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Fabrication and characterization of titanium-matrix composite with 20 vol% hydroxyapatite for use as heavy load-bearing hard tissue replacement

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Titanium-matrix composite with 20 vol% HA ceramic was fabricated by hot pressing technique and the microstructure of the composite was studied by transmission electron microscope (TEM). The mechanical and biological properties of the composite were investigated by mechanical and *in vivo* studies. The experimental results by TEM observation show the bonding state of Ti/HA interface in Ti-20 vol% HA composite with the relative density of 97.86% is good, however, there exists an interfacial transition zone between Ti and HA. In Ti matrix of the composite and pure Ti metal, an interesting substructure comprised of screw dislocations with Burgers vectors b of $1/3\langle 11\bar{2}0\rangle$ was found. Screw dislocations are straight and regularly distributed, and cross slip can be observed. The subgrain boundaries consist of dislocation network walls with equidistant dislocation lines in the same direction. Elastic modulus and Vicker's hardness of Ti-20 vol%HA composite are 102.6 GPa and 3.41 GPa respectively. Owing to the existence of 20 vol% HA ceramic, bending strength and fracture toughness of the composite decrease sharply to 170.1 MPa and 3.57 $MPa{\cdot}m^{1/2}$ respectively, which are only about 17.5 and 12% of those of pure Ti metal. *In vivo* studies indicate Ti-20 vol% HA composite has good biocompatibility, and even better osteointegration ability than pure titanium, especially in the early stage after the implantation. In conclusion, Ti-20 vol% HA composite is suitable for heavy load-bearing hard tissue replacement from the point of view of both mechanical properties and biocompatibility.

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has the excellent biocompatibility and can directly bond to the bone[1, 2]. Unfortunately, it cannot be used for heavy load-bearing hard tissue replacement due to its poor mechanical properties and low reliability [3, 4]. The characteristics of HA ceramic have been discussed in detail by Hench [1], Williams [2], Suchanek and Yoshimura [3] respectively. The ideal biomaterials for heavy load-bearing hard tissue replacement can be obtained by fabricating HA ceramic composites, e.g. the polyethylene (PE)-HA composite developed by Bonfield [4].

Although titanium (Ti) and its alloys are the preferred metal materials for orthopaedics and dentistry because

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of their high strength and good biocompatibility [5, 6], they are bioinert biomaterials and cannot directly bond to the bone. Moreover, HA coatings to improve the surface bioactivity of titanium and its alloys often flake off as a result of poor ceramic/metal interface bonding, which may make the surgery fail [7, 8].

The problems mentioned above can be solved by the fabrication of HA-Ti composites. Recently the studies on the fabrication and characterization of HA-based composites reinforced with Ti particles have been reported [9, 10]. The significant toughening effect by energy-absorbing mechanism due to the plastic deformation of ductile Ti particles at the tips of cracks was found in both HA-20 vol%Ti composite and HA-40 vol%Ti composite [9, 10]. However, until now, systematical investigations on Ti-matrix composites doped with HA ceramic have not been reported.

In this paper, Ti-matrix composite with 20 vol% HA ceramic was fabricated by a powder metallurgical process. The microstructure of Ti-20 vol% HA composite was studied by transmission electron microscope (TEM). The mechanical and biological properties of the composite were investigated by mechanical and *in vivo* studies.

2. Materials and methods

2.1. Raw materials and powder processing

The chemical composition of titanium powders with an average size of 45.2 μm was (wt%): Ti 99.3, Fe 0.039, O 0.35, N 0.035, C 0.025, CL 0.034, H 0.024 and Si 0.0018. HA powders with an average size of 1.75 μm were fabricated by the reaction between $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$. The Ca/P ratio of HA was $1.67 \pm 2.0\%$. The content of heavy metals in HA powders, such as Pb, As, Hg and Cd is less than 1.0 ppm. The mixed powders of Ti and HA with 20 vol% HA were blended by ball milling for 24 hours and then compacted at 200 MPa. Finally, green compacts were hot-pressed at 1100 °C under a pressure of 20 MPa in a nitrogen atmosphere for 30 min with a heating rate of 10 °C/min and a cooling rate of 6 °C/min. Pure Ti metal and pure HA ceramic in comparison with the composite were also produced in the same way.

2.2. Characterization

Disk specimens with 0.3 mm in thickness and 3 mm in diameter were cut from the composite and pure Ti samples, mechanically thinned to 0.1 mm and finally ion-thinned. The resulting specimens were examined in a JEOL-2000EX transmission electron microscope (TEM) equipped with a double-tilt holder and operating at 160 KV. The density of sintered samples was measured accurately using distilled water by Archimedes method. The relative density was calculated using the measured density divided by the theoretical one. The phase constitution was analyzed by X-ray diffraction (XRD). Vickers' hardness was tested on polished surfaces under a load of 98 N. Three-point bending tests were performed on Instron testing machine (1186 type) to determine elastic modulus, bending strength and fracture toughness. Samples for optical observations were cut with a diamond saw, and their surfaces were ground and polished. The fracture surfaces of the samples were covered with a thin film of gold by vacuum-deposition and then examined by scanning electron microscope (SEM).

2.3. *In vivo* study

2.3.1. Implant preparation and surgical operation

As shown in Fig. 1(a), Ti-20 vol% HA composite and pure Ti were cut into rectangular specimens about 3.3 mm × 3.3 mm × 5–6 mm in dimension using a diamond saw. The cross-sectional view of the predrilled hole with implant in the skull of several New Zealand White rabbits of 2.5 kg weight is illustrated in Fig. 1(b). The defective bone (DB) region was designed for bone healing. Before implantation, all implants were cleaned with distilled water and sterilized by autoclaving at 121 °C for

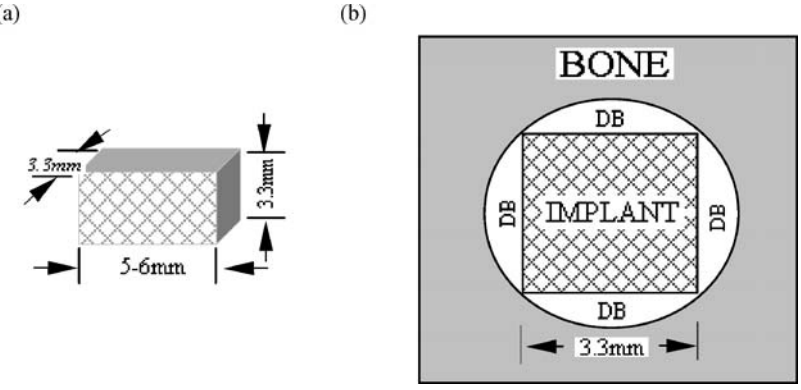

Figure 1 Schematic configuration of the implant model. (a) Rectangular specimen for implantation; (b) Cross-sectional view of the predrilled hole with implant in the skull (DB-defective bone region).

30 min. Prophylactic antibiotic was given once during operation. The rectangular implants were inserted into predrilled holes of 4.76 mm diameter using sterile surgical techniques. With implants randomly distributed, each rabbit contained six implants (three each of Ti-20 vol% HA composite and pure Ti metal).

2.3.2. Observations of tissues and interfaces between bone and implants

After 2, 4 or 8 weeks, two rabbits were sacrificed. The harvested samples were fixed in 10% buffered formalin. The fixed samples were decalcified in an acid compound (1000 ml solution containing 8.5 g sodium chloride, 100 ml formalin, 70 ml 37% hydrochloric acid, 80 ml formic acid, 40 g aluminum chloride and 25 ml acetic acid glacial). Dehydrated in alcohol and embedded in paraffin, decalcified sections were stained with haematoxylin and eosin (HE) for light microscopic observation.

3. Results and discussion

3.1. Fabrication and mechanical properties of Ti-20 vol% HA composite

To be suitable for heavy load-bearing hard tissue replacement, Ti-20 vol% HA composite must have high strength and toughness. Thus the dense Ti-20 vol% HA composite with a high relative density is necessary. However, the dehydration and decomposition reaction of HA phase into tricalcium phosphate (α-$Ca_3(PO_4)_2$, TCP) and tetracalcium phosphate ($Ca_4O(PO_4)_2$, TCPM) is the common feature for HA-Ti composites fabricated by thermal processing because the existence of Ti phase can degrade the structural stability of HA crystal [9, 10]. As a result of the decomposition reaction of HA phase with the generation of new phases and the difference of sintering shrinkages between particles of HA and Ti, the sintering ability of HA-Ti composite compacts is inferior to that of the constituents [9, 11].

Table I shows the characteristics of Ti-20 vol% HA composite sintered by hot-pressing at 1100 °C. For comparison purposes, the characteristics of pure Ti metal and pure HA ceramic fabricated in the same way are also listed in Table I. It could be found that the relative density of pure Ti metal and pure HA ceramic is 99.69 and 98.23% respectively, while the one of Ti-20 vol% HA composite only reached 97.86%, which is higher than those of HA-40 vol%Ti composite (93.30%) and HA-20 vol% Ti composite (90.17%) reported in the literature [9, 10]. Under a given pressure at 1100°, both Ti matrix and HA ceramic have good sintering ability. Moreover, the resistance to plastic deformation of the Ti matrix in the composite at a high temperature above 1000° is small and HA ceramic has the superplastic behavior at a temperature near 1100 °C [12]. During the sintering process, the plastic deformation and flow of Ti matrix and HA ceramic under the pressure can reduce the pores and cracks deriving from the decomposition reaction of HA phase and the difference of sintering shrinkages between Ti matrix and HA ceramic, which can promote the sintering densification and improve the mechanical properties of HA-Ti composites. Thus it is possible that the dense Ti-20 vol% HA composite suitable for heavy load-bearing hard tissue replacement can be fabricated by hot-pressing.

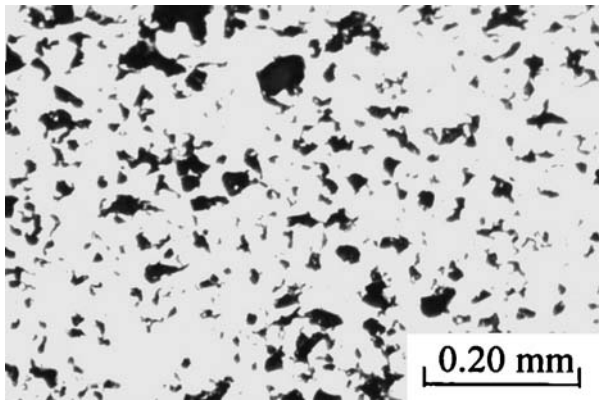

Figure 2 Optical micrograph of Ti-20 vol% HA composite sintered by hot-pressing at 1100 °C.

Fig. 2 is the optical micrograph of Ti-20vol%HA composite sintered by hot-pressing at 1100 °C, in which the white phase is titanium and the dark one is HA. HA

TABLE I Characteristics of Ti-20 vol% HA composites, pure Ti metal and pure HA ceramic

Materials	ρ (g/cm^3)	$\rho_{rel.}$ (%)	Porosity (%)	E (GPa)	σ_{bs} (MPa)	K_{IC} (MPa·m$^{1/2}$)	HV (GPa)
Ti-20 vol% HA composite	4.182	97.86	2.14	102.6	170.1	3.57	3.41
Pure Ti	4.526	99.69	0.31	108.0	971.9	29.69	3.09
Pure HA	3.161	98.23	1.77	110.9	36.9	0.66	4.72

ρ — density of materials sintered by hot-pressing at 1100 °C.
$\rho_{rel.}$—relatively density of materials sintered by hot-press at 1100 °C.
E, σ_{bs}, K_{IC} and HV—Young's modulus, bending strength, fracture toughness and Vickers hardness of materials sintered by hot-pressing at 1100 °C.

ceramic particles are homogeneously distributed in Ti matrix. The phase constitution of Ti-20 vol% HA composite analyzed by X-ray diffraction is similar to those of HA-40 vol% Ti composite and HA-20 vol% Ti composite [9, 10]; i.e. Ti and HA phases are the predominant phases. In addition, the decomposed products of HA phase, such as α-$Ca_3(PO_4)_2$ and $Ca_4O(PO_4)_2$, were also found in a small quantity.

As shown in Table I, Vicker's hardness of Ti-20 vol% HA composite is higher than that of pure Ti metal (3.09 GPa) and reaches 3.41 GPa, which is due to a higher hardness (4.72 GPa) of HA phase. Elastic modulus of pure Ti metal and pure HA ceramic is 108.0 and 110.9 GPa respectively, while that of Ti-20 vol% HA composite is only 102.6 GPa, which is lower than those of the two components in the composite. Elastic modulus is usually determined by the phase constitution and the porosity in the materials. The experiential relationship between elastic modulus of HA-Ti composite (E_{HA-Ti}) and the porosity (p) of the composite and the volume fraction of HA ceramic (f) can be expressed as the following after the literature [10, 13].

$$E_{\mathrm{HA-Ti}} = 107 + (10 - 235p)f \qquad (1)$$

The theoretical value of elastic modulus of Ti-20 vol% HA composite calculated by the above expression is 108.0 GPa, which is higher than the value tested.

Bending strength and fracture toughness of pure Ti prepared by hot-pressing process can reach up to 971.9 and 29.69 MPa $\cdot$ $m^{1/2}$ respectively. However, bending strength and fracture toughness of Ti-20 vol% HA composite decrease sharply to 170.1 and 3.57 MPa$\cdot m^{1/2}$, which is only about 17.5 and 12% of those of pure Ti. Both bending strength and fracture toughness are sensitive to the microstructure of the materials. In other words, they are associated with the configuration and distribution of the constitutional phases and the pores in the materials with a given chemical compositions. The pores reduce the effective area bearing the load and can result in the stress concentration in the materials. As a consequence, bending strength and fracture toughness of the materials decrease sharply according to the approximately exponential relation with the increase of the porosity. For example, the experiential relationship between the strength (σ) and the porosity (p) of the materials can be expressed by the following Ryskewitsch expression [14],

$$\sigma = \sigma_0 \exp(-np) \qquad (2)$$

Where n is between 4 and 7. p is the porosity and σ_0 is the strength of the material without pores. According to the Ryskewitsch experiential expression, the strength of the material with a porosity of 10% can decrease down to 50% of the one of the material without pores. Because bending strength and fracture toughness of pure HA ceramic (37 and 0.663 MPa$\cdot m^{1/2}$) are far lower than those of pure Ti metal, the effect of HA phase on the bending strength and fracture toughness of Ti-20 vol% HA composite is similar to the one of the pores in Ti-matrix of the composite. Thus the sharp decrease of bending strength and fracture toughness of Ti-20 vol% HA composite to only about 17.5 and 12% of those of pure Ti metal can be contributed to the existence of 20 vol% HA phase and the porosity of 2.14%.

Fig. 3 shows the fracture surface characteristics of Ti-20 vol% HA composite and pure Ti metal. It could be found that both Ti matrix in the composite and pure Ti metal fabricated by hot-pressing process present quasi-cleavage fracture. There are some residual pores in the composite and HA ceramic particles in Ti-20 vol% HA composite are fine. In addition, more tearing edges appear on the fracture surfaces of pure Ti metal than Ti matrix in Ti-20 vol% HA composite, which indicates that the plasticity of Ti-20 vol% HA composite is lower than that of pure Ti metal.

It should be pointed out that bending strength and fracture toughness of a compact human bone for heavy load-bearing applications can reach 121–149 MPa and above 2 MPa$\cdot m^{1/2}$ respectively [1, 15]. Obviously Ti-20 vol% HA composite has a higher bending strength and toughness than the compact human bone, and can

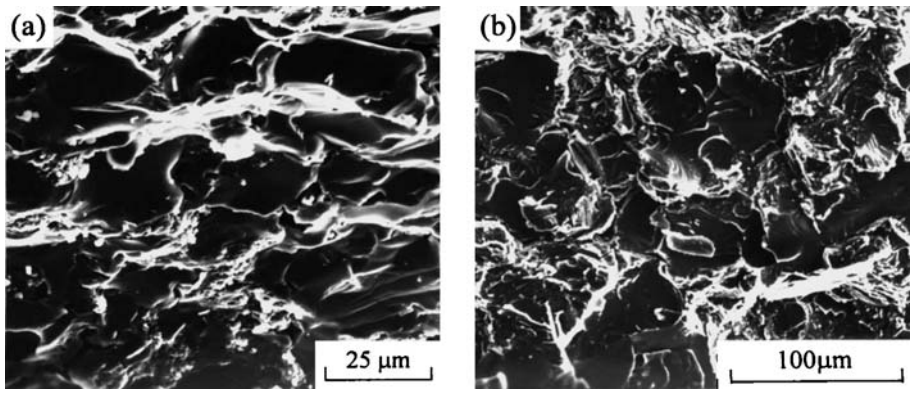

Figure 3 Fracture surface characteristics of Ti-20 vol% HA composite (a) and pure Ti metal (b) sintered by hot-pressing at 1100 °C.

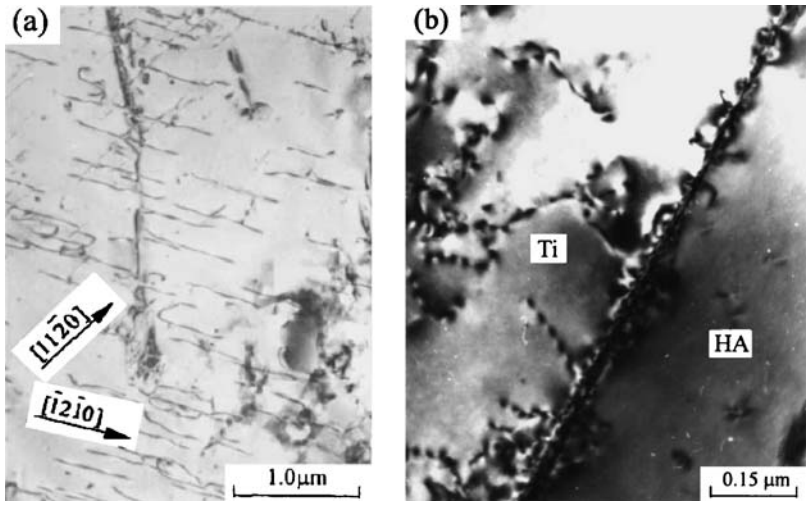

Figure 4 TEM photographs of dislocation substructure in Ti metal observed from [0001] direction (a) and HA/Ti phase interface (b) in Ti-20 vol% HA composite.

meet the basic toughness demands of the replaced hard tissues for heavy load-bearing applications. Thus Ti-20 vol% HA composite prepared by hot-pressing process is suitable for heavy load-bearing hard tissue replacement from the point of view of mechanical properties.

3.2. Microstructure of Ti-20 vol% HA composite

In Ti matrix of Ti-20 vol% HA composite and pure Ti metal, an interesting substructure mainly comprised of screw dislocations was found by TEM and there are no deformation twins. The typical dislocation substructure in pure Ti metal and Ti matrix of Ti-20 vol% HA composite observed from [0001] direction is shown in Fig. 4(a). It is found that there are many straight dislocations that lie mainly along $\langle 11\bar{2}0\rangle$ directions. The character of the straight dislocations was determined by the condition of dual beam and the invisibility condition of dislocation as the screw dislocations, whose Burgers vectors b are $1/3\langle 11\bar{2}0\rangle$. Screw dislocations are straight and regularly distributed, and cross slip can be observed to have occurred.

Fig. 4(b) is the TEM micrograph showing the morphology of Ti/HA interface in Ti-20 vol% HA composite. It was found that the bonding state of Ti/HA interface is good, however, there exists an interfacial transition zone between Ti and HA, which needs further studies. As shown in Fig. 5, subgrain boundaries consisting of dislocation network walls with equidistant dislocation lines in the same direction were found in Ti matrix of Ti-20 vol% HA composite.

It is well known that twinning mode offers an important contribution for the plastic deformation of hcp α-Ti phase under the allotropic transformation temperature (about 882.5 °) of $\alpha \leftrightarrow \beta$-Ti phase [16–18]. However,

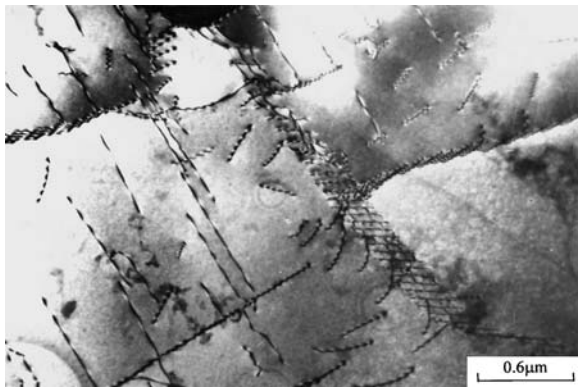

Figure 5 TEM photographs of subgrain boundaries with dislocation walls in Ti-20 vol% HA composite sintered by hot-pressing at 1100 °C.

Ti-20vol% HA composite and pure Ti metal in this work were fabricated by powder metallurgical process with hot pressing at 1100 °C. Therefore, the plastic deformation of Ti matrix in the composite and pure Ti metal mainly occurred in the high temperature bcc β-Ti phase region. Because the screw dislocation is often the main dislocation configuration which controls the slip characteristics of bcc metals [19], the slip mode of screw dislocation is the chief plastic deformation mechanism for Ti matrix of the composite and pure Ti metal above the allotropic transformation temperature of $\alpha \leftrightarrow \beta$-Ti phase, which has also been verified by TEM observation as shown in Figs. 4 and 5.

Since it is difficult for the dislocations in bcc metals to form thermo-bending and thermo-folding [19], screw dislocation lines observed in Ti matrix of the composite and pure Ti metal present a linear configuration. Large plastic deformation at a high temperature about of 1100 °C can lead to the formation and the movement of high density of dislocations more easily, which

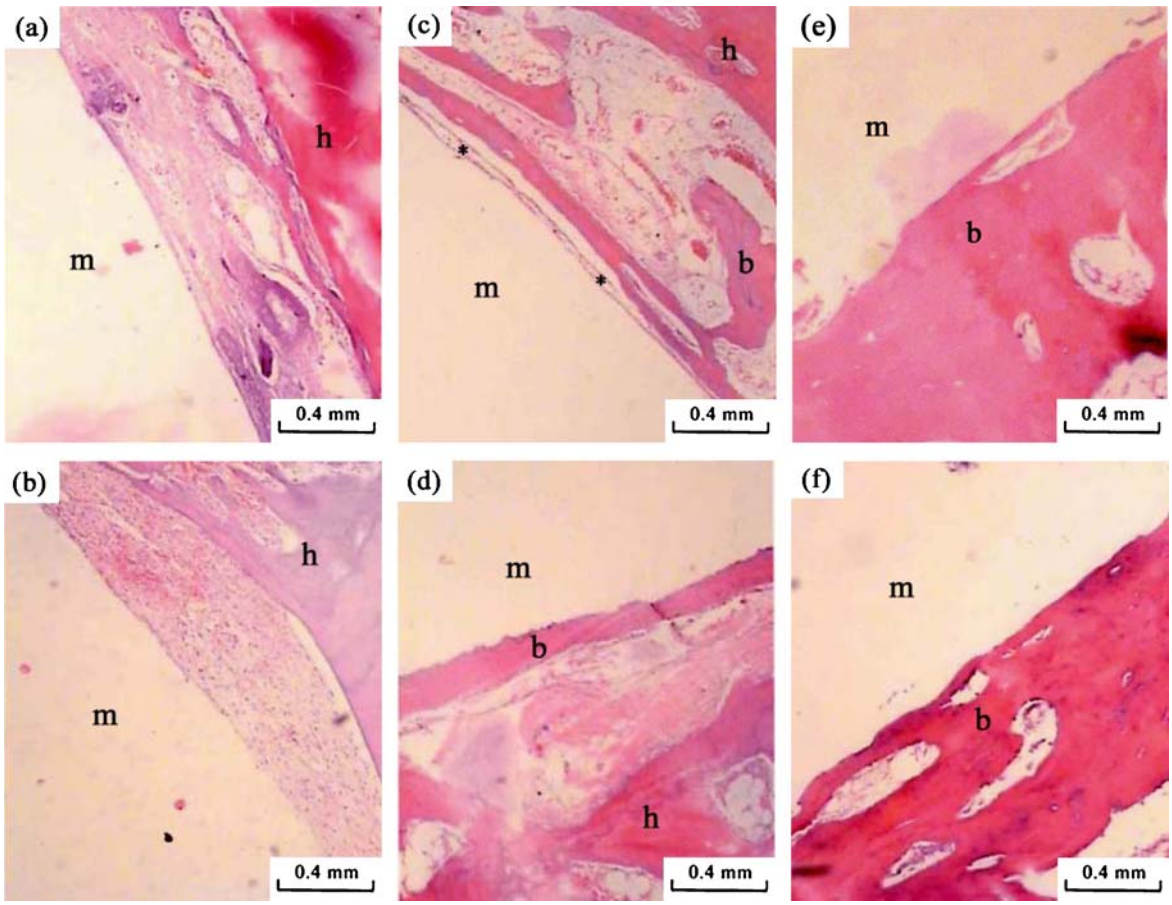

Figure 6 The growing status of newborn bones in defective bone region around the implants and the interfacial morphology between the implant and newborn bone after the implantation of different time observed by light microscopic after stained with haematoxylin and eosin (HE). (a) Pure Ti, 2 weeks; (b) Ti-20 vol% HA composite, 2 weeks; (c) Pure Ti, 4 weeks; (d) Ti-20 vol% HA composite, 4 weeks; (e) Pure Ti, 8 weeks; (f) Ti-20 vol% HA composite, 8 weeks. *m*, implant; *b*, newborn bone; *h*, host bone; *, fibrous tissue.

can result in an increase of strength and a decrease of plasticity for Ti matrix of the composite and pure Ti metal.

3.3. Biological properties of Ti-20 vol% HA composite

The growing status of newborn bones in defective bone region around the implants and the interfacial morphology between the implant and newborn bone after the implantation of different time was observed by light microscopic after staining with haematoxylin and eosin (HE) as shown in Fig. 6. Histological observations after 2 weeks of the implantation show that some immature newborn osteoids could be found in DB regions for both pure Ti metal and Ti-20 vol% HA composite as shown in Fig. 6(a) and (b).

After 4 weeks of the implantation, the DB regions around pure Ti metal and the composite were partially filled with newborn bones. However, there is some fibrous tissue existing at the partial interface between pure Ti implant and newborn bone (Fig. 6(c)). By contrast, new bone tissues can contact directly with the composite and no fibrous tissue was observed at the interface between the composite implants and new bones (Fig. 6(d)). The composite implant could integrate with bone. After 8 weeks of the implantation, the full osteointegration with newborn bone tissues could be found for both pure Ti metal and Ti-20vol%HA composite implants as shown in Figs. 6(e) and (f). New bone tissues were maturer than those of 4 weeks.

The *in vivo* studies indicate that Ti-20 vol% HA composite has good biocompatibility and can integrate with bone. The osteointegration ability of the composite is better than that of pure titanium, especially in the early stage after the implantation, which may be due to the presence of HA ceramic in the Ti-matrix composite.

4. Conclusions

Ti-20 vol% HA composite with a relative density of 97.86% was fabricated by a hot pressing technique. The phase constitution of Ti-20 vol% HA composite

is similar to that of HA-based composite with Ti and HA as the predominant phases. TEM observation shows the bonding state of Ti/HA interface is good, however, there exists an interfacial transition zone between Ti and HA. In Ti matrix of Ti-20 vol% HA composite and pure Ti metal, an interesting substructure comprised of screw dislocations with Burgers vectors b of $1/3\langle 11\bar{2}0\rangle$ was found and there are no deformation twins. Screw dislocations are straight and regularly distributed, and cross slip can be observed. Additionally the subgrain boundaries consist of dislocation network walls with equidistant dislocation lines in the same direction.

Elastic modulus and Vicker's hardness of Ti-20 vol% HA composite are 102.6 and 3.41 GPa respectively. In comparison with pure Ti metal fabricated under the same conditions, the composite has the much lower bending strength (170.1 MPa) and fracture toughness (3.57 $MPa \cdot m^{1/2}$), which are only about 17.5 and 12% of those of pure Ti metal, nevertheless it can meet the basic strength and toughness demands of replacing hard tissue in heavy load-bearing applications. Both Ti matrix in the composite and pure Ti metal fabricated by hot-pressing process present quasi-cleavage fracture.

The *in vivo* studies indicate that Ti-20 vol% HA composite has good biocompatibility and can integrate with bone. The osteointegration ability of the composite is better than that of pure titanium, especially in the early stage after the implantation, which may be due to the presence of HA ceramic in the Ti-matrix composite.

In conclusion, Ti-20 vol% HA composite is suitable for heavy load-bearing hard tissue replacement from the point of view of both mechanical properties and biocompatibility.

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