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Enhanced in vitro bioactivity of porous NiTi–HA composites with interconnected pore characteristics prepared by spark plasma sintering

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ABSTRACT

Porous NiTi possesses suitable mechanical characteristics for orthopaedic implants. However, its poor bioactivity is a major challenge in the clinical application. Composite structures of porous NiTi and hydroxyapatite (HA) can be used to promote the bone ingrowth and integration of the implant with the surrounding tissue. But the differences in physical and mechanical properties of these composites are the main problem during sintering. Hence, we report a rapid fabrication of porous NiTi–HA composites using spark plasma sintering (SPS) with space holder method. Effect of HA on pore characteristics, mechanical properties and in vitro bioactivity (corrosion behaviors, ion release and apatite formation ability) of the porous NiTi–HA was investigated. Results showed that interconnected pore characteristics and 29%–37% porosity could be achieved by adding HA from 3 to 10 wt.%. Compression test revealed that porous NiTi–HA possessed not only low elastic modulus of 5.6–8.1 GPa (close to that of human bone) but also high compressive strength. Furthermore, the addition of HA could improve the bioactivity of porous NiTi significantly. The bioactivity mechanism and a relationship of HA concentration in the NiTi matrix are also discussed. The combination of interconnected pore characteristics, low elastic modulus, high strength and good bioactivity might make this material a candidate for hard tissue implants.

1. Introduction

Porous near-equiatomic NiTi alloys have been recently considered as excellent biomaterials with potential use in the fields of orthopaedic implant and cardiovascular applications due to their unique properties, such as shape memory effects, superelasticity and good biocompatibility [1–3]. Moreover, the pore structures and mechanical properties can be easily tailored by controlling the sintering process, hence, promoting bone tissue ingrowth and making them more biologically compatible to surrounding bone [4,5]. Also, pore structure is crucial for reducing the stress-shielding effect, which may cause bone resorption and weaken bone locally [6–8].

Previously several powder metallurgy (PM) techniques had been used to fabricate porous NiTi alloys [6,9–15], but they often had limitations due to complexity. Besides, they could easily cause oxidation and tended to form undesired phases (Ti_2Ni, Ni_4Ti_3 and Ni_3Ti) due to the composition fluctuation in the specimen. Fully NiTi phase material generally has good mechanical properties and superelasticity for surgical implantation [16]. Ti_2Ni, Ni_3Ti and Ni_4Ti_3 phases existing in porous NiTi might increase the brittleness of the implants. Besides, they could lead to the cavitation corrosion and deteriorate the biocompatibility of porous NiTi in the physiological environments [17,18].

Spark plasma sintering (SPS), the most efficient sintering method for ceramics, metals, and alloys, is a pressure assisted pulsed current sintering process based on spark discharge momentarily generated in the gaps between particles [19]. The particles are activated on its surface by spark discharge and neck formation easily occurs at low temperature in very short time compared with conventional sintering technologies. Furthermore, the effect of electrical field diffusion generated by spark discharge purifies the surface of powder particles, which guarantees neck formation and high quality of sintered materials [20,21]. Zhao et al. [22] successfully prepared NiTi alloys with 13% and 25% porosity through SPS method. The porous NiTi appears to possess a sound microstructure with high ductility. In our recent study [23], we reported that a method of one-step SPS technique was used to fabricate porous NiTi alloy. The results showed that porous NiTi alloys with 18%–61% porosity and 21–415 μm average pore size consisted of nearly single NiTi phase with few undesired phases Ti_2Ni and Ni_3Ti. However, porous NiTi alloy has poor bioactivity in spite of its good mechanical properties. Besides, it should also be noted that the high Ni content released from porous NiTi alloys might result in potentially negative effects on the surrounding tissue by inducing allergic responses [24,25].

The chemical structure of Hydroxyapatite (HA) is similar to the human bone. Its excellent bioactivity could enhance the growth of human bone tissue [26,27]. But HA has poor mechanical properties

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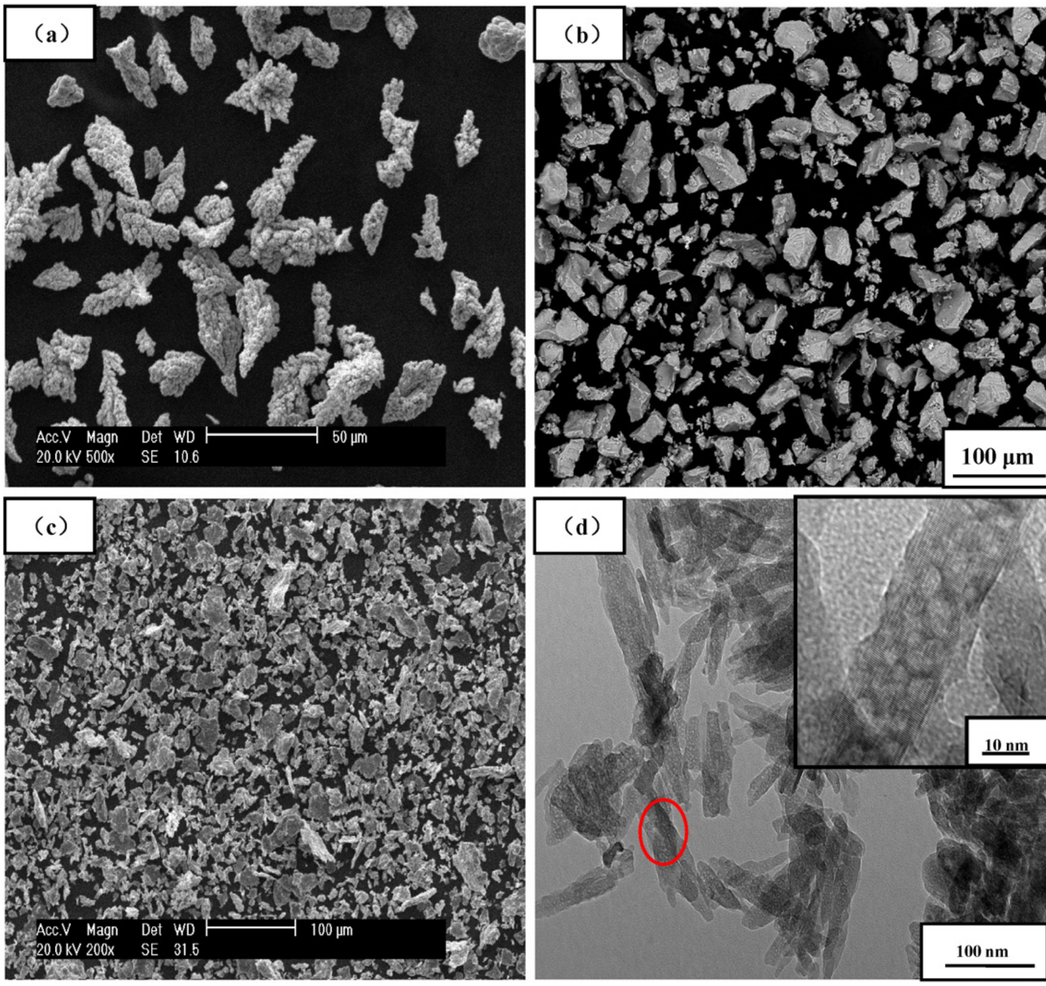

Fig. 1. The morphologies of raw powders: (a) Ni powders; (b) Ti powders; (c) Ni–Ti powders after ball-milling; and (d) HA powders (the inset is the interplanar spacing of HA and magnified image of the region enclosed by the red circle. It shows the HA has good crystalline state).

that it cannot be solely used in larger loading areas. To meet the demand of stable osteointegration, many researchers focus on the development of novel biomaterials. Achieving a good combination of the bioactivity of HA and favorable mechanical properties of metals is considered to be a promising approach to fabricating desirable biomedical composites for load-bearing applications [28–36]. Several surface treatments, including machining, porous coating, electrophoretic deposition and plasma spraying, utilizing HA as a bioactive coating on the metal implant have attracted extensive attention [30,37,38]. But the main disadvantages of the current coating techniques are their susceptibility to degrading, wearing, nonuniform coating (particularly for those implants with interconnected porous structure) and peeling off from the metal substrate [39]. Thus, it would be desirable if the two phases could be interconnected allowing the integration of the native tissue and the implant while reducing the risk of the detachment of the metal substrate from the rest of the construct.

SPS method can easily sinter ceramic, metal and alloy powders applying high energy pulsed current [40,41]. Thus the local surfaces of the particles melt and then vaporize, allowing high quality of junctions to be formed between particles in contact. Therefore, this advantage might further enhance the bioactivity of porous NiTi–HA composite with interconnected pore characteristics. However, the effect of HA powder content, SPS parameters and pore structure on the characteristics of porous NiTi–HA composite are not well documented.

In the present work, porous NiTi–HA composites with interconnected pore characteristics were prepared by SPS and space holder technique. Meanwhile, porous NiTi alloy without bioactive HA ceramics sintered at optimal SPS parameters was used to carry out the comparative study on in vitro bioactivity of porous NiTi–HA composites with different contents of HA. It is expected that SPS technique and bioactive HA ceramic can improve the bioactivity of porous NiTi alloy.

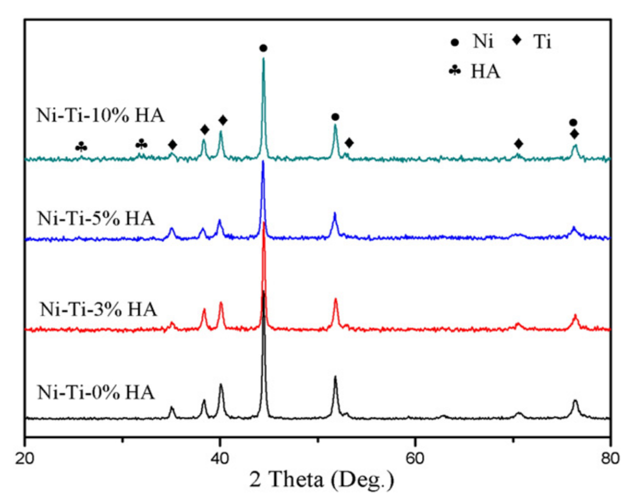

Fig. 2. XRD patterns of raw powder materials.