Cancellous bone from porous Ti6Al4V by multiple coating technique

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A highly porous Ti6Al4V with interconnected porous structure has been developed in our previous study. By using a so-called "Multiple coating" technique, the porous Ti6Al4V can be tailored to resemble cancellous bone in terms of porous structure and mechanical properties. A thin layer of Ti6Al4V slurry was coated on the struts of base porous Ti6Al4V to improve the pore structure. After two additional coating, pore sizes ranged from 100 μm to 700 μm, and the porosity was decreased from ~90% to ~75%, while the compressive strength was increased from 10.3 ± 3.3 MPa to 59.4 ± 20.3 MPa and the Young's modulus increased from 0.8 ± 0.3 GPa to 1.8 ± 0.3 GPa. The pore size and porosity are similar to that of cancellous bone, meanwhile the compressive strength is higher than that of cancellous bone, and the Young's modulus is between that of cancellous bone and cortical bone. Porosity, pore size and mechanical properties can be controlled by the parameters in such multiple coating processes. Therefore the porous Ti6Al4V with the characteristics of cancellous bone is expected to be a promising biomaterial for biomedical applications.

1. Introduction

Development of porous metallic biomaterials associated with their applications in orthopaedics is becoming an increasingly important research project, compared with that of dense metallic biomaterials. Porous metallic biomaterials facilitate bone ingrowth and thereafter improve the interlock between implants and bone. While developing a new porous metallic biomaterial, we have to consider a number of requirements. Firstly, the material must be biocompatible. Secondly, the porous metallic biomaterials should have a high porosity and a porous structure similar to that of human cancellous bone, which therefore can provide sufficient space for tissue ingrowth and exchange of body fluids. A number of research groups have reported porosity and pore size of porous biomaterials are important parameters for bone ingrowth [1–3]. Although there are wide discrepancies regarding the optimal pore size for effective bone ingrowth, a minimum pore size of 100-150 μm is generally considered acceptable for healthy bone ingrowth. Besides porosity and pore size, pore size distribution, pore shape, fenestration size and interconnectivity of the pores [3–5] have also shown their influences on bone formation. Thirdly, the porous metallic material must have suitable mechanical properties [6, 7] including a higher compressive strength and an appropriate Young's modulus [8].

Due to their excellent biocompatibility and corrosion resistance as compared to conventional stainless steels and cobalt-based alloys [6, 9], titanium and its alloy have been widely used as biomaterials in biomedical devices for a long time. Although there are several methods to make porous titanium and its alloy, such as sintering particles and fibres together [10], or processing a mixture of titanium powder and a polymer pore-former [11], the mechanical properties and pore structure of the resulting porous materials could not be compared with those of human cancellous bone. Accordingly, we developed a new processing technique to make porous Ti6Al4V for biomedical applications.

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The porous Ti6Al4V was fabricated by a polymeric sponge replication process, which involves the following steps: impregnation of a polymeric sponge by immersing it in a Ti6Al4V slurry, removal of excess slurry, drying, debinding (the sponge is burned out) and sintering, resulting in a positive replica in Ti6Al4V of the original polymeric sponge [12]. The porous Ti6Al4V obtained possesses a reticulated network with pore size ranging from 100 μm to 1000 μm. After the polymeric sponge was burned out, thin struts ,cracks and triangular voids were left inside the structure, which would be sensitive to structural stresses [13, 14]. The purpose of this study was to develop a new method to produce porous Ti6Al4V, which may better resemble cancellous bone mechanically and structurally.

2. Materials and methods

2.1. Study design

2.1.1. A suitable slurry for multiple-coating

A Ti6Al4V slurry allowing homogenously coating onto a porous Ti6Al4V was developed with regard to composition and viscosity.

2.1.2. Porosity and pore size versus coating times

The influence of coating times on the porosity and pore size of porous Ti6Al4V was investigated.

2.1.3. Permeability

The influence of coating times on permeability of porous Ti6Al4V was studied.

2.1.4. Mechanical properties

The influence of porosity on the mechanical properties of the porous Ti6Al4V with respect to compressive strength and Young's modulus was evaluated. Micro hardness was measured before or after multiple coating.

2.2. Multiple-coating technique

2.2.1. Materials

Base porous Ti6Al4V with a pore size of 100–1000 μm was fabricated by 'polymeric sponge replication' method as described previously [15]. The samples were subjected to ultrasonic cleaning in acetone, ethanol (70%), and demineralised water for 15 min respectively. The slurry used in this process was termed as "Slurry I [16]". Cancellous bone was obtained through boiling goat cancellous bone for one week to remove collagens and other components.

2.2.2. Thin Ti6Al4V slurry (slurry II) for coating

The slurry used has the following chemical composition (in weight percentage wt%): 63.4% Ti6Al4V powder (North-west no-ferrous institute, China), 31.7% demineralised water, 1.5% Polyethyleneglycol4000 (PEG4000, Fluka Chemie GmbH, Germany), 0.4% methylcellulose (MC, Fisher Scientific B.V, The Netherlands), 1% dispersant (Dolapix, Aschimmer&Schwarz GmbH Germany), 1%ammonia solution (25%, Merck) and 1% 1-Octanol. Firstly, demineralised water was mixed with PEG4000 and MC by stirring for 1h, then Ti6Al4V powder was added and stirring continued for 1.5 hrs, finally, Dolapix, ammonia solution and 1-octanol were added to improve rheological behavior. Stirring was subsequently continued for another 1 h to achieve homogeneous slurry. The viscosity of the thin Ti6Al4V slurry was measured by viscometry (Brookfield Engineering Labs DV-II+ viscometer) with a spindle of RV4 at the speed of 20 rpm at room temperature.

2.2.3. Multiple coating

The base porous Ti6Al4V was dipped into Slurry II for 30 seconds and then taken out. High-pressure air was used to remove excess slurry to achieve a thin homogenous coating on the struts and to prevent the slurry from blocking the pores. After coating, the samples were dried for 1h at 80 °C and for 24 hrs at room temperature. Finally, the samples were sintered at 1250 °C under high vacuum (10^{-5} mbar) with a dwell time of 2 hrs. The coating procedure can be repeated before sintering to obtain samples with multiple coating.

2.3. Characterization

2.3.1. Porosity

The porosity of porous Ti6Al4V sample was calculated from its weight and volume by comparing the bulk density of cylindrical samples ($n = 10$) with the theoretical one of Ti6Al4V: 4.45 g/cm^3.

2.3.2. Pore size and porous structure

By using an environment scanning electron microscope (ESEM, XL30 ESEM-FEG, Philips, The Netherlands), the structure of porous Ti6Al4V were analyzed from cross-sections of the samples. From these cross-sections, estimations of the pore sizes were made by linear measurements. Pieces of porous Ti6Al4V (dimensions ∅ 10 × 12) were cut off by using a WOCO50 sawing machine and a WOCO 997 sawing blade (Wolfgang Conrad) and polished with a series of SiC sand papers (types from 800, 1200 and 2400). After sawing the samples ($n = 5$, respectively) were cleaned in an ultrasound water bath and dried before ESEM observation.

2.3.3. Permeability

A permeability test was performed with a self-designed permeability-meter [17]. Briefly, a cylindrical sample was mounted in a tube connected to a wide diameter water reservoir which was positioned at a certain constant height. The flow of water through the sample was measured in ml/sec. Normalized for the dimensions of the sample, it provided measure of the sample's permeability. The samples with different porosity (coating times) were tested to study the relationship between permeability and the number of additional coating times.

2.3.4. Mechanical properties

Before and after coating, micro hardness was measured under a micro hardness tester (SHIMADZU, Japan). Based on the trial testing, a load of 500 g applied for 35s to a diamond shaped indents was chosen. Ten samples from each batch were randomly chosen. The compression tests of porous Ti6Al4V samples ($\varnothing 10 \times 12$ mm, $n = 10$) were performed at room temperature with a crosshead speed of 1 mm/min (Zwick/Z050, Germany). The Young's modulus was calculated by the load increment and the corresponding deflection increment between the two points on the straight-line part.

3. Results

3.1. Ti6Al4V slurry (slurry II) for coating

The chemical composition of the two slurries used for sponge replication (Slurry I) and later multiple coating (Slurry II) were listed in Table I, showing they share the same ingredients but different concentrations of Ti6Al4V powders and binders and therefore resulting in rheological behavior. Fig. 1 shows the viscosity of Slurry I [15] and Slurry II.

TABLE I Ti6Al4V slurry composition for polymeric sponge replication and multiple coating

Composition	Slurry I coating foam (wt%)	Slurry II Multiple-coating (wt%)
Demi water	18.5	31.7
PEG4000	3	1.5
Dolapix	1	1
Ammonia	1	1
Octanol	1	1
Methylcellulose	0.5	0.4
Ti powder	75	63.4

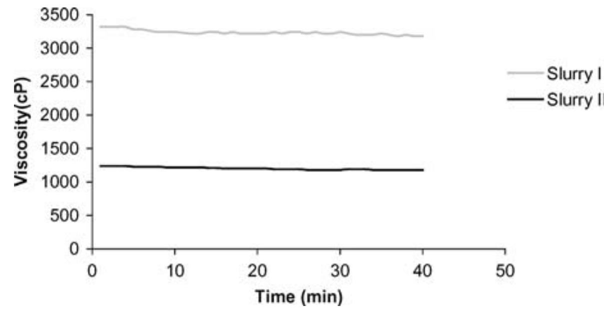

Figure 1 Viscosity data of Ti6Al4V slurry I and slurry II.

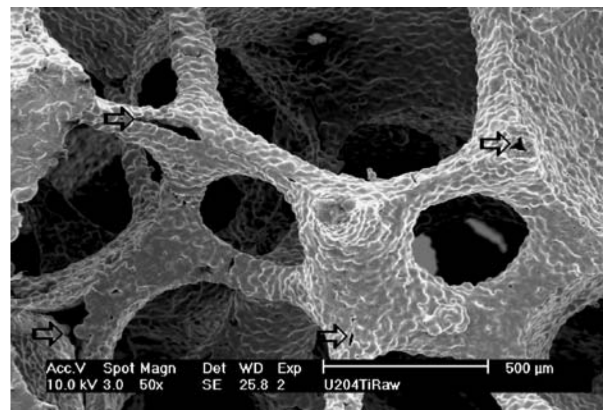

Figure 2 Macrostructure of porous Ti6Al4V (Arrows indicated the crack and triangle hole).

3.2. Pore structure

Fig. 2 shows macrostructure of the base porous Ti6Al4V under high magnification. Some large flaws can be seen, such as cracks and triangular voids (denoted by arrows in the figure) in the struts. These flaws and a number of thin struts will contribute significantly to the strength. The macrostructure of the base porous Ti6Al4V and after one additional coating are shown in Fig. 3(a) and (b). As prepared, without extra coating, the porous structure looked too thin. However, these drawbacks were overcome greatly by one extra coating: the cracks being filled by titanium powder turned the porous body denser. It appears that the macro structure of porous Ti6Al4V is not affected significantly by an additional coating treatment. It was found that the pores of porous Ti6Al4V are spherical in shape, and the porous body retains its interconnected porous structure. The struts without or with one additional coating are shown in Fig. 3(c) and (d). Fig. 3(e) shows the macrostructure of cancellous bone, displaying a striking similarity with the structure of Fig. 3(a) and (b).

3.3. Porosity and pore size

Fig. 4 shows the porosity and pore size versus coating times. It can be seen that the porosity and pore size are dependent on the number of additional coating times,

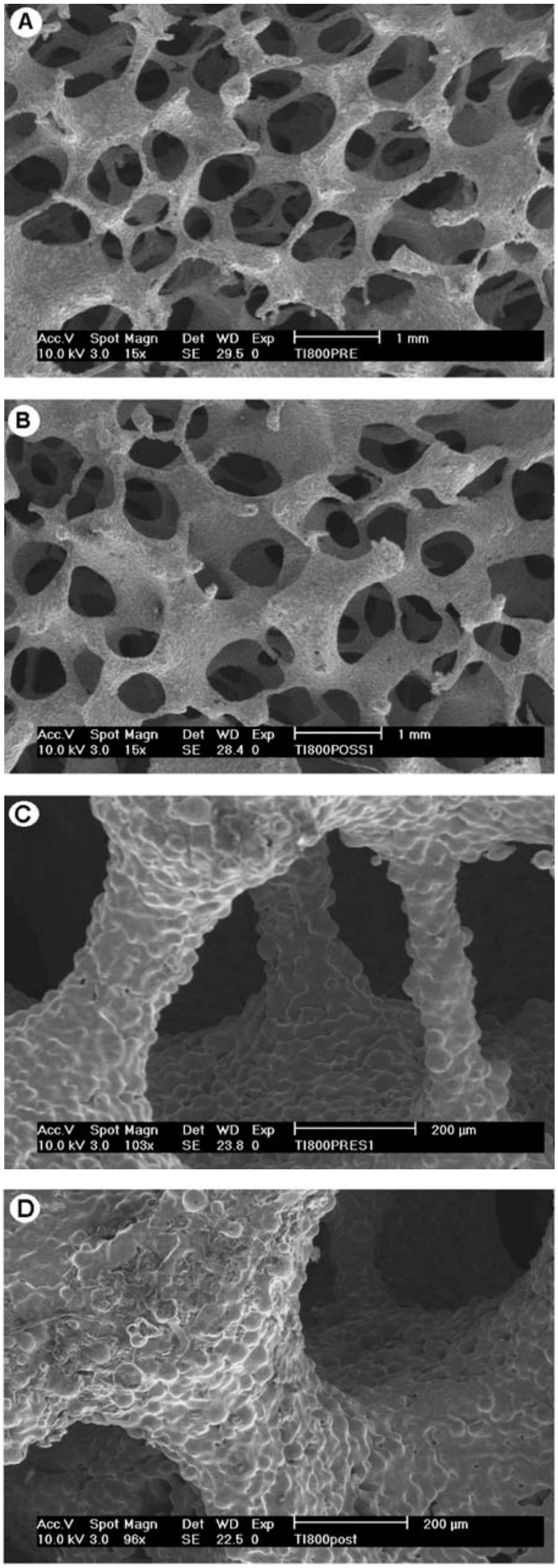

Figure 3 Macrostructure and microstructure of porous Ti6Al4V. (a) Macrostructure without any additional coating, (b) Macrostructure with one time coating, (c) Struts without any extra coating, (d) Struts with one time coating, (e) Cancellous bone. *(Continued on next page.)*

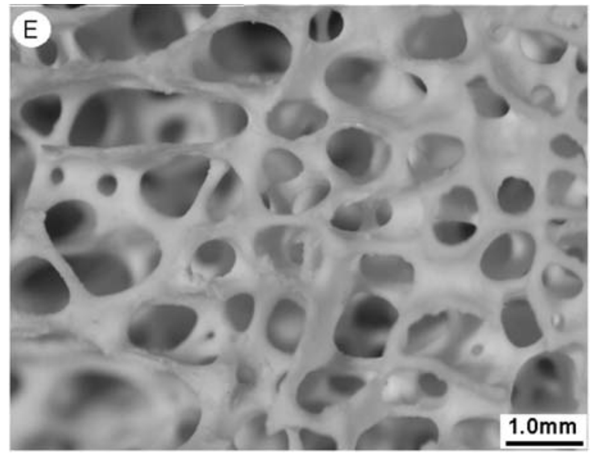

Figure 3 (*Continued*.)

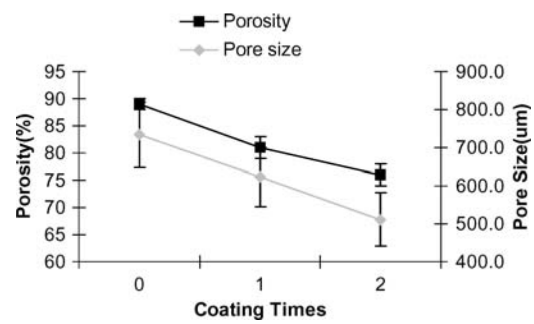

Figure 4 Porosity /Pore size of porous Ti6Al4V as function of the number of additional coating times.

decreasing with increasing coating times. It implies the porosity and pore size of porous Ti6Al4V can be controlled by multiple coating. However, the increase of coating times might result in pore isolation and pore closing.

3.4. Permeability

Fig. 5 shows the permeability data of porous Ti6Al4V with different porosities and human cancellous bone

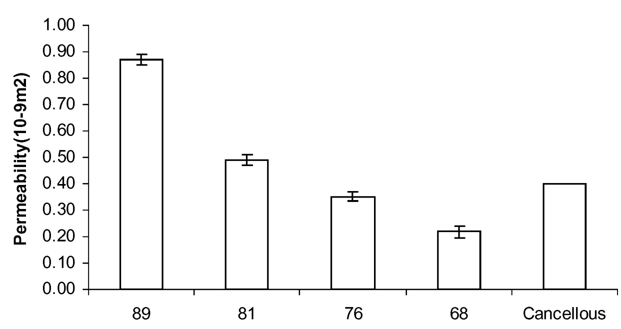

Figure 5 Permeability data of porous Ti6Al4V with various porosities and human cancellous bone.

TABLE II Mechanical properties of porous Ti6Al4V

Sample	Additional coating times	Porosity	Compressive strength (MPa)	Young's modulus (GPa)	Micro hardness (HV)	Sample number
PTC0	0	89 ± 1	10.3 ± 3.3	0.8 ± 0.3	373 ± 17	10
PTC1	1	81 ± 2	35.5 ± 7.2	1.5 ± 0.3	369 ± 14	10
PTC2	2	76 ± 2	59.4 ± 20.3	1.8 ± 0.3	379 ± 16	10

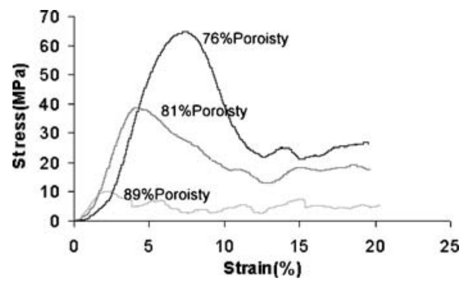

Figure 6 The stress-strain curves of porous Ti6Al4V with different porosities.

under transverse direction [18]. It can be seen that the permeability increases with porosity. Porous Ti6Al4V with high porosity has a high value of permeability. The first coating significantly decreased the permeability, additional coating having less effect. It is clear that porous Ti6Al4V after multi coating has similar permeability as human cancellous bone. The permeability test also enables to check repeatability of the coating process. In one batch of samples after coating, the standard deviation in permeability is relative low. The measured porosities (listed in Table II)also prove the repeatability of the coating process.

3.5. Mechanical properties

The mechanical properties of porous Ti6Al4V were evaluated by compressive strength, Young's modulus and micro hardness, and the results are listed in Table II. Results of Vickers (Hv) micro hardness showed that no difference in micro hardness was caused by additional coating treatment. However, the compressive strength increased from 10 to 35.5 MPa after one extra coating. The Young's modulus also increases with the number of extra coating times. This suggests that the compressive strength and Young's modulus can be adjusted by the number of additional coating. Fig. 6 shows the stress-strain curves of porous Ti6Al4V with different porosities. It can be seen that the plateau stresses increase with decreasing porosity.

4. Discussion

4.1. Ti6Al4V slurry for multiple coating (Slurry II)

The base porous Ti6Al4V with interconnected macro and micro structure has a high surface area and high affinity to the slurry, providing the possibility of producing porous Ti6Al4V with higher strength by multiple coating techniques, and further improving the material structure. The viscosity of the Ti6Al4V slurry is an important parameter. It was known that a stable slurry with high solids content and a certain value of viscosity is a prerequisite to an evenly distributed coating on the struts of the sponge [19]. Given the type of the binder, the higher concentration of the binder, the higher the viscosity of the resulting slurry will be. Considering the process of coating a sponge, it is suggested that a thicker coating on the sponge struts is beneficial to maintain the reticulated pre-forms after the sponge substrate is burned out. When coating sponges, the excess slurry can be removed by rolling-pressing while the sponges are immersed in the slurry so that high viscosity slurry can be used. On the other hand, in case of additional coating, the excess slurry has to be removed by high pressure air, so the viscosity of the slurry should be low and posses a good fluidity for going through the network of the base porous Ti6Al4V. However, if the slurry is too thin, only a limited area of the base porous is coated, making it difficult to achieve evenly distributed coating on the struts. Our experimental outcomes show the two slurries are optimal for fabricating the base body and the additional coating.

4.2. Permeability

The permeability of porous Ti6Al4V after two times extra coating is quite comparable to that of human cancellous bone. Therefore the porous Ti6Al4V after multiple coating can be expected to be a promising biomaterial for biomedical applications. In general, when porous materials are studied, two parameters are widely used: porosity and pore size, including mean value and distribution. The other parameters like interconnectivity, interconnection pore sizes are seldom mentioned. It was found that measuring permeability is an easy and effective method to reveal the structural properties of porous materials. Permeability data reflect a combination of (1) porosity, (2) pore size and distribution, (3) interconnectivity, (4) interconnection pore size and distribution, (5) orientation of pores with respect to flow direction. Therefore, permeability can be taken as a comprehensive intrinsic parameter for describing macroporous structure precisely and quantitatively in the future, and probably more relevant than porosity and mean pore size in characterizing porous materials structure.

4.3. Mechanical properties

The mechanical properties of porous Ti6Al4V were studied by compressive strength, which increased significantly as the porosity decreased with the increasing of coating times. For metallic foams, the mechanical parameters are affected by the relative density of foam ($\rho_r = \rho/\rho_s$, the density of the foam ρ divided by that of the solid material ρ_s). Gibson and Ashby [20] suggested a general model, in which the relationship between the relative strength, Young's modulus, and relative density are given by:

$$\sigma_{pl}/\sigma_{ys} = C_1(\rho/\rho_s)^{N1} \quad (1)$$

$$E/E_s = C_2(\rho/\rho_s)^{N2} \quad (2)$$

where σ_{pl} is the plateau stress of the foam; σ_{ys} is the yield stress of solid material; E is the Young's modulus of the foam; E_s is the Young's modulus of solid materials, and C1, C2, N1 and N2 are constants, depending on cell structure parameters. For the case of aluminium foam with lower density ($\rho_r < 0.2$), Gibson and Ashby found the following coefficients and exponents for the model:

$$\sigma_{pl}/\sigma_{ys} = 0.3(\rho/\rho_s)^{3/2} \quad (3)$$

$$E/E_s = (\rho/\rho_s)^2 \quad (4)$$

with C1 = 0.3, N1 = 3/2, C2 = 1, N2 = 2. Fig. 7 shows the effect of porosity on the compressive strength

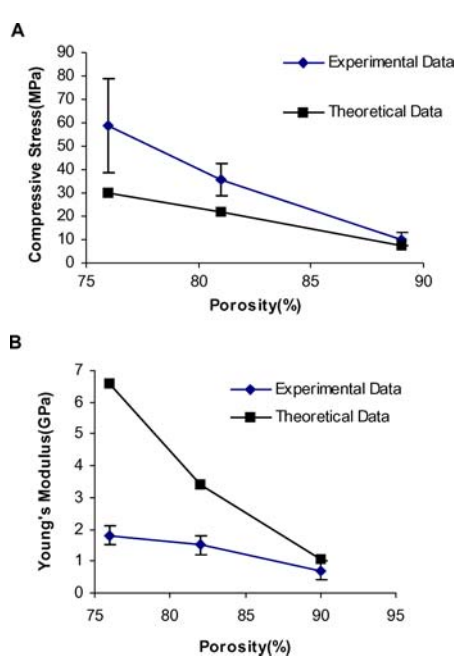

Figure 7 Effect of porosity on the compressive strength and Young's modulus of porous Ti6Al4V (comparison of experimental data and data from theoretical data). (a) Effect of porosity on the compressive strength; (b) Effect of porosity on the Young's modulus.

(shown in Fig. 7(a)) and Young's modulus (shown in Fig. 7(b)) of the porous Ti6Al4V according to the experimental data and theoretical data calculated from Gibson and Ashby's model. The experimental data do not fit the Gibson-Ashby's model. The reason is obviously that the different processing techniques of porous aluminium and porous Ti6Al4V resulted in different pore morphology, and therefore different constitution relationship.

With regard to the effect of the relative density on the mechanical properties of porous Ti6Al4V, based on the Gibson and Ashby model expressed in Equation 1 and Equation 2, coefficients fitting our experimental results are calculated as:

$$\sigma_{pl}/\sigma_{ys} = 0.5(\rho/\rho_s)^{3/2} \quad (5)$$

$$E/E_s = 0.76(\rho/\rho_s) \quad (6)$$

Where C1 = 0.5, N1 = 3/2, C2 = 0.78, N2 = 1, for $E = 210$ GPa, and $\sigma_{ys} = 827$ MPa [9].

The main problems of implant materials generally used in load bearing application are twofold: (1) The high Young's Modulus of the dense metallic materials and the low strength of polymers and brittleness of ceramics as compared with human bone. A number of reports showed that lower Young's moduli of implants resulted in stresses and strains that are close to those of intact bone, and may better reduce the stress shielding due to too high Young's moduli [21–23]. Although dense Ti6Al4V has a Young's modulus only about half of those of 316L stainless steel or CoCrMo alloy, it is still about 10–20 times higher than the Young's modulus of human bone. Recently there has been an increasing interest in developing new titanium alloys with lower Young's modulus, such as Ti-15Mo [24], Ti-15Zr-4Nb-2Ta-0.2Pd [25] and Ti-35Nb-5Ta-7Zr [26], but they are still higher than that of human bone. Fig. 8 shows the Young's modulus of commonly used implant materials [27, 28]. It can be seen that the Young's modulus's of porous TI6Al4V is between that of cancellous and cortical bone. (2) Although ceramics are good bone substitutes (osteoconductive), they are too brittle and weak to provide sufficient strength for load-bearing condition. Fig. 9 shows the compressive strength of various implant materials [27, 28]. It can be found that porous Ti6Al4V has much higher compressive strength than that of porous ceramics and polymers. The porous Ti6Al4V with a porosity of 76% has a strength of 59 MPa, the strength of trabecular-bone with 75% porosity is in the range of 10–50 MPa. As it is shown previously that we can adjust the strength and Young's modulus of porous Ti6Al4V by our multiple-coating technique to meet the requirements of porous bone substitute.

Three mechanisms can be used to explained the improvement of the strength of porous Ti6Al4V by multiple coating. Firstly, some large flaws, such as cracks,

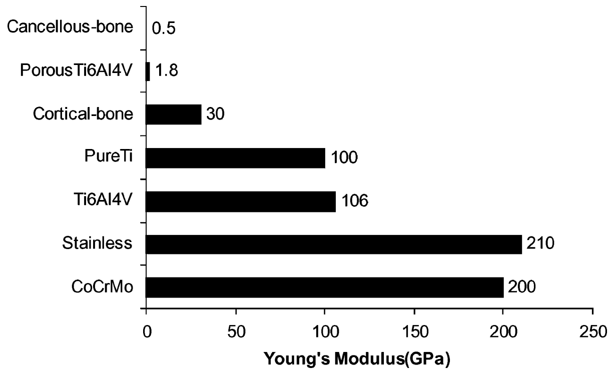

Figure 8 Young's Modulus of different implant biomaterials.

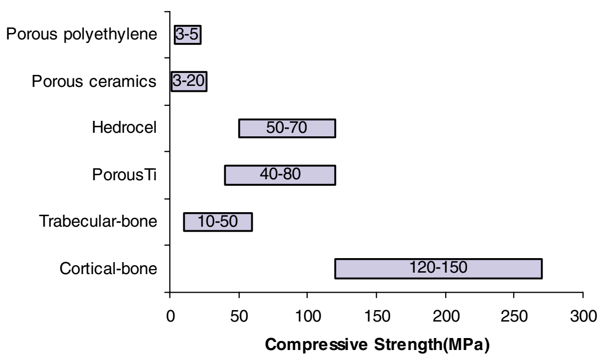

Figure 9 Compressive strength of different porous implant biomaterial comparing with bone.

were filled with Ti6Al4V powder. Secondly, the additional high vacuum sintering has a further advantage of reducing any contaminations existing on the surface of the powder particle and base body. Therefore, the fusion of Ti6Al4V particles was enhanced by the less absence of titanium carbide, titanium nitrides and oxides in the outer surfaces, resulting in increased mechanical properties of the final porous body. Thirdly, the porosity was decreased by multiple coating, as discussed above.

5. Conclusions
Porous Ti6Al4V with cancellous bone properties was successfully made by multiple coating techniques. Porosity, pore size and mechanical properties can be adjusted to correspond with bone. The permeability test proved the repeatability of the multiple coating process, and the permeability value increases with porosity of porous Ti6Al4V. Our findings show that both structural and mechanical properties of porous Ti6Al4V are comparable to those of human cancellous bone. Therefore this material can be expected to find better practical application for tissue engineering scaffolds and orthopedic implants

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