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Rapid fabrication of function-structure-integrated NiTi alloys: Towards a combination of excellent superelasticity and favorable bioactivity

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ABSTRACT

Porous NiTi has brought new expectations to the field of orthopaedic implants due to its excellent mechanical properties such as high strength and superelasticity together with good biocompatibility. In order to facilitate the surrounding bone tissue ingrowth into the implanted porous alloy, reasonably large sized pores and a high amount of porosity are required. There is, however, a major challenge for clinical applications: the higher the porosity, the worse are the mechanical properties and the superelasticity. In this work, therefore, function-structure-integrated NiTi alloys consisting of a central solid and an outer porous layer were fabricated by spark plasma sintering (SPS). When sintered at 750 °C, the NiTi alloy with 14% porosity in the inner part and 49% porosity as well as 350 μm average pore size in the outer layer exhibits an exceptionally high compressive strength (~1375 MPa), together with an excellent superelastic recovery strain (>4%) and favorable cellular affinity (ROS1728 osteoblasts). Altogether, this work provides a strategy to design materials with function-structure integration and suggests that properly designed function-structure integrated NiTi alloys may be promising as advanced bone implants.

1. Introduction

Porous near-equiatomic NiTi alloys have brought new expectations to the field of orthopaedic implants and cardiovascular applications due to their unique properties, such as shape memory effect, superelasticity, and excellent biocompatibility [1–3]. The pore structure of metallic implant biomaterials is crucial for tissue ingrowth and thus for improving the fixation and remodeling between the implant and the human tissue. Moreover, biomaterials with porous structure also lower the elastic modulus and stiffness considerably, which is beneficial for reducing the extent of stress shielding [4–6]. In addition, the superelasticity of the alloys enables the implant to undergo extra-large recoverable deformation, thus decreasing the possible concentration of stress and the risk of periprosthetic fracture after surgery [7–11]. However, porous NiTi shape memory alloys are yet unable to satisfy the requirements for load-bearing biomedical applications. In order to facilitate tissue cell ingrowth into the implanted porous alloy, reasonably large sized pores (e.g. 100–500 μm) and high porosity (30%–50%) are required [12,13]. But there is a problem: the higher the porosity, the worse are the mechanical properties and the superelasticity. Besides, the properties of porous NiTi also strongly depend on the pore characteristics, such as interconnected pore structure, pore

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distribution and pore orientation [8,11,12,14,15].

To enhance the applicability of porous NiTi, therefore, it is imperative to design new implants and prostheses with function-structure integration. One approach for developing such advanced implants is related to materials with gradient porous structure [16–18]. This would allow reducing stress-shielding and improving bioactivity, without any important detrimental effect on mechanical strength and superelasticity. Thus, an ideal radial gradient porosity sample includes two layers at least: (a) an outside layer with much higher porosity and larger pore size; (b) an inner part with much higher density. This can not only provide a favorable environment for bone tissue ingrowth, but also avoids the deterioration of mechanical properties and superelasticity, which promises to thus obtain a metallic implant biomaterial with good biocompatibility, low elastic modulus, enhanced compressive strength and high superelasticity for load-bearing applications. In fact, human bones with distinct pore structures and densities at different positions correspond to different mechanical properties [15].

Recently, several techniques have been proposed to produce porous NiTi implant materials, such as powder metallurgy (PM), metal injection molding (MIM), isostatic pressing (IP), microwave sintering (MS) and additive manufacturing (AM) [4,9,19–23]. The spark plasma sintering (SPS) technique, which is a pressure assisted pulsed current sintering process based on spark discharge momentarily generated in the gaps between particles and has the capability of fast densification and minimal grain growth, has emerged as the most efficient and convenient sintering method for ceramics, metals, alloys, composites and porous scaffolds [24–27]. The particles are activated on their surface by spark discharge, and neck formation can occur easily at low temperature in a 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 efficient neck formation and a high quality of the sintered material [26,28–30]. Latest work [31] on fabricating porous NiTi shape memory alloys with high porosity (18%–61%) and large pore size (21–415 μm) by using a one-step SPS method, has shown that this method is suitable for obtaining nearly single-phase NiTi with few undesired phases such as Ti_2Ni or Ni_3Ti as byproducts.

In this work, we report a method for the rapid fabrication of biomedical NiTi alloys with radial gradient dense - porous structure by the SPS method using a modified mold and space holder technique without binder. The effects of pore characteristics (porosity and pore size) and microstructure on mechanical properties, superelastic behavior, fracture mechanism and bioactivity of the Radial Gradient Porous NiTi alloys (RGP NiTi alloys) were investigated.

2. Materials and methods

2.1. Spark plasma sintering

Titanium powders (purity > 99.5%, average particle size ~ 45 μm) and nickel powders (purity > 99.7%, average particle size ~ 70 μm) with a nominal atomic ratio of 50.8 to 49.2 were weighed using an FA-2004N electronic balance with a precision of 0.1 mg and were put into stainless steel containers together with some stainless steel balls. The powder-to-ball mass ratio was 3:1. Before mixing, the containers with the powder mixture were purged with argon gas (purity > 99.999%) for 1 h in order to minimize oxidation of the powders during mixing. The materials were mixed in a planetary ball mill (XQM-4) at a speed of 300 rpm for 10 h. Afterwards, 20 wt % of 100–500 μm sieved pure ammonium hydrogen carbonate (NH_4HCO_3) particles were thoroughly mixed into the Ni-Ti powders as space holder. No binder or lubricant was added during mixing to ensure biosecurity. The milled Ni-Ti powders (powder B) and Ni-Ti-20 wt% NH_4HCO_3 mixtures (powder A) were then sequentially pressed into green compacts with a geometry of 15 mm × 24 mm in a specially designed steel mold using a hydraulic press at a cold compaction pressure of 300 MPa. A schematic diagram illustrating the individual processing steps and the mold details to form a radial gradient porous NiTi sample is shown in Fig. 1.

In order to investigate the effect of the applied sintering temperature, the green compacts were sintered using a SPS system (SPS-515S, Syntex Inc, Japan) at a constant heating rate of 50 °C min^{-1} up to different temperatures (holding time: 5min.), e.g., 600 °C, 650 °C, 700 °C, 750 °C, 800 °C, 900 °C and 1000 °C. During the whole preparation process, the vacuum in the SPS chamber was maintained at ~6 Pa.

2.2. Microstructure and mechanical properties

The pore morphology and microstructure of the specimens were evaluated by scanning electron microscopy (SEM) (FEI QUANTA200, Holland) and optical microscopy (BH2-UMA, Olympus, Japan). The average pore sizes and the porosity were analyzed by the Image Pro-Plus 6.0 software. The phase constituents of sintered samples were determined by X-Ray diffraction (XRD) (D8 Advance, Bruker, Germany) with Cu Kα radiation at 40 kV within diffraction angles ranging from 10° to 90° at a scanning speed of $2°•min^{-1}$. In order to further investigate whether NH_4HCO_3 was completely removed from the sintered samples, X-ray fluorescence (XRF) (ZSX 100e, Rigaku Corporation, Japan) analysis was performed on the wall of the internal pores to determine the chemical composition of the internal surface of the pores. Compression tests were carried out with a compression testing machine (AG-X100 KN, SHIMADZU, Japan) at a strain rate of 3×10^{-3} s^{-1}. The compressive strength and the elastic modulus were investigated by the single experiment mode, and the superelasticity was investigated by a controlled experiment mode. At the same time, compressive cyclic loading-unloading curves of the samples under different pre-strain and different cycles were carried out. The samples for the compression tests were machined into a cylindrical shape with a length-to-diameter ratio of L/D = 2.0 (according to ASTM standard E9-09).

2.3. In vitro experiments

Osteoblasts of rats (ROS1728) were selected to comprehensively evaluate the cytotoxicity of the RGP NiTi alloys by both indirect and direct contact tests, which simulated the implantation of biomaterials into the marrow cavity in vivo. The cells were cultured in Dulbecco's modified eagle's medium (DMEM) supplemented with 10% fetal bovine serum (FBS) at 37 °C in a humidified atmosphere with 5% CO_2. The cell culture medium was then diluted to obtain 100%, 75%, 50% and 25% concentrations. Because the outer porous structure was designed to providing a favorable environment for bone tissue ingrowth, the cytotoxicity test samples (2 mm thick and 1 mm diameter) were selected from the outer layer (49% ± 5% porosity) of the RGP NiTi alloys.

In the indirect tests, extracts of samples were obtained by choosing a serum-free medium as extraction medium. 12 samples were prepared, with 3 samples in each of the four groups. The samples were polished, cleaned, dried, and then sterilized. For each sample, a total of 1 ml leaching solution with different concentrations (100%, 75%, 50% and 25%) was added for the experimental groups. The DMEM medium was used as negative control groups. Cells were incubated in 96-well plates at a density of approximately 5×10^3 cells per 100 μl culture medium in each well for 24 h.