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Original Research

Low temperature spark plasma sintering of TC4/HA composites

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ABSTRACT

Ti6Al4V/hydroxyapatite composites (TC4/HA) have been prepared by high energy ball milling and low temperature spark plasma sintering at 600 °C, 550 °C, 500 °C and 450 °C, respectively. The sintering temperature of the composites was sharply decreased as the result of the activation and surficial modification effects induced from high energy ball milling. The decomposition and reaction of hydroxyapatite was successfully avoided, which offers the composites superior biocompatibility. The hydroxyapatite in the composites was distributed in gap uniformly, and formed an ideal network structure. The lowest hardness, compressive strength and Young's modulus of the composites satisfy the requirements of human bone.

1. Introduction

Recently, the metal materials (mainly titanium and titanium alloys) and ceramics (mainly hydroxyapatite and tricalcium phosphate) have been used to repair and replace human bones [1]. TC4 (Ti6Al4V) belongs to a+β type titanium based alloy with excellent corrosion resistance and mechanical processing properties. Moreover, the material will not be affected by thunderstorms affect in human body. However, the element of Al reduces the biocompatibility of this alloy [2,3].

Hydroxyapatite ($Ca_{10}(PO4)_6(OH)_2$, HA) is a major inorganic component of the animal bones and teeth. Thus, hydroxyapatite has excellent biocompatibility and is absence of toxic elements. It can be implanted safely, and can also be used for the bone conduction and guidance. But, HA has a low strength, and is very brittle. It cannot be used to host the site. On the other hand, TC4 has excellent mechanical processing properties [4]. Therefore the composite of HA and TC4 combines their respective advantages, which not only has high strength and toughness of TC4, but also has superior biological activities of hydroxyapatite. Nevertheless, it is still hard to fabricate TC4/HA by conventional processing because hydroxyapatite will decompose or react with Ti at high temperature [5]. The decomposition or reaction of hydroxyapatite can hinder the sintering process, which reduces the binding force of Ti and HA and changes the matrix structure. These problems have a great impact on the mechanical properties of the composites. The composites prepared at low temperature cannot only prevent crystallization, but also avoid the decomposition of HA and reduce the elastic modulus, which avoid the phenomenon of stress shielding [6,7].

2. Experimental

The composites were prepared by mechanically alloying TC4 (95 wt%) powder of about 50–70 μm grain size and HA (5 wt%) power of about Φ20 × 150 nm grain size with high-energy ball-milling QM-3SP04. The TC4/HA composites were fabricated by SPS-625 under 600 MPa and at different sintering temperatures of 600 °C, 550 °C, 500 °C, 450 °C respectively. The temperature was increased at the same rate of 100 °C /min for each sintering. The vacuum degree of sintering chamber was monitored by the SPS analysis unit. The specimens are disk in shape with a diameter of 15 mm and a thickness of 3 mm. The phase analysis of the composites was conducted by X-ray diffraction, and their microstructures were observed by scanning electron microscope (SEM). X-ray energy dispersive spectroscopy (EDS) was used to determine the composition of the specimens. The densities of sintered samples were measured with Archimedes density tool (Mettler Toledo ML 204). HV-1000 type micro-sclerometer was used to measure the micro-hardness of the sintered samples with a load of 9.8 N and a load-dwell time of 10 s. The compressive curves of sintered samples were also measured using a WDW-200 type mechanical property instrument with strain rate of 5×10^{-4}.

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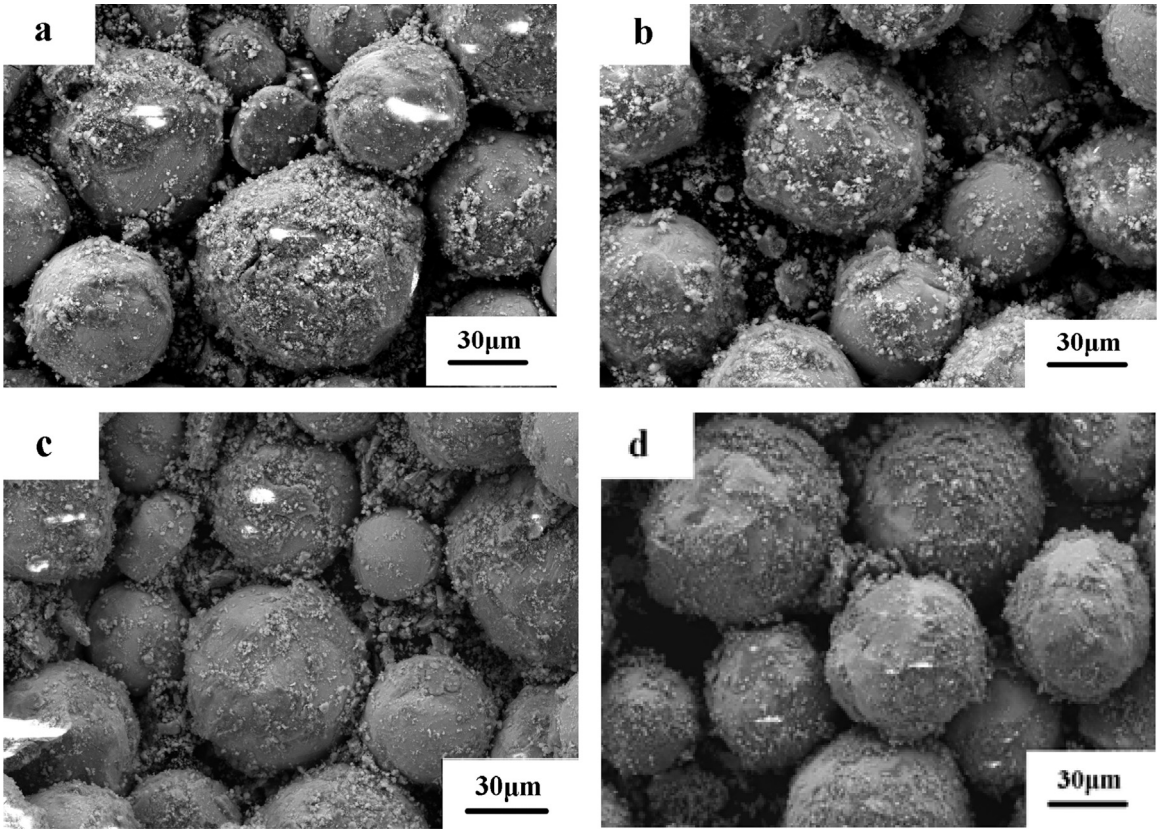

Fig. 1. SEM micrographs of powder mixture of TC4+5% HA by high energy ball milling with different ball milling times: 1 h (a), 2 h (b), 3 h (c) and 4 h (d).

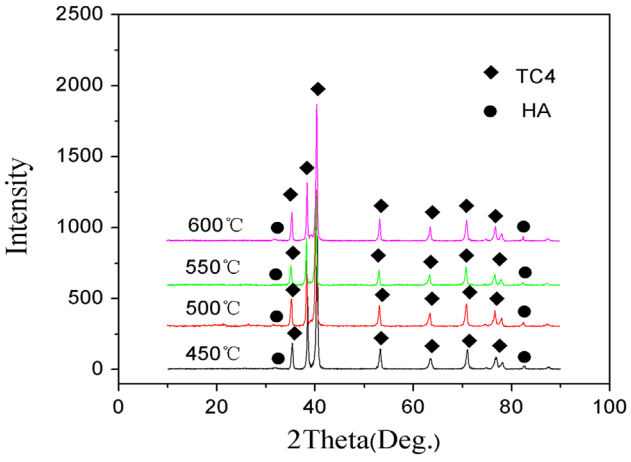

Fig. 2. XRD patterns of composites sintered at different temperatures.

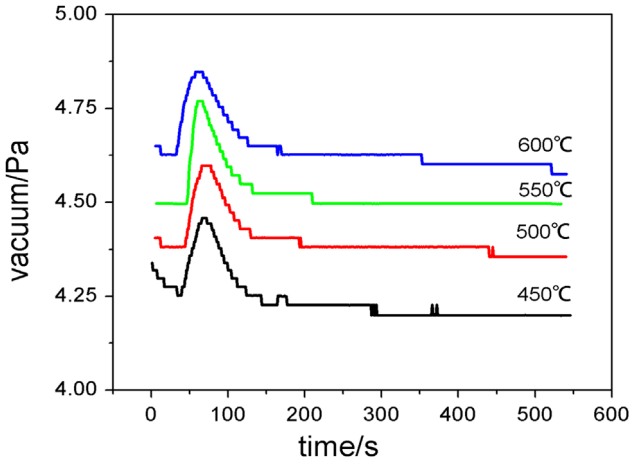

Fig. 3. Curves of vacuum degree at different temperatures.

3. Results and discussion

3.1. Process parameters of high-energy ball milling and coating

During the high-energy milling, the purpose of this experiment is to change the crystal structure of the material surface, store energy properly, improve the material surface energy, decrease the material activation energy, and eventually reduce the sintering temperature [8,9]. The ball milling time is 1 h, 2 h, 3 h, 4 h respectively, under the same charge ratio.

Fig. 1 shows the SEM morphology of TC4+5%HA after ball milling. It can be seen that the particle size of TC4 is not reduce after ball milling, and the agglomeration of HA is also not obvious. With the increasing milling time, many more fine particles are gradually attached to the surface of TC4 particle, and their distributions become more homogeneous. Since the grain size of HA is relatively small, it has high activity. It is easy for HA to embed on the surface of TC4 under the mechanical force. The increase of milling time makes the coating effect better. Therefore, the optimum milling time is 4 h to obtain the mixture powder for sintering.

3.2. XRD analysis

Fig. 2 displays the XRD patterns of the composites sintered at 600 °C, 550 °C, 500 °C, 450 °C. As seen from the figure, the diffraction peak position of each sintered samples does not changes, therefore, the results showed that no new phase is generated in the sintering process at different temperatures. Due to the low content of HA, its diffraction peak does not emerge obviously. So it

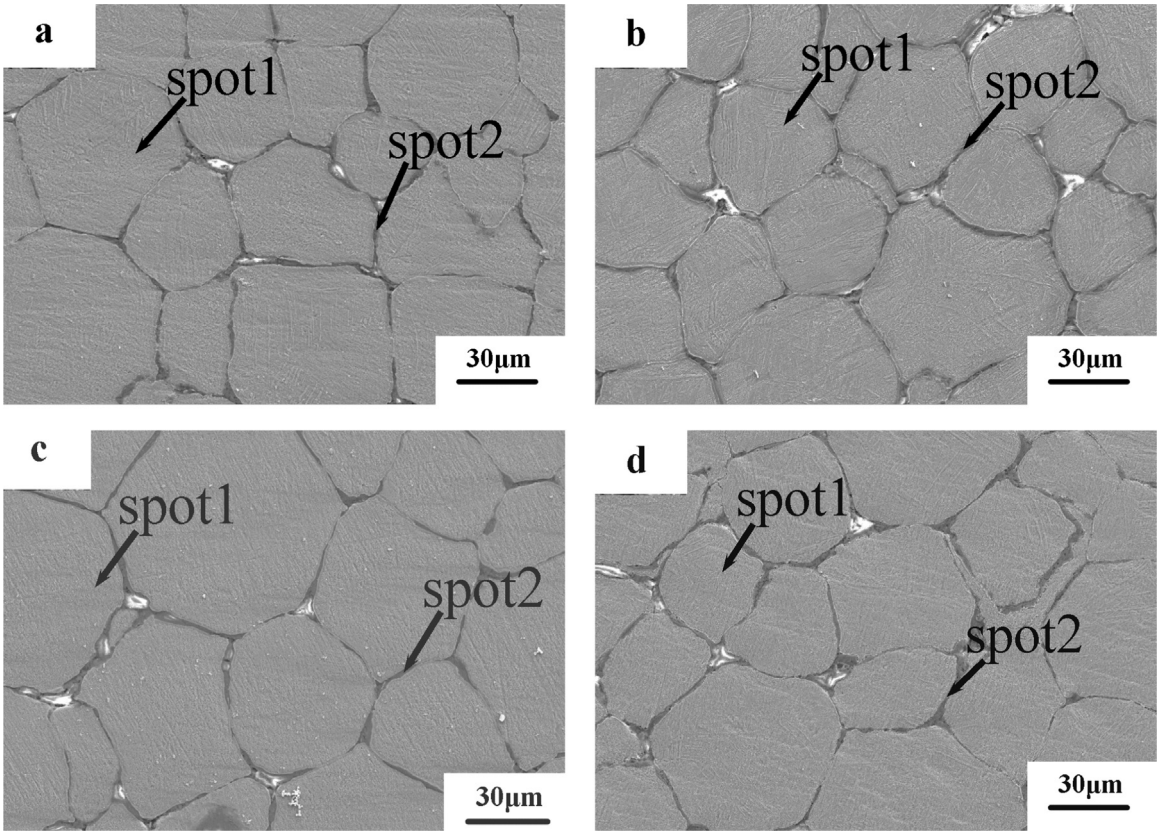

Fig. 4. Microstructure of TC4+5%HA composites sintered at different temperatures: (a) 600 °C, (b) 550 °C, (c) 500 °C and (d) 450 °C.

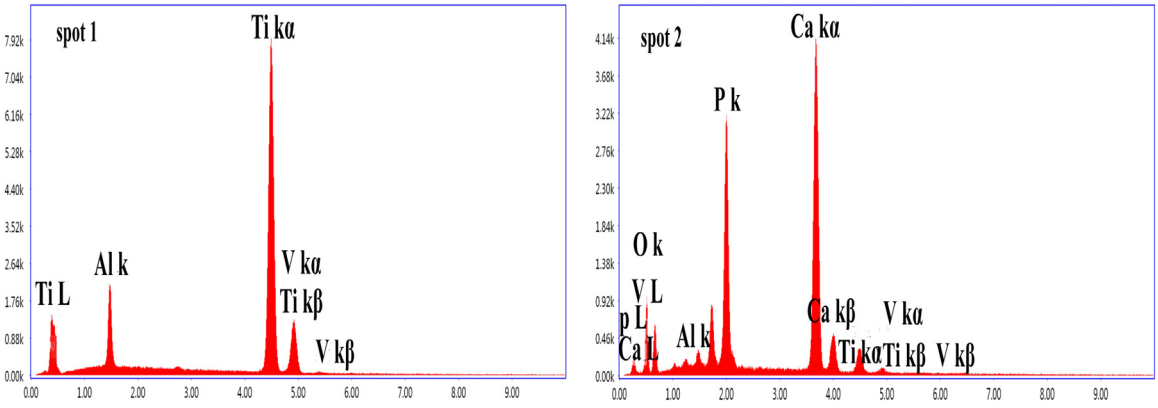

Fig. 5. EDS results of spot 1 and spot 2 on the TC4+5%HA composites sintered at 450 °C.

Table 1
Hardness of the composites.

Specimen (°C)	Spot 1 (GPa)	Spot 2 (GPa)
450	4.036	4.089
500	4.156	4.422
550	4.125	4.356
600	4.173	4.396

is hard to detect whether HA decompose or generate other phases.

The vacuum is sensitive to the released gas from the sintering body during sintering procedure. Whether HA decomposes can be deduced from the curve of vacuum (Fig. 3). Fig. 3 shows that a peak appears in the vacuum curve in the early stage, which is a progress of powder degassing. The particle size is relatively small and has large surface area, which results in a strong adsorption capacity. A large amount of gas adsorbed in powder will be released during the procedure of evacuating. After the initial evacuating stage of about 150 s, the pressure of the sintering system becomes gentle gradually, and no additional peak appears. HA does not decompose. Therefore, the mainly component of specimen is TC4, and the minor component is HA.

3.3. Microstructure analysis

Fig. 4 shows the microstructure of the composites sintered at 600 °C, 550 °C, 500 °C and 450 °C. These images show similar compact structures of composites. Fig. 5 displays the energy spectrum analysis results at two locations of the composites. According to the surface of scanning spectrum analysis, the gray tissue is TC4 and void, whereas the black tissue is the mixture of HA and TC4. TC4 exhibits an ideal network structure, and HA

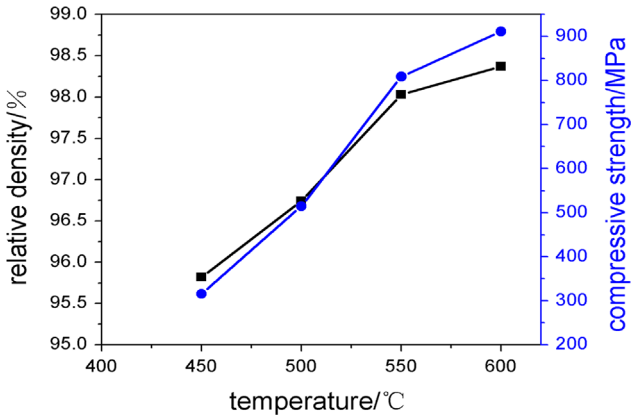

Fig. 6. Relative density and compressive strength of composites sintered at different temperatures.

distributed around TC4 uniformly. This structure allows TC4 to act as the mainly force. The distribution of the hydroxyapatite in the gap and surface can promote the growth of tone in the gap and surface, and improve wear resistance and the strength of the material. Overall, TC4 and HA bind denser. With the decrease of the sintering temperature, the molten extent of the powder surface is not enough, which reduces the binding force of the powder. When the sintering temperature is 450 °C, since the binding force is too low, the individual particles fall off during polishing. Therefore, it is vital to increase the sintering pressure to obtain denser composites.

3.4. Hardness analysis of the composite

Since the hardness of cancellous bone is 0.16–0.58 GPa, the hardness of the cortical bone is 0.15–0.56 GPa [10–13]. Table 1 shows the hardness of the composites sintered at different temperatures. It is found that the hardness values at spot 1 and spot 2 (in Fig. 4) are higher than those of human bone. We propose that HA plays a role in enhancing hardness of the composite. When the sintering temperature changes from 450 to 600 °C, the hardness values of the composites are basically same at different positions, indicating that the extent of sintering is better HA distributed very uniformly. With the decreasing sintering temperature, HA is distributed more uniformly, and the micro-hardness also decreases slightly. The lowest hardness value is 4.06 GPa, which is higher than human bone, but meets the requirement of hardness value for the implant materials.

3.5. Relative density and compressive strength

Fig. 6 is the density and compressive strength of the composites sintered at different temperatures. With the increasing sintering temperature, the relative density the compressive strength of the composites increases apparently. When the sintering temperature is low, the growth of neck is hindered which reduces the relative density. According to the literature, the compressive strength is 130–90 MPa [11]. The relative density and compressive strength of the specimen sintered at 450 °C is 95.82% and 312.58 GPa, which is higher than the compressive strength of human bone.

Fig. 7 shows the compression stress–strain curves of the composites. The Young's modulus required for implant-materials is 10–20 GPa [12,13]. With the decreasing sintering temperature from 600 to 450 °C, the Young's modulus of the composites are 18.632, 15.473, 14.738 and 8.442 GPa, respectively, which can meet the requirement for implant materials and avoid the phenomenon of stress shielding.

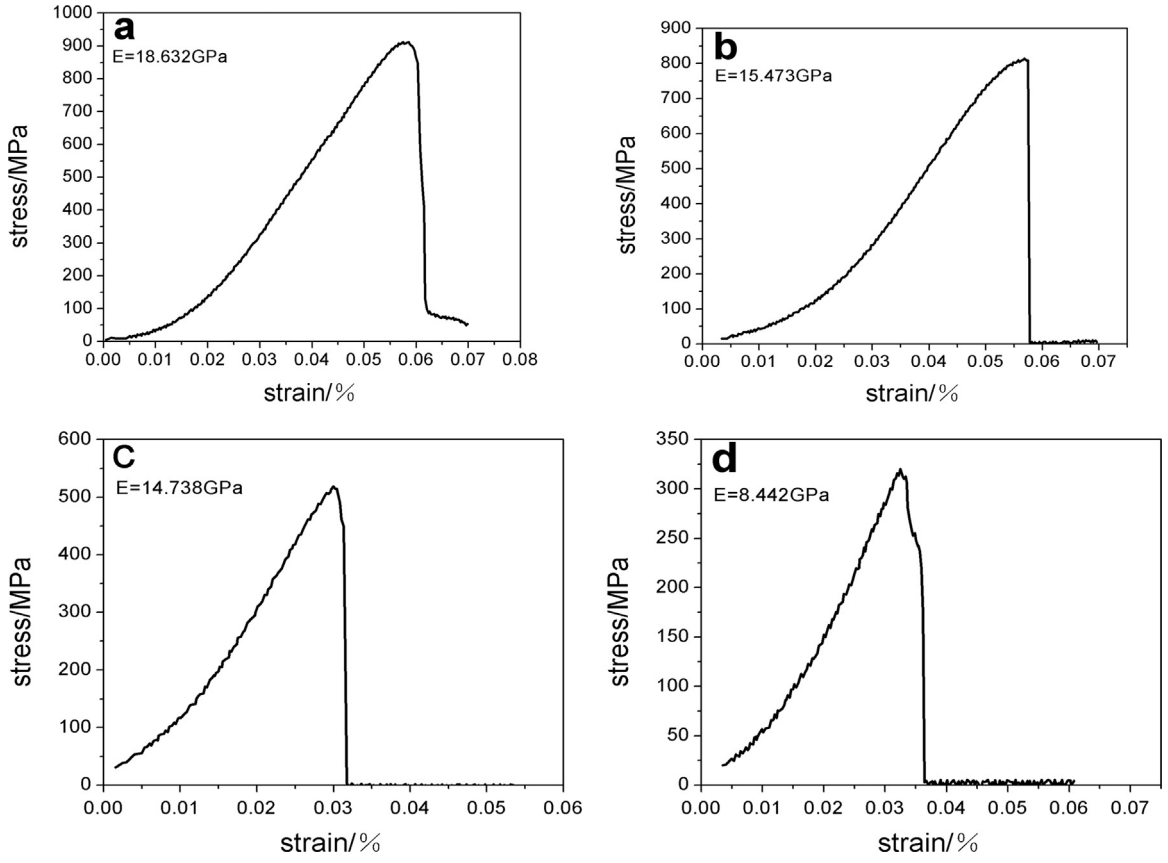

Fig. 7. Compression stress–strain curves of the composites sintered at different temperatures (a) 600 °C, (b) 550 °C, (c) 500 °C and (d) 450 °C.

4. Conclusions

1) By high energy ball milling, HA can be decorated at the surface of TC4 uniformly, which enhances the activity of the surface of powder, and achieves surficial modification of materials.
2) Since the decomposition of HA does not occur, the low-temperature SPSed TC4/HA composites have a superior biocompatibility, which meets the requirements of implant.
3) With the decrease of sintering temperature, the hardness, compressive strength and Young's modulus of the TC4/HA composites reduce, which satisfy the requirements of human bone.

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