Recent progress of biomedical porous titanium for bone implants

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Biocompatible porous titanium could be used for surgical implants like bones, joint prostheses or dental roots due to its excellent biocompatibility and osteoconductivity. Porous structure permits ingrowth of bone tissue, transportation of body fluid and nutrients. Mechanical property like elastic modulus and compressive strength depends on the pore characteristics like porosity, pore size, pore morphology of the porous titanium fabricated by different methods. The tailored elastic modulus of porous titanium matches that of cancellous bones. Deposition of hydroxyapatite coating on the surface of porous titanium can improve its bioactivity and biocompatibility. The fabrication method, surface modification, in vitro and in vivo studies and future research directions of porous titanium are reviewed in this literature.

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1. Introduction

In recent decades, the necessity for repairing or replacing human hard tissues like bones, joint prostheses or dental roots using artificial biomaterials is increasing significantly owing to the hereditary or traumatic reasons. Among the common biomaterials, commercially pure titanium and its alloys like Ti6Al4V ELI have been developed and used widely as surgical load-bearing implants like joint prostheses or dental roots due to good tissue compatibility and corrosion resistance. However, Ti6Al4V alloy may cause health problems like alzheimer's and other diseases related to the released aluminum and vanadium ions [1]. Additionally, traditional biomedical metals may cause bone resorption, osteoporosis or even loosening resulted from the "stress shielding effect", i.e. the significant mismatch of elastic modulus between the implant and bone tissue. The stress shielding effect would affect the desired implant osteointegration. As presented in Table1, the elastic modulus of pure titanium or Ti6Al4V ELI alloy is much higher than that of cancellous or compact bone [1-25].

One promising and effective solution to resolve the above-mentioned biomechanical compatibility problem is to fabricate porous titanium and/or its alloys containing biocompatible elements with appropriate mechanical property like elastic modulus and strength that could be altered and adjusted by pore characteristics, including pore size, porosity and interconnectivity. As shown in Table1, the elastic modulus of porous titanium or porous Ti-15Mo alloy is comparable to that of cancellous or compact bone [2-22]. Some researches reveal that porous materials with pore size between 100 and 500μm could allow the ingrowth of bone tissue, transportation of body fluid and nutrients [2, 17].

A number of authors have attempted to propose and develop some processes to fabricate porous titanium with controllable pore structure and mechanical property matching those of hard tissue, respectively, and to clarify the relationships between pore structure and mechanical property of porous titanium [3-22].

Bioactivity is another important issue of the artificial biomaterial. Nearly all the implanted metallic biomaterials are bioinert because they are usually encapsulated by fibrous tissue isolated from the surrounding bone. Surface modification like deposition of calcium phosphate coating on metal is an alternative method to solve this problem. Calcium phosphate exhibits good bioactivity and biocompatibility. But their applications may be limited to unloaded implants and coatings due to the poor mechanical properties [2, 23-30].

Hydroxyapatite (HA, chemical formula $Ca_{10}(PO_4)_6(OH)_2$) may be an appropriate biomedical ceramic because its structure and composition are similar to the mineral phase of the human hard tissue. HA coating could form a bioactive surface on a metallic implant to promote bone growth and induce a bonding between the implant and the surrounding bone tissue [2, 23-30].

Therefore, deposition of HA coating on the surface of porous titanium may be a proper surface modification route to achieve advantages combination of good biomechanical compatibility of porous titanium scaffold with the bioactivity of hydroxyapatite [2, 23-30].

There are some processes including physical approaches like plasma spraying and ion beam-assisted deposition, wet-chemical approaches like biomimetic method, sol-gel technique, micro-arc oxidation to fabricate HA coatings on the surface of metallic biomaterials [23-30]. The commonly used physical approaches are difficult to deposit HA coating on the surface of porous metals with complex contour like inner pores [23-30].

The wet-chemical approaches can be used to deposit HA coating on the surface of porous titanium or its alloys because the solution could access the inner pores and then form calcium phosphate coating at low temperature [23-30].

In the present literature, the recent progress of porous titanium is reviewed in the following four sections. The first covers the fabrication approaches of porous titanium with tailored pore structure and mechanical property. The second summarizes the surface modification of porous titanium with biocompatible HA coating. The last addresses the *in vitro* and *in vivo* behaviors of porous titanium.

Table 1. Elastic moduli of biomedical metals and bones [1-22].

Bones and biomaterials	Young's modulus [GPa]
Compact bone	
Cancellous bone	17-27
Pure titanium	0.05-2
Ti6Al4V ELI alloy	108
Porous Ti-15Mo alloy with	120
porosity of (30-63%)	4.6~25.6
Porous titanium with porosity	1~17.5
of (25~77%)	

2. Fabrication methods

Approaches of powder sintering, freeze casting, rapid prototyping and metal injection modeling and fiber/wire sintering have been developed to produce porous titanium [3-22].

2.1 Powder sintering

Power sintering is a conventional approach to fabricate porous titanium with controlled pore structure and tailored mechanical property [4-15]. Fig.1 illustrates schematically the procedures for powder sintering of porous titanium. Commercially pure titanium or TiH_2 powders and space-holder materials like NH_4HCO_3, Mg, NaCl or urea powders are mixed and blended thoroughly according to the theoretical or empirical ratios. The green compacts are compressed in a mould from the blended powders followed by spacer removal using different methods. The compact placed in the furnace are sintered in vacuum and cooled to obtain porous titanium [4-15].

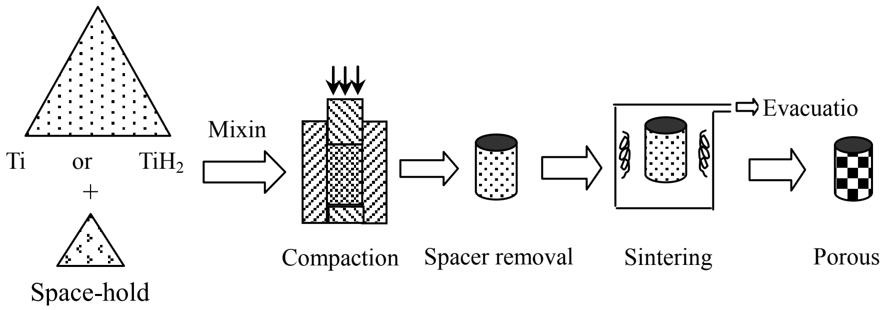

Fig.1. Schematic illustration of procedures for powder sintering of porous titanium.

Li et al fabricated porous titanium using powder sintering method from TiH_2 and space-holder of NH_4HCO_3 powders. The green compacts made from the mixed powders were heated to 473 K for 2h to decompose ammonium bicarbonate completely into gases of NH_3, H_2O and CO_2 and then sintered at 1473K for 4h in vacuum. TiH_2 powders were dehydrogenated into titanium powders and hydrogen during heating process. The latter can serve as a protective atmosphere [4]. The typical pore morphology of the sintered porous titanium was presented in Fig.2. It was characterized by partially interconnected porous structure. Porous structure with average pore size bigger than 100μm and porosity of 38.5~56.2% of the sintered porous titanium matches that of cancellous bone. Elastic modulus ranged between 17.5 and 7.9GPa of the sintered porous titanium was close to that of human bone [4]

Singh et al prepared porous titanium by powder sintering from powers of elemental titanium powders and space-holder of NH_4HCO_3. The research revealed that the permeability of the sintered porous titanium with porosity between 51 and 78% was close to that of spinal fusion devices [5].

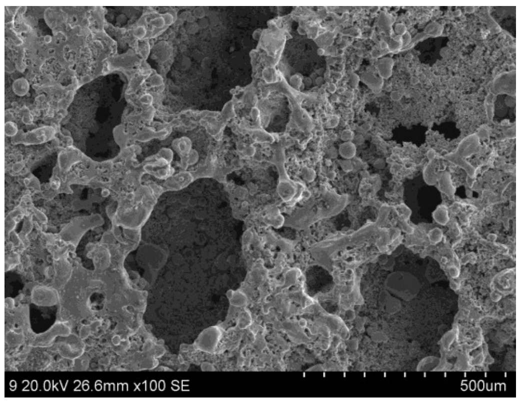

Fig. 2. SEM image of pore morphology of porous titanium.

Kim et al prepared porous titanium from Ti and space-holder of Mg powders by powder sintering. The mixed powders were made into compacts followed by dipping in HCl and ethanol solutions to remove space-holder of Mg. Finally, the green compacts were dried and sintered in vacuum to fabricate porous titanium with porosity of 50~70% and low elastic modulus of 1.7±0.8 GPa [6].

Titanium and space-holder of NaCl powders were mixed to fabricate porous titanium using powder sintering [7, 8]. Prior to sintering, the spacer of NaCl in compacts were dissolved in water. The elastic modulus ranged between 4 and 11GPa of the sintered porous titanium with porosity of 50~67% match that of cancellous bone [8].

It can be concluded from the reports that the pores result mainly from the vacancies that occupied by the space-holder powders. The pore characteristics (porosity, pore size and distribution, morphology) and mechanical property of the porous titanium can be regulated by the amount of space-holder material [4-15].

2.2 Freeze casting

Freeze casting has been developed to fabricate porous titanium with controlled pore characteristics like porosity, pore size, morphology and orientation. It utilizes the dendritic growth of a freezing vehicle like camphene, which can be removed by freeze-drying to form aligned pores [16].

Yook et al prepared porous titanium using camphene-based freeze casting [16]. The ball milled TiH_2 /camphene slurry was poured into a mold and freeze-dried to remove the camphene. TiH_2 powders were thoroughly hydride decomposed when the samples were heated to 673K and then sintered at 1573K. The prepared porous titanium scaffold with porosity of 64% and compressive strength up to 110±17MPa was a promising implant biomaterial [16].

2.3 Rapid prototyping (RP) technology

Recently, rapid prototyping technology which combined with computer-aided design (CAD) model has developed rapidly to produce variety of materials [17, 18].

Selective laser melting (SLM) is a fabrication process that involves manufacturing a part with given architecture in a layer by layer mode by fusing the metallic powders using high energy laser beam [17, 18]. Cylindrical titanium with four longitudinal square channels was prepared by using SLM method. It can be used to fabricate scaffolds or orthopedic implants [17].

2.4 Metal injection molding

The metal injection molding (MIM) could be a promising approach to fabricate porous titanium owing to the combination of characteristics of injection molding and powder sintering. It consists of mixing of the powders, molding of the feedstock, debinding and final sintering [19, 20]. Tuncer et al produced porous titanium by MIM. Pure titanium powders and space holder of NaCl particles were mixed with binder system of paraffin wax, polyethylene and stearic acid. The homogenous feedstock was compacted into samples by injection molding, followed by debinding of the binder and removal of space holder. Paraffin wax and stearic acid as polyethylene were removed by solvent and thermal debinding, respectively. The space holder was removed by water dissolving. The dried samples were sintered at 1473K under vacuum. The as-received porous titanium with porosity of 65% has elastic modulus of 7.7GPa [20]. The volume fraction of the space holder, temperature and pressure of the injection molding, temperature and time of the sintering process have significant influences on the pore characteristics of porosity, pore size and morphology as mechanical property of the MIM-ed porous titanium [20].

2.5 Fiber/wire sintering

Porous titanium can also be produced by fiber/wire sintering from woven or non-woven titanium fiber/wires. The mechanical property, pore characteristics of porous titanium depend on the fiber/wire diameter, architecture and pressure during the compaction of the green compact, etc [21, 22]. He et al fabricated porous titanium with entangled wire structure. The titanium wire entangled by winding or twisting was compacted in a mould and then sintered. It was characterized by low elastic modulus, high strength and flexibility [21]. Zhang et al prepared porous titanium using fiber sintering. The commercially pure titanium fibers were compacted in a mould into a green samples and then sintered in vacuum to obtain porous titanium with porosity of 67% [22].

3. Surface modification to form biocompatible surfaces

Recently, research on surface modification of porous titanium and its alloys has focused on deposition of HA coating using biomimetic method, micro-arc oxidation and sol-gel technique [23-30].

3.1 Biomimetic method

Biomimetic method is a widely used wet-chemical technique to prepare biocompatible HA coating on titanium and its alloys by inducing formation of bone-like apatite in simulated body fluid (SBF) on bioactive layer formed by treatment of the substrate in acid, alkali and/or other solutions. This convenient approach can improve the bonding strength by introducing chemical bond to the interface between the metallic substrate and host bone tissue [23-27]. The procedures of the biomimetic (or chemical treatment) method consist mainly of acid and/or alkali treatments and immersion of the sample in SBF [23-27].

Liang et al prepared porous titanium layer with thickness of approximately 2mm and porosity of 40% by powder sintering of pure titanium powders on dense titanium substrate. The cleaned porous samples were immersed in NaOH aqueous solution (alkali treatment) and then heat treated. The alkali-heat treated samples were soaked in SBF to deposit HA coating on its surface. The results indicated that alkali treatment could induce formation of the network structure, sodium titanate and titanium oxide on the porous sample. Moreover, heat treatment could densify the network structure. The final SBF immersion could induce deposition of uniform HA coating [23].

Li et al deposited HA coating on the sintered porous titanium using pre-calcification assisted biomimetic method. The cleaned samples were soaked in HNO_3 and NaOH aqueous solutions in turn. Prior to the final immersion in SBF, the acid-alkali treated samples were immersed in Na_2HPO_4 and $Ca(OH)_2$ solutions in turn to be pre-calcified. The research revealed that this pre-calcification could accelerate the apatite formation [24].

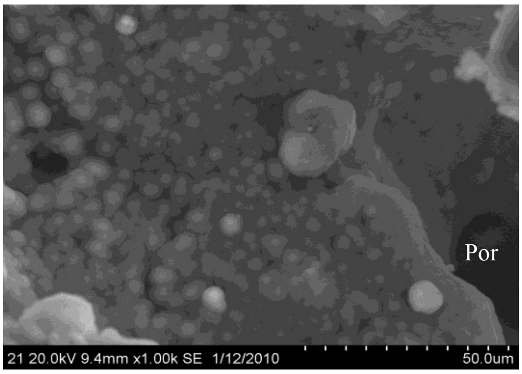

Fig. 3. SEM image of HA coating deposited on porous titanium.

The acid and alkali treatments aim to thicken titanium oxide film and form sodium titanate hydrogel, respectively. The pre-calcification could promote the sufficient adsorption of Ca^{2+} and HPO_4^{2-} ions. And the SBF immersion may induce the nucleation and deposition of hydroxyapatite [24]. As shown in Fig.3, HA coating was deposited on the surface of porous titanium by biomimetic method. It suggested that this wet-chemical approach could be an effective and convenient alternative to produce uniform HA coating on porous titanium without blocking the pores [24].

Zhao et al deposited HA coating on porous titanium using biomimetic method. The acid-alkali or alkali-heat treated porous samples were immersed in supersaturated calcium phosphate solution to form HA coating [25].

Fujibayashi et al suggested that sodium removal by hot water or dilute HCl immersion could improve the bioactivity of alkali-heat treated porous titanium, compared with other conventional treatment like alkali-heat prior to soaking in SBF. Moreover, the dilute HCl-treatment could promote the apatite-forming ability on porous titanium [26].

Xie et al deposited HA coating on porous titanium by electrochemical activation treatment followed by chemo-biomimetic treatment (SBF solution with increased Ca^{2+} and HPO_4^{2-} concentrations by a factor of five). During the electrochemical activation treatment in NaOH solution, nanometer bone-like porous structure and hydrated titanium oxide as $Ti\text{-}OH^-$ hydrogel layer were formed on the surface of porous sample. The absorbed Ca^{2+} and PO_4^{3-} ions reacted with OH^- to form HA coating. The chemo-biomimetic method could accelerate the deposition speed of HA coating [27].

The thickness, phase composition, Ca/P ratio and microstructure of the HA coating deposited on surface of porous titanium can be regulated by the parameters of concentration, temperature and immersion time of the acid, alkali and SBF solutions used in the biomimetic method [23-27].

3.2 Micro-arc oxidation

Micro-arc oxidation (MAO), a kind of anodic oxidation technique in electrochemical field, can be used to form a porous ceramic film of oxide containing elements from the substrate metal and the electrolyte on the surface of titanium, magnesium, aluminum and its alloys. The composition, phase constituents of the film can be controlled by the applied voltage, frequency, duty cycle and oxidizing time, compositions and concentration of the electrolyte. This promising technique has advantages of good interfacial bonding between the film and the substrate, etc. HA coating on porous titanium can be commonly prepared by MAO-treatment followed by hydrothermal treatment or soaking in SBF [28, 29].

Lee et al prepared HA/TiO_2 hybrid coating on porous titanium by MAO method in an electrolyte solution containing HA particles. The morphology and phase composition of the hybrid coating depended on the content of HA in the electrolyte solution [28].

Zhou et al deposited HA coating on the sintered porous titanium by MAO treatment followed by soaking the sample in SBF. The research result indicated that MAO film containing Si, Ca and Na could promote the formation of apatite on porous titanium. Additionally, the proper pore size could contribute to the deposition of HA because more necessary ions could be absorbed onto the MAO coating [29].

3.3 Sol-gel method

Sol-gel method is a conventional approach to produce HA coating on the surface of porous metal [30, 31]. The metal was dipped in and coated with the sol made of the precursors and then heat treated to prepare HA gel coating on the surface. The sol-gel technique is characterized by low cost, convenient process, and controlled composition, phase constituent, microstructure as thickness of the HA coating [30, 31].

Ag/HA coating can combine the biocompatibility and biological affinity advantages of hydroxyapatite with the good antimicrobial activity of silver. Two precursors prepared by diluting of calcium nitrate tetrahydrate and phosphoric pentoxide with ethyl alcohol, respectively were mixed according to the Ca/P molar ratio of 1.67 to obtain the HA sol. Porous titanium samples were dipped in the HA sol stirred with solution of silver nitrate and then dried followed by sintering. This dipping/withdrawing process was repeated to produce Ag/HA composite coating with a desired thickness [30]. The research indicated that Ag/HA coated porous titanium exhibited good antibacterial property and biocompatibility [30].

4. *In vitro* and *in vivo* biological studies

Recently, some researchers have performed some investigations on the *in vitro* and *in vivo* biological studies of porous titanium. Rubshteina et al conducted *in vitro* studies by evaluation of the adherent cell fraction of autologous bone marrow of rabbits on porous titanium with porosity of 40%. The results indicated that the stromal coating formed in the culture medium containing marrow cells showed good osteointegration [32]. The *in vitro* cell test research revealed that the HA/TiO_2 hybrid coating could improve the bioactivity of porous titanium [28]. The *in vivo* investigations were performed on implantation of porous titanium into adult rabbits. The research revealed that the pores of porous titanium were filled with neogenic bone tissue whose ratio of Ca/P was comparable to that of mature bone tissue. Meanwhile, osteogenic cells appeared on the surface of porous titanium. The interconnected porous structure of porous titanium could be convenient for the formation of bone tissue inside the pores [32]. Zhang et al performed *in vivo* investigations by implantation of Si-HA, HA- coated and uncoated porous titanium sintered into femora of New Zealand White rabbits [22]. The research indicated that Si-HA coating porous titanium had higher bone ingrowth rate than HA coated and uncoated one. Additionally, Si-HA coating porous titanium had better bioactivity due to the contribution of silicon to cell proliferation and osteoconductivity [22]. Takemoto et al investigated the osteoconductivity of the HA coated porous titanium by implantation into the back muscles of adult beagle dogs [26]. The *in vivo* research proved that the dilute HCl-alkali-heat treated porous titanium samples exhibited better osteoinductivity and induced ectopic bone growth in the back muscles of beagle dogs, compared with other prerequisite treatments like alkali-heat prior to immersion in SBF [26]. Fukada et al carried out *in vivo* studies by implantation of the porous titanium coated with apatite into the dorsal muscles of mature beagle dogs [17]. The result showed the strong dependence of osteoconduction on the interconnective pore size of porous titanium [17]. The researches confirmed that porous titanium with bioactive HA coating exhibited good osteoconductivity and tissue compatibility.

5. Concluding remarks

Studies of porous titanium used for bone implants have achieved great progress in recent decades. Currently, some techniques have been developed to fabricate porous titanium with controllable and desirable elastic modulus and pore size that meet the requirements of bone implant applications. Some methods have been used to improve the bioactivity by means of surface modification, e.g. producing biocompatible calcium phosphate coatings on the surface of porous titanium. Some *in vitro* and *in vivo* investigations have been performed to study the tissue biocompatibility of porous titanium. So far, there are still some unclear issues relating to the porous titanium. In the future, more comprehensive studies on porous titanium are expected in the following directions:

(1) In terms of different fabrication of porous titanium, it is important to clarify the relationship between the strength, elastic modulus and porosity, pore size. Therefore, the standardized technological procedures are needed to prepare porous titanium with desirable and precise mechanical property and pore characteristics by regulating the process parameters.

(2) In terms of the HA coating on porous titanium, it is imperative to ensure the enough bonding strength and long-term stability. The HA coating containing silver, silicon, or other elements are expected to exhibit special biological functions like antibacteria, enhanced osteoconductivity, drug delivery or release and other properties in the early implantation period.

(3) Further *in vitro* and *in vivo* investigations on porous titanium should focus on the long-term clinical safety and the effects of composition and structure as thickness of HA coating, pore characteristics, mechanical property on the osteoconductivity and biocompatibility of porous titanium.

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