method and mixed element method [12]. The mixed element method is a method of uniformly mixing Ti powder and other alloy element powders in a ball mill, using processes such as hot isostatic pressing molding, injection molding, and injection molding for fixed molding, and finally sintering to produce related products. This method has the advantages of changing the alloy ratio and low production costs; The pre alloying method is a method of obtaining relevant titanium alloy powders in advance through various means, and then obtaining products through relevant molding and sintering techniques. This method obtains products with a fine and uniform structure [13,14]. Porous titanium alloys prepared by powder metallurgy technology are easily affected by pore forming agents and sintering processes.



(a) Mixed Element Morphology (b) Prealloy Powder Morphology

Figure 2. Powder Morphology of Titanium Alloys Prepared by Two Powder Metallurgy Methods [12]

2.1.1 Effect of Pore Forming Agents on the Properties of Porous Titanium Alloys

According to the literature, urea, ammonium bicarbonate, PMMA, NaCl, and stearic acid are often used as pore forming agents, which directly affect the pore size and porosity of implanted materials. The pore size and porosity of porous alloys can affect the biocompatibility of porous titanium alloys. Research has found that when the implant aperture is between 15 and 400 μ m, it is beneficial to the growth of bone tissue cells; When the porosity is greater than 30%, it is beneficial for the transportation of body fluids and the growth of cells [15,16]. Zhang Meili [17] and others prepared Ti-10% Mg porous materials, using urea as a pore forming agent, and studied the effect of pore forming agents on the mechanical properties of porous materials. It was found that when the urea content increased, the pore size and porosity of the alloy material increased. When the urea content is 25%, the pore size distribution of the alloy material is more uniform, and the elastic modulus and compressive strength meet the requirements of bone implant materials. Zhang Shuai [18] and others

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prepared Ti-14Mo-2.1Ta-0.9Nb-7Zr alloy using ammonium bicarbonate as a pore forming agent. With the increase of the pore forming agent, the pore size and porosity of the alloy material increase, while the elastic modulus and compressive strength decrease. When the content of porogen is 20%, the porosity of the alloy is 38.9%, the elastic modulus is 9.19 GPa, and the compressive strength is 405 MPa, which conforms to the porosity and mechanical properties of bone implant materials.

The results show that adding different kinds of pore forming agents has no significant effect on the phase structure of porous titanium alloy materials; With the increase of the content of pore forming agent, the pore size and porosity of porous titanium alloy materials increase, the elastic modulus decreases, and the compressive strength decreases.

2.1.2 Effect of Sintering Process on Properties of Porous Titanium Alloy

The sintering process mainly includes sintering temperature and time. The sintering process has a significant impact on the mechanical properties of the alloy. With the increase of sintering temperature and time, the pore diameter of the alloy gradually tends to be circular, the porosity gradually decreases, and the pore wall gradually becomes thinner, resulting in an increase in the elastic modulus of the material, an increase in compressive and flexural strength, and a greater density. Bone implant materials not only require that the porosity of the alloy be similar to human bone, And the mechanical properties (compressive strength: 80~150MPa, flexural strength: 50~120MPa [19]) should also be similar to them. Therefore, it is particularly important to find the best sintering process.

Li Xia [20] prepared Ti-24Nb-4Zr-8Sn non-toxic medical titanium alloy by powder metallurgy method. After sintering, the alloy was subjected to quenching treatment. The experiment showed that the optimal sample sintering temperature was 1400 ℃, quenching temperature was 980 ℃, its elastic modulus was 57.2GPa, and its ultimate tensile strength was 725MPa, showing good plasticity. In order to improve the biocompatibility of titanium alloys, our research group redesigned the alloy composition and prepared Ti-29Nb-4Mo-13Ta-9Zr alloy. We studied the effect of sintering temperature on the comprehensive properties of the alloy [21]. The research shows that when the temperature is 1350 ℃, the elastic modulus is 66 GPa, and the compressive strength is 780 MPa, the corrosion resistance of the alloy is significantly improved.

When selecting the sintering temperature range, the temperature range should be determined based on the boiling point and atomic diffusion rate of each element in the alloy. The sintering temperature should not be too high to prevent the volatilization of alloy elements from leading to poor mechanical properties and reduced biological activity; When the sintering temperature is too low, during the sintering process, the atomic diffusion speed and distance of alloy elements are small, and there are many defects that affect the mechanical properties of the composite material. The mechanical properties of the alloy sample obtained from the above research have significantly improved, but there is still a gap with the requirements of bone implant materials, mainly manifested by a high elastic modulus. Using this sample as a bone implant material will create a "stress shield". The main reason for this phenomenon is the influence of the second phase. When the temperature rises within a certain range, the substrate β Will grow α Phase, α Phase will increase the elastic modulus of the sample; However, when the temperature exceeds this range, martensitic transformation occurs in the sample, α Phase transformation β Phase, β The presence of phases can reduce the elastic modulus. As the sintering temperature increases, small spherical pores appear in the alloy, and cracks appear when the second phase cooperates with the pores, seriously affecting the mechanical properties of the alloy [22].

Powder metallurgy technology can be used to obtain near net shaped titanium alloy products, with flexible proportioning design, fine and uniform microstructure, and good mechanical properties; However, the utilization rate of materials is relatively low (generally around 50%), and the powder shape is easily affected by the set process parameters, resulting in significant changes in the shape of the final product [23].

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2.2 Additive Manufacturing Method

Additive manufacturing is also known as 3D printing. This method is based on the discrete stacking principle, using methods such as laser beams and hot melt nozzles to stack materials layer by layer to create a 3D three-dimensional model [24,25]. The product prepared by additive manufacturing method has high precision and can be quickly and accurately prepared into any shape. According to different molding technologies, additive manufacturing methods can be divided into selective laser melting (SLM) technology, laser selective sintering (SLS) technology, electron beam selective melting (EBM) technology, and laser cladding (LC) technology [26]. SLM technology and EBM technology are widely used in the preparation of titanium alloys due to their high precision compared to other technologies.

2.2.1 Preparation of Porous Titanium Alloy Material for Bone Implantation Using SLM Technology

SLM technology uses metal powders as raw materials and selectively irradiates them with a laser beam. The metal powders are melted and stacked layer by layer, eventually forming a three-dimensional structure. This technology requires a large amount of power, but its production efficiency is extremely fast [27,28].

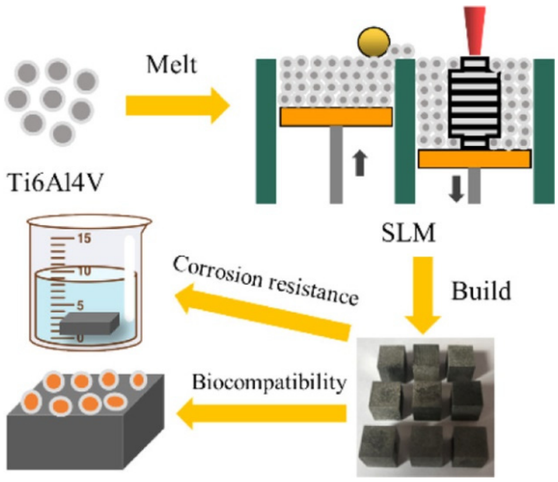
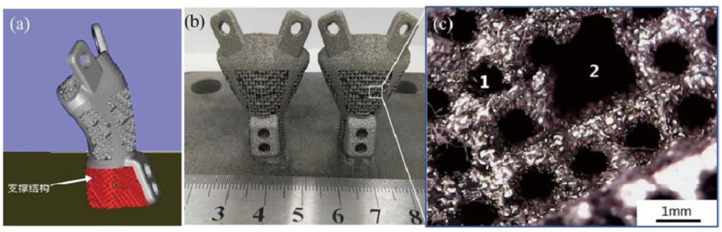


Figure 3. Working principle of SLM [29]

Chen Xiaojun [30] used Ti6Al4V as the raw material, analyzed the impact of process parameters on the performance of titanium alloy materials, and optimized the process parameters. According to the structural characteristics of the spinal vertebrae, SLM molding was performed using a vertical placement method. The resulting physical structure was good, consistent with the actual design, and free of obvious defects (as shown in Figure 3). Cheng Huihua [31] prepared Ti-35Nb-7Zr-5Ta (TNTZ) porous titanium alloy using SLM technology, and studied the effect of porous structure on properties. The experimental results show that the elastic modulus and yield strength of the alloy decrease with the increase of porosity; The lower the porosity, the higher the mechanical properties and cell proliferation level of the alloy. When the porosity is 70%, it is most conducive to cell adhesion.



(a) Supports addition results (b) SLM manufacturing results and (c) microscopic characteristics of porous structures (1 being primary pores, 2 being secondary pores)

Figure 4. SLM manufacturing of implants [30]

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2.2.2 Preparation of Porous Titanium Alloy Material for Bone Implantation using EBM Technology

EBM technology is to slice and layer parts, convert three-dimensional information into two-dimensional information, and use an electron laser beam to melt the powder in a vacuum environment. After processing one layer of powder, the workbench will drop by a height, and the next layer of powder will be processed and stacked layer by layer until the part is processed [32,33]. This technology has high work efficiency and high material repeatability.

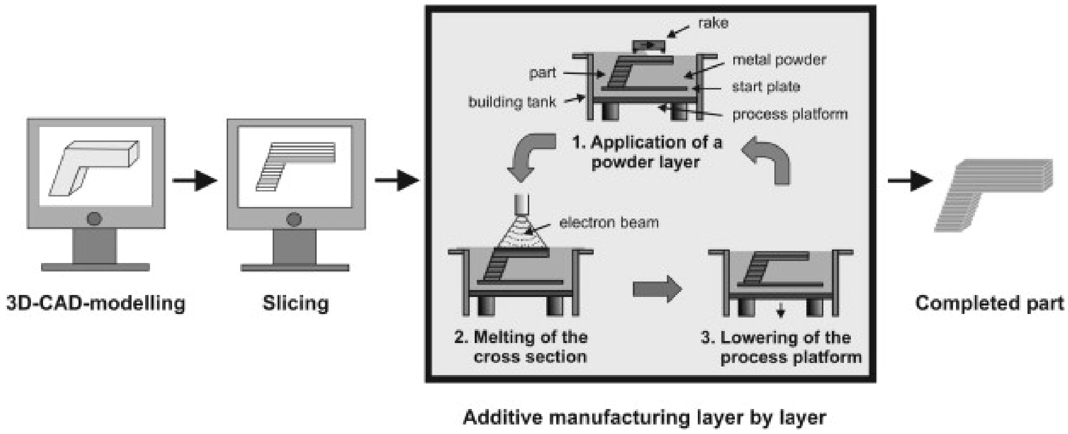

Figure 5. EBM technology workflow diagram [34]

Xu Jingzhong [35] and others prepared Ti-6Al-4V alloy using EBM technology, and analyzed the effect of pore structure on the friction behavior and mechanical properties of the material. The study found that when the porosity is the same, the pore compressive strength of the triangular structure is the largest, because the triangle itself has good stability; However, pores with disordered structures exhibit minimal wear when subjected to friction, making them suitable for use as pore structure types for bone implant materials. ZHANG [36] used EBM technology to prepare a titanium alloy stent simulating the trabecular structure of bone. Studies have shown that compared to titanium alloy dense metal structures, the elastic modulus of the stent decreases by 96% to 93%, and the apparent elastic modulus of the stent is 0.39 to 0.618 GPa, which is close to natural bone and can reduce stress shielding.

The additive manufacturing method can reconstruct a patient's damaged bone model based on medical images to produce bone implant materials with high precision; At the same time, the prepared material has a porous structure, which is conducive to the growth of cells within it, and improves biocompatibility. However, the raw materials used for additive manufacturing are generally pure titanium or Ti-6Al-4V, which is expensive. Ti-6Al-4V contains harmful elements such as Al and V, which can lead to peripheral tissue lesions when implanted into the body; Although the powder manufactured with additives has a high reuse rate, the powder may exhibit adhesion, which seriously affects the biocompatibility of implant materials.

2.3 Gel Injection Molding Method

Gel injection molding technology is a forming process that combines polymer chemistry and manufacturing process to achieve the purpose of rapid prototyping. It is more and more widely used by virtue of many advantages such as high strength, uniform composition, simple process flow and so on [37-39]. The technology mainly includes the steps of slurry preparation, molding, gel curing, mold turning, sintering, etc. The viscosity of slurry and sintering process are the key to prepare qualified bone implant materials [40]. The factors that affect the viscosity of the slurry include monomer concentration, solid content, and alloy composition. With the increase of solid content and monomer concentration, the viscosity of the slurry will significantly increase, leading to an increase in the elastic modulus of the material. Adding appropriate alloy components can effectively avoid

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this problem. Therefore, the alloy composition is a key factor affecting the viscosity of the slurry. The sintering process includes sintering temperature, sintering time, and sintering atmosphere.

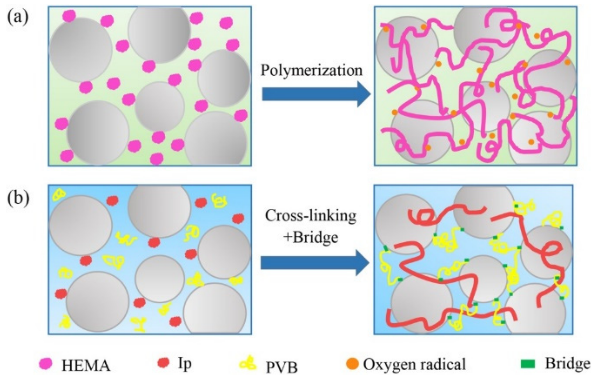

Figure 6. Schematic Diagram of Solidification Mechanism [39]

2.3.1 Effect of Alloy Composition on Viscosity

Fan Lianpeng [41] and others compared the viscosity of titanium cobalt alloy and pure titanium at room temperature, and research showed that when the solid content of the two is the same, the viscosity of titanium cobalt alloy is significantly lower than that of pure titanium. Yang Donghua [42] and others added Mo to Ti to make composite materials. Compared to pure Ti, when the solid content is the same, the viscosity of Ti-7.5Mo at room temperature significantly decreases, and with the increase of solid content, its viscosity growth trend is also slower than that of pure Ti. The above research results indicate that at room temperature, adding different alloy components can effectively reduce the viscosity of the material to prevent cracking during sintering.

2.3.2 Effect of Sintering on Mechanical Properties of Porous Alloys

Hong Haixia [43] determined the optimal sintering process for porous NiTi alloy through experiments, that is, under a high vacuum environment, sintering at 1050 ℃ for 2 to 4 hours. At this time, the alloy's tensile strength is 144.32 to 196.55 MPa, compressive modulus of elasticity is 16.86 to 19.68 GPa, porosity is 37.05% to 44.85%, and pore size is between 20 μ m and 200 μ m, meeting the basic requirements for medical implant materials. Shi Yongliang [44] and others used vacuum sintered Ti-6Al-4V alloy at a sintering temperature of 1200 ℃. After holding for 2 hours, the axial and radial shrinkage of the sample was uniform, presenting a three-dimensional connected honeycomb shape, with a porosity of 70.56%, a compressive strength of 194MPa, and a flexural strength of 105MPa. The structure and properties met the requirements of human bone tissue.

The gel casting process is simple, time saving, and the precision of the prepared products is high, but the dependence on the mold is large. It can only prepare specific shapes according to the mold, and cannot carry out large-scale production.

2.4 Discharge Plasma Sintering Method

Spark plasma sintering (SPS) technology is a technology that directly applies a pulse voltage between powder particles, and generates plasma by electric spark to heat the particles. It integrates plasma activation, hot pressing, and resistance heating. This technology has the advantages of fast heating rate, energy saving, and uniform grain size [45,46].

Liu Kaige [47] and others used spark plasma sintering technology to prepare (Ti-35Nb-7Zr-5Ta) - 15HA biological composite materials, and studied the effects of different sintering temperatures (950~1150 ℃) on the mechanical properties and biological activity of the composite materials. The results show that with the increase of temperature, the biological activity of the composite gradually decreases, and the elastic modulus gradually increases. When the sintering temperature is 950 ℃, the elastic modulus of the composite material is 30 GPa, which has the best biological activity and is suitable for use as a bone implant material. Zhang et al. [48] prepared a radial gradient porous composite using SPS technology. The composite has a layered porous structure, extremely low elastic modulus (16.8 GPa), and high compressive strength (1248 MPa), which meets the conditions for bone implant materials.

Using spark plasma sintering technology can improve the plasticity and strength of titanium alloys, prepare implant materials with porous structures, but the overall porosity is low, which is not conducive to the combination of human bone tissue and implant materials and the growth of tissue cells.

3. Conclusion and Outlook

(1) At present, titanium based alloy composites have shown significant advantages over metal materials in the application of orthopedic materials, and have been widely used in spinal correction, tissue repair, and the production of orthopedic prostheses, providing tremendous assistance to patients [49]. However, there are still certain differences between the mechanical properties and biocompatibility of fabricated bone implant materials and human bone. Therefore, future researchers should focus on improving the mechanical properties and biocompatibility of titanium alloys to better benefit patients.

(2) Powder metallurgy technology can produce titanium alloy materials with near net shape and uniform and dense microstructure through a shorter manufacturing process, which not only has low cost but also can produce high-performance titanium alloys [50]. In recent years, the manufacturing, forming, and sintering processes of titanium alloy powders have been continuously developing, and it is believed that in the future, powder metallurgy technology in China will exhibit a vigorous development trend.

(3) Additive manufacturing, as an emerging preparation technology, is still in the process of gradual development [51]. Although additive manufacturing technology produces titanium alloy materials with high precision and can quickly produce any shape, greatly saving production time, the high cost of raw materials required to produce titanium alloys using additive manufacturing technology is also the reason why this technology cannot be produced on a large scale. The titanium alloy produced by gel casting technology has high precision but needs specific molds, which greatly reduces the production efficiency [53]. In the preparation of porous titanium alloy materials in the future, titanium alloy can be produced by the combination of additive manufacturing and gel casting, which can greatly reduce costs and improve production efficiency.

(4) Spark plasma sintering (SPS) is a relatively new and rapid sintering technology developed in recent years, which combines the plasma activation method, also known as plasma activation sintering method [54]. Due to the surface activation of each particle inside the sintered body, the prepared material has uniform particle size, high density, and good performance. However, there are certain limitations, such as poor process repeatability and high cost of sample preparation.

Acknowledgments

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