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Characterization of transformation behavior in porous Ni-rich NiTi shape memory alloy fabricated by combustion synthesis

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Recently, porous NiTi shape memory alloy (SMA) has been the subject of considerable interest as a promising biomaterial for use as hard tissue implants and medical instruments due to its unique properties such as shape memory effect, superelasticity, excellent corrosion resistance, and good biocompatibility [1, 2]. Moreover, its cellular structures and mechanical characteristics are similar to those of some natural biomaterials, such as bone and wood. Up to now, many porous NiTi SMAs with different pore structures were developed by combustion synthesis or self-propagating high-temperature synthesis (SHS). Chu *et al.* prepared porous NiTi SMAs with close spherical pore structures [3]. Li *et al.* fabricated porous NiTi SMAs with three-dimensionally interconnected anisotropic pore structures [4]. Chu *et al.* recently developed porous NiTi SMAs with high strength and three-dimensionally interconnected isotropic pore structures by an improved SHS method [5].

The shape memory effect of SMA involves the reversible martensitic transformation from a high temperature parent phase to a low temperature martensitic phase, which has been discussed in many papers [6–10]. In general, two martensitic phases, R-phase and B19′, are prone to form from the equilibrium high temperature B2 phase on cooling. The transformation behavior in dense NiTi SMAs, especially in dense Ni-rich NiTi SMAs, has been studied and reported extensively [6–10]. Li *et al.* have reported the transformation behavior in the SHS-synthesized porous NiTi SMA with a chemical composition of Ti-50 at.% Ni [11]. However, the important effects of post-SHS aging and solution heat treatment on the transformation behavior in porous NiTi SMAs have not been reported in the literature. It should be pointed out that few systematic studies have been reported to date on the transformation behavior in porous NiTi SMAs, especially in porous Ni-rich NiTi SMAs fabricated by combustion synthesis.

In this paper, the characterization of transformation behavior in porous Ni-rich NiTi SMA fabricated by combustion synthesis is investigated and discussed in comparison with that of dense Ni-rich NiTi SMA with the same chemical composition prepared by a conventional arc-melting method (CAM).

The raw materials used in the fabrication of porous NiTi SMA by SHS were titanium and nickel powders. The chemical composition of titanium powders with an average size of 45.2 μm was (wt.%): Ti 99.3, Fe 0.039, O 0.035, N 0.035, C 0.025, CL 0.034, H 0.024 and Si 0.0018. The chemical composition of nickel powders with an average size of 33.8 μm was (wt.%): Ni 99.5, Fe 0.03, Zn 0.002, Ca 0.03, C 0.05, Mg 0.015, Mn 0.03 and Si 0.01. The mixed powders of Ni and Ti with 51 at.% Ni were blended by ball milling for 12 hrs. firstly, and then pressed into cylindrical compacts of 50 mm in diameter and 25 mm in height. The pressure used was sufficient to give a green density of 45 ± 2% theoretical. The preheating temperature varied from 300 to 500 °C. The preheated pellet was ignited at one end by an ignition reagent (4 g in weight) composed of Ti and C powders with 50 at.% Ti in the SHS equipment under an atmosphere pressure (about 0.1 MPa) of 99.98% pure argon flowing. Once ignited, the combustion wave could self-propagate along the axis to the other end of the compact in a very short time, and then porous NiTi SMA was synthesized. The conventional tungsten arc-melting technique was employed to prepare dense NiTi SMA with the same chemical composition of Ti-51 at.% Ni. Titanium (99.7 wt.%) and nickel (99.98 wt.%), totaling nearly 200 g, were melted and remelted at least six times in an argon atmosphere.

Both SHS-synthesized porous NiTi SMA and CAM-synthesized dense NiTi SMA were solution treated at 1050 °C for 2 hr, then quenched in water and finally aged at 500 °C for 1 hr. The phase constituents of the specimen were determined by X-ray diffraction (XRD) analysis. The general porosity of porous NiTi SMA was determined by weight and dimensional measurements. The porous NiTi SMA in this work has an average porosity of 55 vol.%. Optical micrographs show that porous NiTi SMA has an isotropic pore structure in terms of pore morphology and distribution, and the size of the pores is about 200–600 μm.

From the aged materials, specimens were cut from one region for DSC measurements. The transformation

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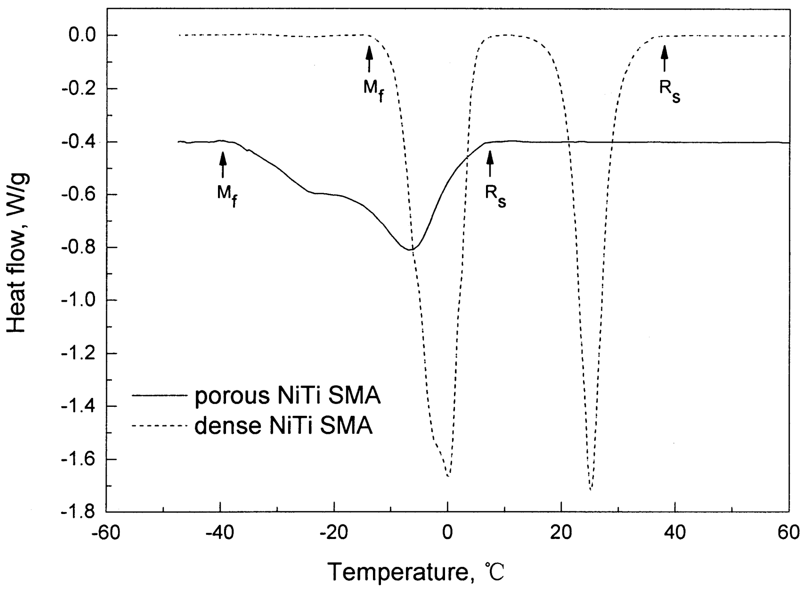

Figure 1 DSC charts on cooling of SHS-synthesized porous NiTi SMA and CAM-synthesized dense NiTi SMA after solution treatment at 1050 °C for 2 hr and aging treatment at 500 °C for 1 hr.

behavior during heating and cooling was investigated using a differential scanning calorimeter (DSC) of type 2910 from TA Instruments. The heating and cooling rates were kept at 5 °C/min. DSC specimens with weights between 20 and 50 mg were heated up to 60 °C where they were held for three minutes to establish thermal equilibrium. Then the DSC measurement started by cooling down to −60 °C. At −60 °C the specimen was again held for three minutes and then heated up to 60 °C.

DSC charts which were obtained during cooling and heating are shown in Figs 1 and 2. It was found that there were two overlapping peaks for porous NiTi SMA and two distinct peaks for dense NiTi SMA on the cooling curves as shown in Fig. 1, which is referred to as a two-step transformation, namely first from B2 to R-phase and then from R to B19′ martensite [9]. On the heating curves, there is one single peak corresponding to the transformation of B19′ to B2 for porous NiTi SMA and two peaks corresponding to the two-step transformation B19′→R→B2.

The following three characteristic features of the transformation behavior in porous Ni-rich NiTi SMA fabricated by SHS in comparison with the dense Ni-rich NiTi SMA with the same chemical composition prepared by CAM after the same heat treatment were identified from Figs 1 and 2: (1) The phase transformation temperatures (austenite start temperature A_s, austenite finish temperature A_f, R-phase start temperature R_s, and martensite finish temperature M_f) of porous NiTi SMA are lower than the corresponding ones of dense NiTi SMA. (2) The intensity of each thermal peak associated with phase transformation in porous NiTi SMA is weaker than that of the corresponding one in dense

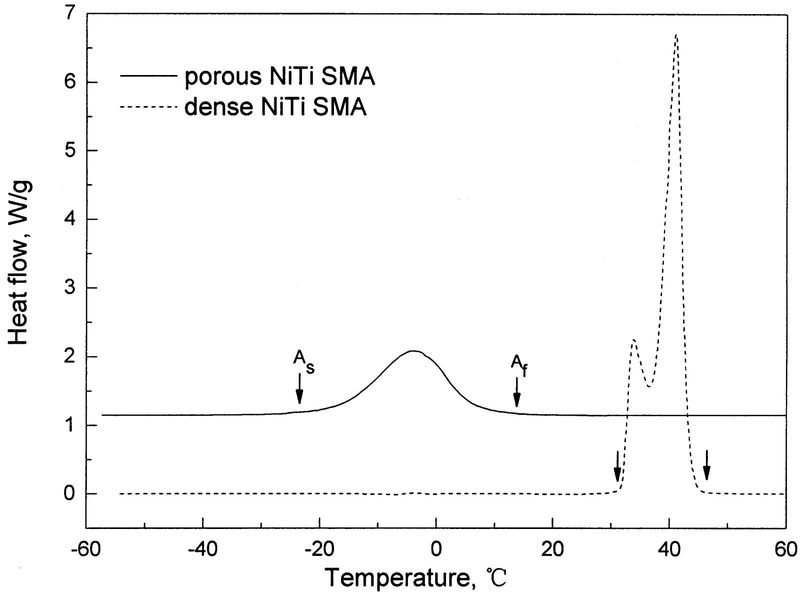

Figure 2 DSC charts on heating of SHS-synthesized porous NiTi SMA and CAM-synthesized dense NiTi SMA after solution treatment at 1050 °C for 2 hr and aging treatment at 500 °C for 1 hr.

NiTi SMA, which may suggest that the phase transformations in porous NiTi SMA are incomplete. (3) The width of the thermal peak associated with phase transformation in porous NiTi SMA is larger than that of the corresponding one in dense NiTi SMA, e.g., A_s and A_f of porous NiTi SMA are at about $-23.5\,^\circ$C and $15\,^\circ$C, and the temperature gap between them is about $38.5\,^\circ$C. However, A_s and A_f of dense NiTi SMA are much higher (at about 31 and $46\,^\circ$C), and the gap is about $15\,^\circ$C. In addition, the thermal peaks of dense NiTi SMA are sharper, which suggests that phase transformations are finished almost instantly, while in porous NiTi SMA, the phase transformation rate is slower due to the relatively small slopes of the thermal peaks on the DSC curves.

It should be noted that more DSC tests on the samples subjected to different heat treatments, have also been performed. The above-mentioned three features of the transformation behavior in porous Ni-rich NiTi SMA fabricated by SHS in comparison with dense Ni-rich NiTi SMA with the same chemical composition prepared by CAM after the same heat treatment are always present in the results of all tests.

The porosity has little effect on transformation behavior of porous Ni-rich NiTi SMA, which can be easily interpreted from a consideration of thermodynamics and has also been suggested by the experimental results of Li *et al.* [11]. Here we show that the above-mentioned characterization of transformation behavior can simply be explained by considering the microstructural features in porous Ni-rich NiTi SMA fabricated by combustion synthesis. Fig. 3 shows the XRD patterns of SHS-synthesized porous NiTi SMA and CAM-synthesized dense NiTi SMA. It can be seen that the metastable Ni_4Ti_3 phase is the only second phase appearing in dense NiTi SMA besides B2(NiTi) matrix phase. However, in porous NiTi SMA, the stable Ti_2Ni second phase is also present besides metastable Ni_4Ti_3, B2(NiTi) and B19′(NiTi) matrix phases. The presence of the second phase Ti_2Ni is the common feature for porous NiTi SMA prepared by SHS due to the composition fluctuation in the specimen because the raw powders are mixed insufficiently and the particle size of the reactants is not small enough [4, 5, 12]. Moreover, the experimental results after Chu *et al.* [5] indicate that the undesired Ti_2Ni phase in porous NiTi SMA formed during the SHS process could not be removed by solution treatment.

The appearance of the stable Ti-rich Ti_2Ni phase increases the nickel content in NiTi matrix of porous NiTi SMA in comparison with dense NiTi SMA, which is accompanied by a decrease of transformation temperatures because the Ni-content of the NiTi matrix strongly affects phase transformation temperatures and 0.1 at.% increase in Ni-content can lower the phase transformation temperatures by about $20\,^\circ$C [8, 13]. The B19′ martensitic transformation is also associated with high transformation strains (on the order of 10%) [9]. Therefore, the dispersed Ti-rich Ti_2Ni particles in the NiTi matrix can act as an obstacle to make the martensitic transformation more difficult. As indicated by the widened transformation span, the relatively small slope and the relatively weak intensity of the thermal peaks on the DSC curves in Figs 1 and 2, the phase transformations in porous NiTi SMA fabricated by SHS proceed much more gradually and are incomplete.

In conclusion, the transformation temperatures of porous NiTi SMA fabricated by combustion synthesis are lower than the corresponding ones of dense NiTi SMA with the same chemical composition prepared by CAM after the same heat treatment. Moreover, the phase transformations in porous NiTi SMA proceed at a relatively slow rate and are incomplete. A consistent explanation for all characteristic features of the transformation behavior observed in our DSC experiments was provided. Further systematic work required is to investigate the effects of post-SHS aging and solution heat treatment on the transformation behavior in porous NiTi SMAs fabricated by combustion synthesis.

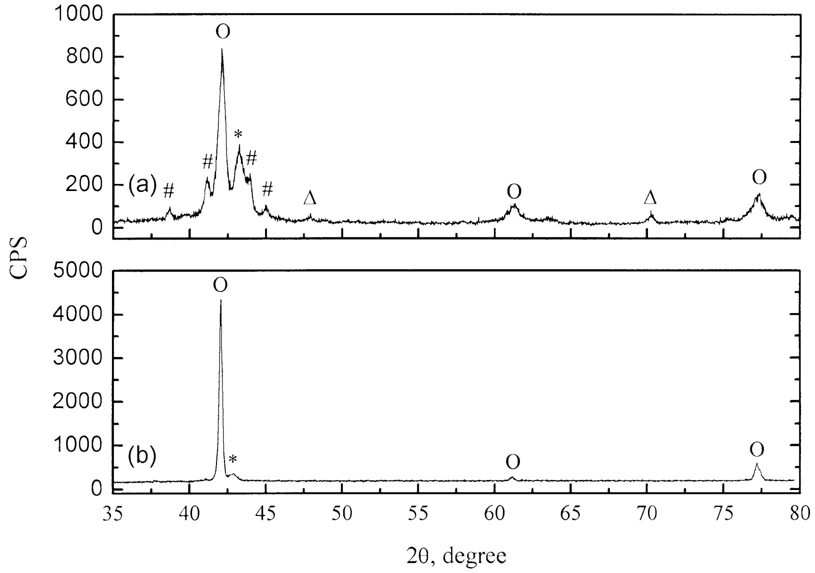

Figure 3 XRD patterns of SHS-synthesized porous NiTi SMA (a) and CAM-synthesized dense NiTi SMA (b). (O) B2(NiTi), (#)B19′(NiTi), (*) Ni_4Ti_3, (Δ) Ti_2Ni.

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