Powder sintering of porous TiNi alloy using pore forming agent of NH_4HCO_3

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Porous TiNi shape memory alloy (SMA) was fabricated by powder sintering using powders of TiH_2, Ni and pore forming agent of NH_4HCO_3. The research results reveal that phase compositions of the sintered porous TiNi SMA are independent of addition of pore forming agent. Microstructures and mechanical properties are dependent strongly on the adding amount of pore forming agent. Average pore size and porosity increase while compressive strength and elastic modulus decrease with the amount of pore forming agent. The appropriate pore structure and mechanical properties meet the demands of cancellous bone, suggesting porous TiNi SMA is fit for orthopedic application.

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1. Introduction

It is well known that TiNi shape memory alloys (SMAs) have been used in biomedical fields because of its unique superelasticity, shape memory effect and corrosion resistance, etc. [1]. However, there is an increasing concern regarding the osteoporosis, which may resulted from the stress shielding effect, i.e. mismatch of elastic moduli between the solid metallic biomaterial and bone tissue [2].

Recently, as a potential implant candidate used for replacement and repair of human hard tissues like dental roots, knee joint and cancellous bone tissue and so on, the research of porous TiNi SMA has attracted much attention due to its exceptional advantages. The porous structure can provide appropriate mechanical property, elastic modulus, bone tissue ingrowth and human body fluid transportation [3-11].

So far, there have been some reports on microstructure, fabrication, corrosion resistance, surface modification, *in vitro* biocompatibility and so on of porous TiNi SMA [3-11]. Some processes like combustion synthesis and powder sintering have been proposed to fabricate porous TiNi SMA [8-11]. Compared to the complex metal injection molding/sintering [9] and capsule-free hot isostatic pressing [10], microwave sintering [11], solid-state replication [12] and laser fabrication method [13], conventional power sintering from elemental powders is featured by low equipment investment, convenient processing and wide porosity range of the product [14]. In this paper, pore forming agent is used to adjust and control the microstructure and mechanical property of porous TiNi SMA prepared by powder sintering.

2. Experimental

2.1 Preparation of porous TiNi SMA

Pure TiH_2 and Ni powders with average size of 14 and 7.6 μm, respectively, were mixed according to the nominal composition of Ti-50.5at.%Ni. The mixed powders were blended in a rotating container for 24h with pore forming agent of NH_4HCO_3 powders (average size of 132μm) with amount of 0, 25 and 35wt.%, respectively. The blended powders were cold pressed under 100MPa into green compacts with size of $\Phi10$ mm × 15 mm and placed into a sintering furnace under vacuum condition. It was heated to 200^oC for 2h to evaporate the pore forming agent and heated to 780^oC for 1h to dehydrogenate the TiH_2 powders. And then it was heated to $990\,^oC$ and sintered for 5h. The sintered porous TiNi SMA was air cooled and cleaned with acetone and ethanol, respectively.

2.2 characterization of porous TiNi SMA

X-ray diffraction (XRD, Rigaku D/max), scanning electron microscopy (SEM, Hitachi S3400N), image analysis and uniaxial compression test at ambient temperature were performed to characterize the phase composition, pore morphology, porosity and average pore size as well as mechanical properties in compression of the sintered porous TiNi SMA.

3. Results and discussions

Fig. 1 shows the XRD patterns of porous TiNi SMAs sintered with different addition amount of pore forming agent. It can be seen clearly that porous TiNi SMAs sintered without and with addition of NH_4HCO_3 are both composed of TiNi (B2), TiNi (B19'), Ti_2Ni and $TiNi_3$ phases, without raw powder phase. Compared to the diffraction peaks shown in Fig. 1(a), the weaker ones presented in Fig. 1(b) may be attributed to the complex pore structure resulted from pore forming agent. Hydrogen dehydrogenated from TiH_2 powder can serve as protective atmosphere during heating process of the green compact. The diffraction data indicate that addition of NH_4HCO_3 has little influence on the phase constituents of the sintered porous TiNi SMA.

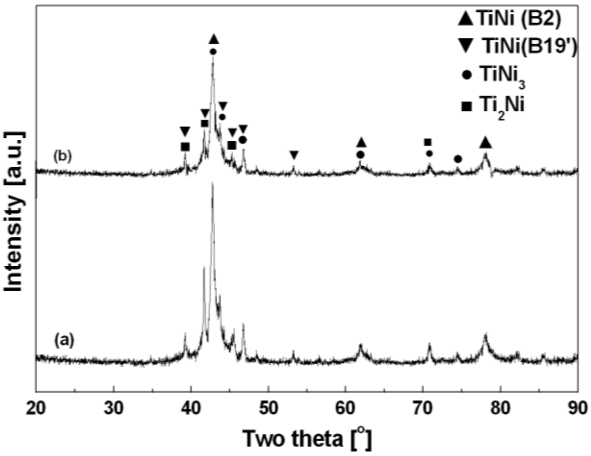

Fig. 1. XRD patterns of the porous TiNi SMA sintered with different amount of pore forming agent (a) 0; (b) 35%.

Fig. 2 presents SEM images of pore morphology of porous TiNi SMAs sintered with different amount of NH_4HCO_3. As shown in Fig. 2 (a), some small and irregular pores exist in porous TiNi SMA sintered without adding any pore forming agent. Meanwhile, pore numbers and size increase substantially with the increase of adding amount of NH_4HCO_3 from 25% to 35%, as illustrated in Figs. 2(b) and (c). The sintered porous TiNi SMAs consist of partially intercommunicating pores and connecting walls. The porous structure of TiNi SMA foam, which is similar to that of cancellous bone, would favor the ingrowth of bone tissue, transportation of body fluid and nutrient [3, 4].

For the sintered porous TiNi SMAs, average pore size increases from 7 to 175 and 296 μm, while porosity from 10 to 42 and 64%, with the increase amount of pore forming agent from 0 to 25 and 35%, respectively.

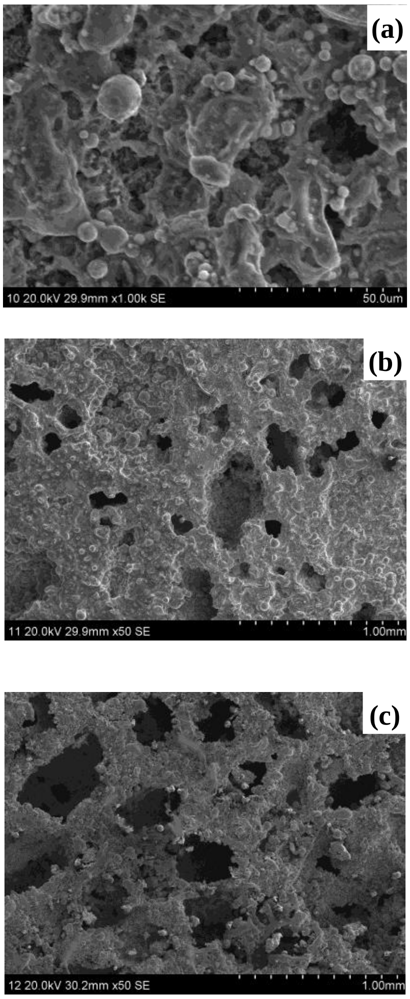

Fig. 2. SEM images of pore morphology of the porous TiNi SMAs sintered with different amount of pore forming agent (a) 0; (b) 25%, (c) 35%.

During the heating process of green compact, pore forming agent of NH_4HCO_3 powders evaporate thoroughly in form of H_2O, NH_3 and CO_2 gases. Therefore pores in porous TiNi SMA sintered without adding NH_4HCO_3 may result from the original pores and the dehydrogenated hydrogen in green compact. While pores in porous alloy sintered with NH_4HCO_3 powder originate mainly from the vacancies left by pore forming agent powders.

Open pore structure with pore size bigger than 100 μm is favorable to bone ingrowth and apposition. Therefore, porous structure and pore parameters of the sintered porous TiNi SMA meets the pore characteristic demand of porous implant.

Fig. 3 illustrates the compressive stress-strain curves of porous TiNi SMAs sintered with different amount of pore forming agent. It consists of elastic, plastic and collapse stages. The approximate ultimate compressive strength decreases from 405.1 to 76.6 and 49.3MPa while approximate elastic modulus in compression from 12.1 to 3.2 and 2.7 GPa with the increase amount of pore forming agent from 0 to 25 and 35%, respectively. The compressive strength and elastic modulus in compression of the sintered porous TiNi SMA can be regulated by the addition amount of pore forming agent. The former is close to that of cancellous bone (<100MPa) while the latter matches that of cancellous bone (<1GPa) [15]. In terms of porous structure and compressive property, the sintered porous TiNi SMA is considered potential reconstructive orthopedic candidate for hard tissue implants.

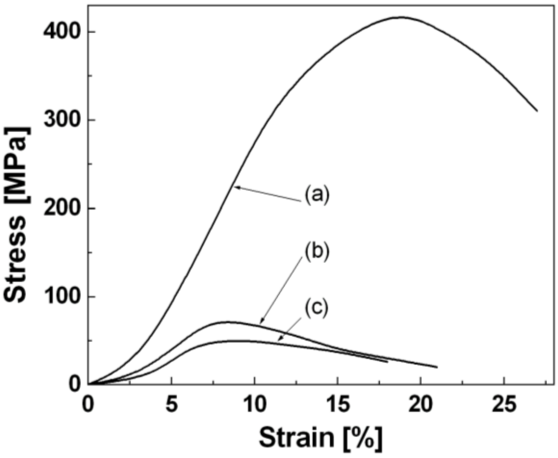

Fig. 3. Compressive stress-strain curves of porous TiNi SMA sintered with different amount of pore forming agent (a) 0; (b) 25%, (c) 35%..

4. Conclusions

Porous TiNi SMA can be prepared by powder sintering from TiH_2, Ni and NH_4HCO_3 powders. Addition of NH_4HCO_3 has little influence on phase constituents of sintered porous TiNi SMA. Pore morphology, average pore size, porosity, compressive strength and elastic modulus of sintered porous TiNi SMA regulated by pore forming agent meet the corresponding demands of porous hard tissue implants. The results indicate the sintered porous TiNi SMA is a promising implant material.

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