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HA/Ti composite for biomedical application by mechanical milling①

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Abstract: In order to overcome the poor mechanical properties of HA and the low bioactivity of Ti, HA/Ti composites with various compositions were prepared by mechanical milling. The effects of milling condition and the composition on the microstructure, the density and the hardness of the composites were studied. The results show that during the ball milling process, Ti particles are refined and the homogeneity of the HA/Ti mixtures is improved; HA will partially decompose due to the existence of Ti and high sintering temperature. The microstructure of HA/Ti composites is highly dependent on the milling condition and the composition. In the microstructure, Ti phase connects to be a continuous network, and HA/Ti mixtures disperse in the network. The longer the milling time, the finer the network will be. The density of HA/Ti composites decreases with the content of HA increasing and the milling time prolonging, because HA deteriorates the sinterability of Ti. The hardness of HA/Ti composites increases firstly with the content of HA increasing, and then drops when the content of HA exceeds 30%. Addition of HA will strengthen the HA/Ti composite but will decrease the density of the composite, which accounts for the effect of HA on the hardness of the composites.

Key words: HA/Ti composite; mechanical milling; microstructure
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1 INTRODUCTION

Titanium and titanium alloys have been widely used as orthopedic and surgical reconstructive implants for their high specific strength, corrosion resistance and excellent biocompatibility[1-3]. In addition, these materials exhibit relatively high fatigue strength and are nonthrombogenic. However titanium and titanium alloys usually lack of bioactivity, and do not induce the formation of a layer of biological apatite on their surface. When they are placed in the human body, a layer of fibrous tissue surrounds them, which prevents a firm union from forming between the implant and the surrounding tissue, and this failure is obviously detrimental when rigid fixation of the implants is sought. Moreover, of recent concern is the presence of Ti ions that have appeared in several clinical studies involving Ti6Al4V and CP(Chemically pure) Ti. Using large amounts Ti may hinder the recovery process by increasing the ammount of local inflammation. With current trends leaning toward longer implantation times and larger surface areas the issue of Ti toxicity becomes a real concern[4-7].

In order to overcome the above problems, coatings with hydroxyapatite (HA) on Ti and Ti alloys become of great interest because the resultant products are composite materials having good mechanical properties supplied by the metal together with the bioactivity given by HA[8-14]. Coatings of HA have been prepared by a variety of processes, including plasma spraying, laser ablation, ion beam sputtering, electro-deposition, sol-gel method. However, problems associated with these processes are obvious.

Studies have shown that these processes have two major drawbacks: difficulty in controlling the chemical and phase composition of HA in the heat-related techniques (e.g. techniques using plasma and laser)[15-17]; poor bonding strength between the coating and Ti alloy substrate[18-23]. Recently, a new chemical coating technique has drawn great interest, involving NaOH-treating followed by biomimetic mineralization. However this coating technique has problems to be overcome, for example, long soaking time, thin coating thickness and unknown bonding strength. This work aims at preparing a composite biomaterial containing homogeneously distributed HA particles in titanium base material, instead of HA coating on Ti substrate. This type of composite structure would have a higher bonding strength between HA and Ti, and would conveniently adjust the mechanical properties of Ti base material.

2 EXPERIMENTAL

2.1 Materials

Calcium nitrate tetrahydrate, ammonium phosphate, and concentrated ammonium hydroxide were obtained from Shanghai Chemicals Company, China and used as received. Titanium powder made by hydrogenization and dehydrogenization (HDDH) process was purchased from

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Xi'an Bangzhen Titanium Company, China.

2.2 Preparation of hydroxyapatite powder

Calcium nitrate and ammonium phosphate (with a Ca/P ratio of 1.67) were dissolved separately in 2 L deionized water, and the pH value of the two solution was adjusted to be 11~12 by adding ammonium hydroxide. Ammonium phosphate solution was added into stirred calcium nitrate solution drop by drop, and the pH value of the reacting solution was maintained as 11~12. The precipitates were washed, dried and crushed into precursor powder. Then the precursor powder was calcined at 900 ℃ for 2 h. Subsequently, the calcined powder was put into an autoclave, and hydrothermally treated at 130 ℃, 10 MPa for 2 h.

2.3 Mechanical milling of composite powders

The HA powder was mixed with titanium powder (mean particle size of 72 μm) in mass proportion of 20∶80, 30∶70, 40∶60, 50∶50 separately. The mixed powders were placed in a plenary mill in Ar atmosphere and milled for 10 h, 20 h and 30 h separately. In order to prevent severe welding of powders, 2% (in mass fraction) stearic acid was used as process controlling agent.

2.4 Densification of powders

The mechanically milled powders were placed in a rigid die and cold pressed into billets of d 20 mm × 10 mm at a pressure of 300 MPa. The billets were then put into a graphite die, and hot pressed in Ar atmosphere at 1 000 ℃, 40 MPa for 30 min.

2.5 Characterization of composite biomaterials

The structure of HA was determined by Fourier transformed infrared respectra (FTIR), and the phase composition of HA/Ti composite was determined by XRD at a scanning rate of 1°/min. The density of the billets were tested by Archimedes method. The billets were then polished and eroded with a solution containing 2% HF and 2% HNO_3 (in volume fraction). Micrograph was observed with a Leitca Optical Microscope and an X650 Scanning Electron Microscope. Owing to the size of the billet, only hardness (HRB) was tested for this composite.

3 RESULTS

3.1 Hydroxyapatite powder

The size of the rodlike HA powder after hydrothermal synthesis is about 10 nm in diameter and 100 nm in length, as shown in Fig. 1. IR spectrum analyses show that the characteristic peak of HA around 660 cm^{-1} is very sharp after hydrothermal treatment, compared with that before hydrothermal treatment, as shown in Fig. 2. It indicates that the structure or the HA obtained is more complete after hydrothermal treatment.

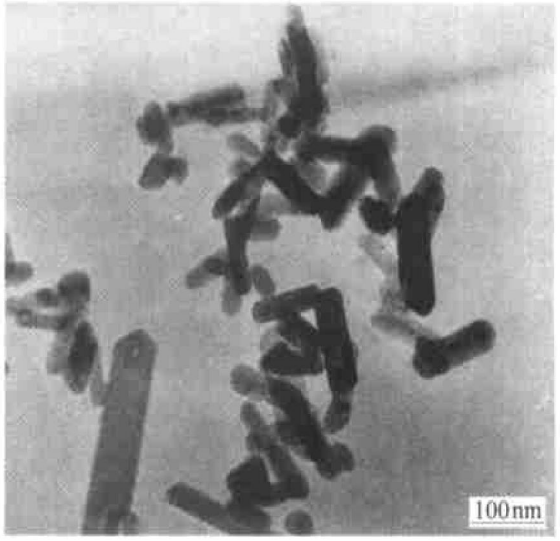

Fig. 1 TEM photograph of HA powders

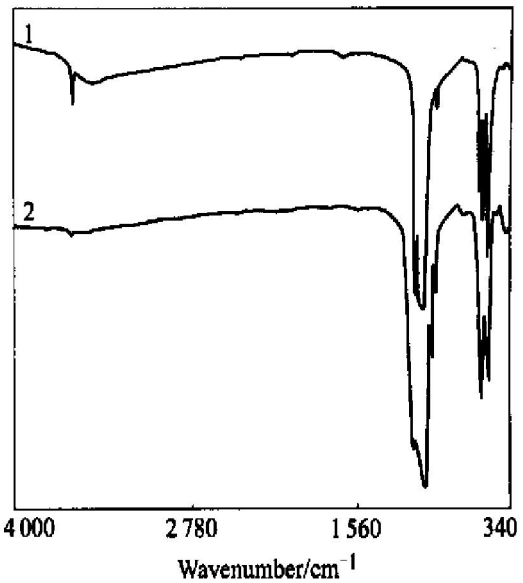

Fig. 2 IR spectra of HA powders
1—Before hydrothermal synthesis;
2—After hydrothermal synthesis)

3.2 Density

The density of HA/Ti composites after milling and hot pressing is shown in Fig. 3. The density of HA/Ti composites decreases with the content of HA increasing, as well as the milling time prolonging.

3.3 Hardness

The hardness of HA/Ti composites increases at first with the content of HA increasing, then drops after it reaches the peak value at 30% HA, as shown in Fig. 4. Fig. 4 also indicates that the hardness of Ti-30HA composite increases with milling time prolonging.

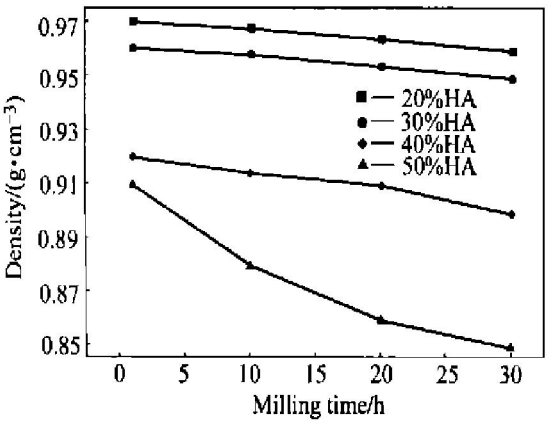

Fig. 3 Density of Ti/HA composites

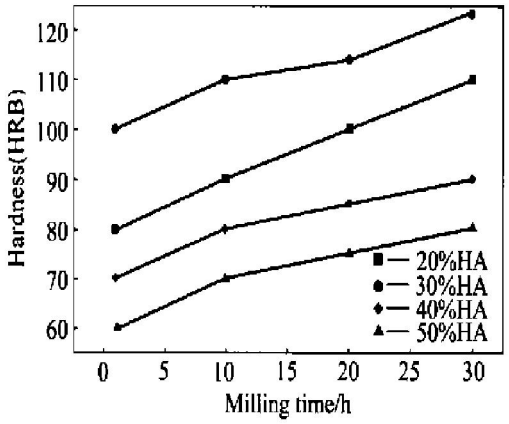

Fig. 4 Hardness of HA/Ti composites

3.4 Phase and microstructure

The XRD analyses of Ti-30HA powder after milling for 1 h and 20 h are shown in Fig. 5. It can be seen that the main phases of the powder are still Ti and HA, while with milling time increasing the content of HA decreases.

The SEM analyses show that the mean size of Ti powder decreases with milling time increasing, but the size distribution is inhomogeneous, ranging from several microns to tens of microns, as shown in Fig. 6. It's hard to detect the size change of HA.

The optical microstructures of Ti-30HA composite are shown in Fig. 7. The bright phase in this figure is Ti particles, and the gray phase is HA/Ti mixture. The Ti particles connect together and form a network surrounding the gray phase. The network structure of Ti particles is refined due to extensive ball milling, therefore, the homogeneity of HA/Ti composite is improved. Moreover, the microstructures, especially the crystal size of the Ti particles is refined.

4 DISCUSSION

4.1 Ball milling process of Ti-HA powders

Ti-HA powders should be considered as ductile-brittle system. The ball milling process of this system

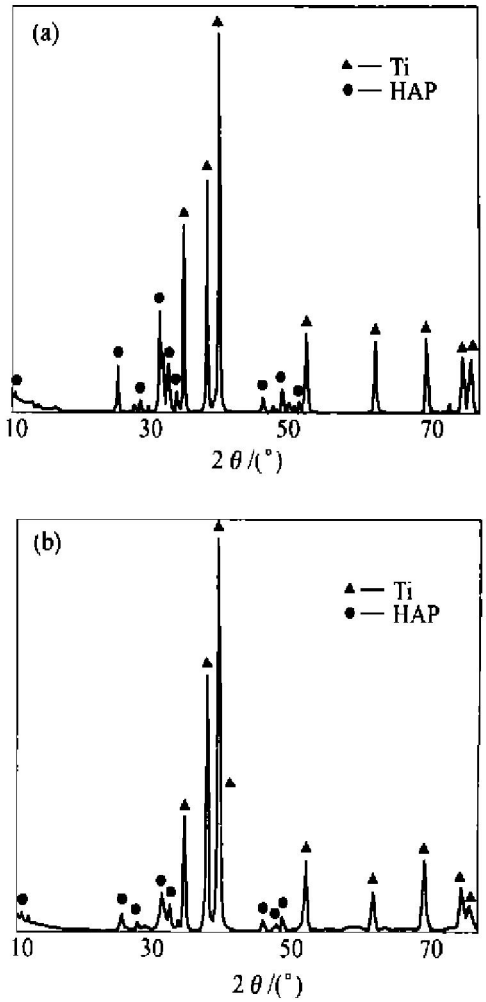

Fig. 5 XRD patterns of Ti-30HA powders
(a) —Milling for 1 h; (b) —Milling for 20 h

includes severe plastic deformation, cold welding and fracture of the ductile phase, disintegration of brittle phase and embedding of brittle phase in ductile phase. The size of HA particle is as small as tens of nanometer, so it would be difficult to further refine its particle size by ball milling. Usually, ductile Ti particles were deformed and formed sandwich-like structure during ball milling process. HA particles were embedded in the layers of Ti phase. As milling proceeded, the layers of Ti phase came closer and HA would be more uniformly distributed. The particle size of HA is so small that its decomposition temperature would be lowered; moreover other studies showed that the decomposition temperature of HA could drop in the presence of Ti[24]. Considering these two aspects, in the ball milling process, the temperature rising in high-impact-energy area would probably be high enough to lead to partial decomposition of HA phase. Therefore, as ball milling proceeded the content of HA decreased.

4.2 Density and microstructure evolution

In order to prevent HA in the composites from

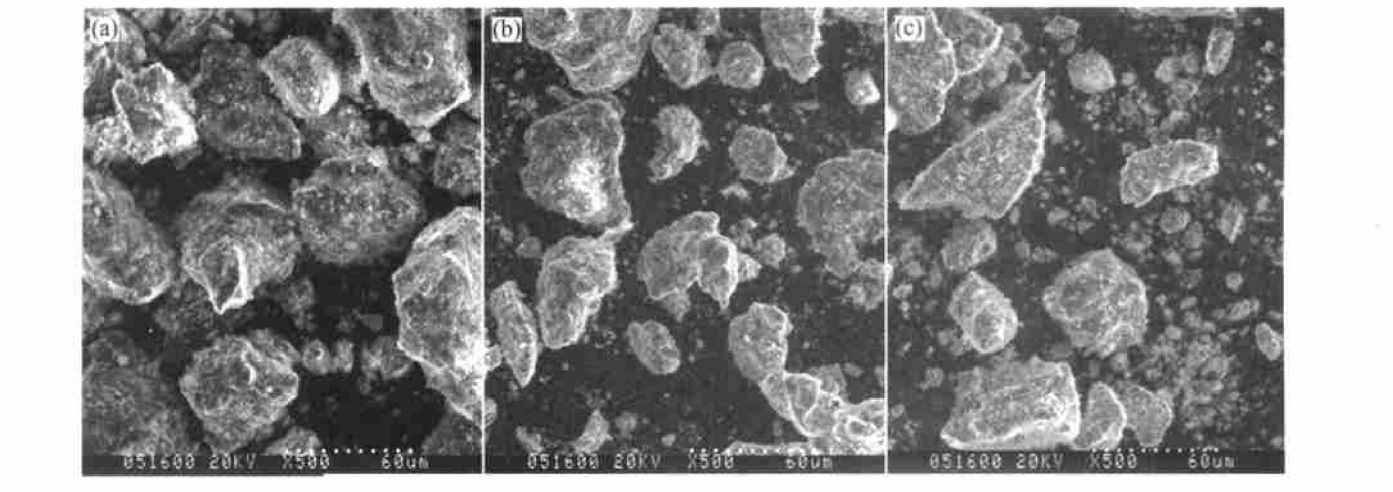

Fig. 6 SEM photographs of Ti powders
(a) —Milling for 1 h; (b) —Milling for 20 h; (c) —Milling for 30 h

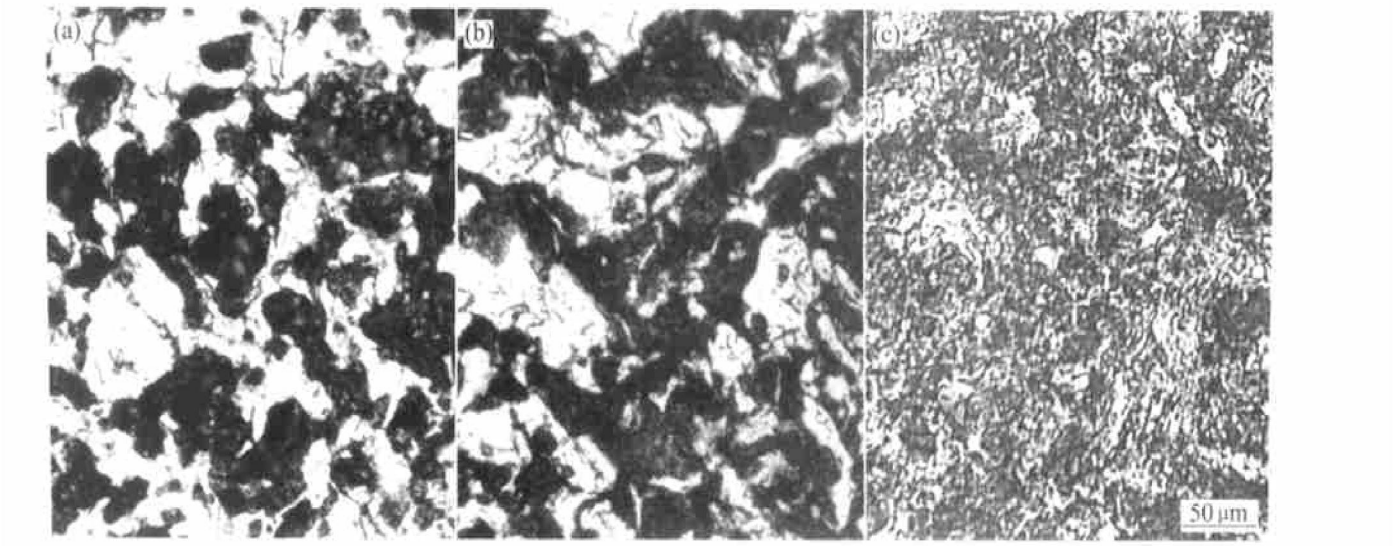

Fig. 7 Optical microstructures of Ti-30HA composites (after etching)
(a) —Milling for 1 h; (b) —Milling for 20 h; (c) —Milling for 30 h

decomposition, low temperature and short-period hot pressing were chosen. The densification mechanism of pure Ti powder during hot pressing could be mainly attributed to high temperature creep. Addition of HA particles would hinder the densification process due to two aspects. Firstly, the strength of the composite HA/Ti powder was increased by addition of hard HA phase, i. e. it would be more difficult for the composite powder to be deformed to fill the pores; secondly, the HA dispersing inside and covering Ti particles would be obstacles for the neck growth between Ti particles. So the density of HA/Ti composites decreased with the HA content increasing. As the milling time prolonged, HA particles were more homogenously dispersed in Ti particles, and would seriously deteriorate their sinterability, hence the density decreased with milling time increasing as well. However, prolonged milling time improved the homogeneity of the composites, and refined the size and the microstructure of Ti particles, and the network structures formed during hot pressing would also be refined and be more homogenous.

4.3 Hardness of composite

The hardness of the HA/Ti composites is mainly influenced by two interacting factors. Firstly, in addition to the improvement of bioactivity, HA can also act as strengthening phase in the composite, so with the content of HA increasing, the hardness increased; secondly, the strength of the composites decreased with density decreasing, which were mainly induced by the increasing of HA.

At a low content of HA, the former factor is prevalent, so the hardness increased with HA content increasing; while at a content of HA above 30%, the later factor is prevalent, so the hardness decreased. It seems that the premium content of HA should be around 30% on the consideration of both strength and bioactivity. The effect of milling time on the hardness of the composite can be

attributed to the continuous refining of the microstructure.

5 CONCLUSIONS

1) During the ball milling process, Ti particles are refined and the homogeneity of the HA/Ti mixtures is improved; HA will partially decompose due to the existence of Ti and the temperature rising effect.

2) The microstructure of HA/Ti composites is highly dependent on the milling condition and the composition. After hot pressing, Ti phase connects to be a continuous network, and HA/Ti mixtures disperse homogenously in the network. The longer the milling time, the finer the network will be. The density of HA/Ti composites decreases with the content of HA increasing and the milling time prolonging, because HA deteriorates the sinterability of Ti.

3) The hardness of HA/Ti composites increases firstly with the content of HA increasing, and then drops when the content of HA exceeds 30%. Addition of HA will strengthen the HA/Ti composite but will decrease the density of the composite, which accounts for the effect of HA on the hardness of the composites.

REFERENCES

[1] Noort R. Titanium: the implant material of today[J]. J Mater Sci, 1987, 22(14): 3801-3811.

[2] Temgralll P, Lunfsytom I. Physico-chemical consideration of titanium as a biomaterial[J]. J Clin Mater, 1992, 9(1): 115-134.

[3] Mitsuo N. Mechanical properties of biomedical titanium alloys [J]. J Mater Sci Eng A, 1998, 243: 231-236.

[4] Ball M D, Downes S, Scotchford C A, et al. Osteoblast growth on titanium foils coated with hydroxyapatite by pulsed laser ablation[J]. J Biomater, 2001, 22(4): 337-347.

[5] Cleries L, Femendez Pradas J M. Behavior in simulated body fluid of calcium phosphate coatings obtained by laser ablation [J]. J Biomater, 2000, 21(18): 1861-1865.

[6] Ramires P A, Romito A, Cosentino P, et al. The influence of titania/hydroxyapatite composite coatings on in vitro osteoblasts behaviour[J]. J Biomater, 2001, 22(12): 1467-1474.

[7] Nonami T, Kamiya A, Naganuma K, et al. Implantation of hydroxyapatite granules into superplastic titanium alloy for biomaterials[J]. J Mater Sci Eng, 1998, 6(4): 281-284.

[8] Yasuda H Y, Mahara S, Nishyama T, et al. Preparation of hydroxyapatite/α-tricalcium phosphate composites by colloidal process[J]. J Mater Sci Eng, 2002, 3(1): 29-33.

[9] Inagaki M, Yokogawa Y, Kameyama T. Influence of plasma gas composition on the adhesiveness of RF thermal plasma sprayed hydroxyapatite/titanium composite coatings[J]. J Key Eng Mater, 2001, 218(14): 47-50.

[10] Watazu A, Naganuma K. Hydroxyapatite granules implanted on titanium alloys[J]. J Key Eng Mater, 2000, 192(22): 745-748.

[11] Kumar R R, Wang M, Ducheyne P. Production and evaluation of hydroxyapatite-tricalcium phosphate functionally graded coating[J]. J Key Eng Mater, 2001, 195(26): 1013-1035.

[12] ZHANG J M, LIN C J, FENG Z W. Hydroxyapatite/metal composite coatings prepared by multi-step electrodeposition method[J]. J Mater Sci Lett, 1998, 17(13): 1077-1079.

[13] CHU Cheng-lin, ZHU Jing-chuan, YIN Zhong-da, et al. Structure optimization and properties of hydroxyapatite-Ti symmetrical functionally graded biomaterial[J]. J Mater Sci Eng, 2001, 316(1-2): 205-210.

[14] Gu Y W, Loh N H, Khor K A, et al. Spark plasma sintering of hydroxyapatite powders[J]. J Biomater, 2002, 23(1): 37-43.

[15] Quek C H, Cheang P. Influence of processing parameters in the plasma spraying of hydroxyapatite/Ti-6Al-4V composite coatings[J]. J Mater Pro Tech, 1999, 89(19): 550-555.

[16] Khor K A, Yip C S, Cheng P. Post-spray hot isostatic pressing of plasma sprayed Ti-6Al-4V/hydroxyapatite composite coatings[J]. J Marter Pro Tech, 1997, 71(2): 280-287.

[17] Tsui Y C, Doyle C, Clyne T W. Plasma sprayed hydroxyapatite coatings on titanium substrates Part 1: Mechanical properties and residual stress levels[J]. J Biomater, 1998, 19(22): 2015-2029.

[18] ZHENG xue-bin, HUANG Mir-hui, DING chuan-xian. Bond strength of plasma-sprayed hydroxyapatite/Ti composite coatings[J]. J Biomater, 2001, 21(8): 841-849.

[19] Yokoyama A, Watari F, Miyao R, et al. Mechanical properties and biocompatibility of titanium-hydroxyapatite implant material prepared by spark plasma sintering method[J]. J Key Eng Mater, 2001, 194(25): 2045-2050.

[20] Slosarczyk A, Klisch M, Blazewice M, et al. Hot pressed hydroxyapatite-carbon fibre composites[J]. J Euro Ceram Soc, 2000, 20(9): 1397-1402.

[21] ZHENG X, HUANG M, DING C. Bond strength of plasma-sprayed hydroxyapatite/Ti composite coatings[J]. J Biomater, 2000, 21(8): 841-849.

[22] Lopes M A, Monteiro F J, Santos J D. Glass-reinforced hydroxyapatite composites: Fracture toughness and hardness dependence on microstructural characteristics[J]. J Biomater, 1999, 20(21): 2085-2090.

[23] Ban S, Hasegawa J, Maruno S. Fabrication and properties of functionally gradient bioactive composites comprising hydroxyapatite containing glass coated titanium[J]. Mater Sci Forum, 1999, 311(29): 350-355.

[24] CHU Cheng-lin, ZHU Jing-chuan, YIN Zhong-da, et al. Hot pressing of hydroxyapatite-Ti material and stability[J]. Trans Nonferrous Metals Society of China, 2000, 10(4): 505-510.

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