

Effects of aging temperature on the martensitic transformation in porous Ni-rich NiTi shape memory alloy fabricated by combustion synthesis

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Shape memory effect (SME) involves the reversible martensitic transformation between a high temperature parent phase and a low temperature martensitic phase. The martensitic transformation behavior in dense NiTi shape memory alloys (SMAs), especially in dense Ni-rich NiTi SMAs, has been studied and reported extensively [1–5]. However, few systematic literatures have been reported to date to study the martensitic transformation behavior in porous NiTi SMAs, especially in porous Ni-rich NiTi SMAs fabricated by combustion synthesis or self-propagating high-temperature synthesis (SHS).

As the promising biomaterials for use as hard tissue implants, many porous NiTi SMAs with different pore structures have been developed by combustion synthesis [6–8]. The transformation behavior in the SHS-synthesized porous Ni-50at%Ti SMA has been reported by Li *et al.* [9]. Nevertheless, the effects of post-SHS aging and solution heat treatment on the transformation behavior in the porous NiTi SMAs have not been investigated in the literature [9]. It should be pointed out that porous NiTi SMAs fabricated by SHS have the common microstructural feature of composition inhomogeneity due to the presence of second phases [7, 8], which can be affected by post-SHS heat treatment. Thus the post-SHS heat treatment can play a very important role on phase transformation behaviors of porous NiTi SMAs.

In the present work, the porous Ni-rich NiTi SMA is fabricated by SHS, then quenched into water at room temperature after solution treated at 1050 °C for 10 h. The effects of aging temperature on the martensitic transformation in the porous Ni-rich NiTi shape memory alloy are investigated using differential scanning calorimeter (DSC) and discussed.

The raw materials were Ti (99.3 wt%) and Ni (99.5 wt%) powders with an average size of 45.2 and 33.8 μm respectively. The mixed powders of Ni and Ti

with 50.8 at% Ni were blended by ball milling for 12 h, and then pressed into cylindrical compacts of 50 mm in diameter and 25 mm in height. The preheating temperature is 350–450 °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 under an atmosphere pressure (about 0.1 MPa) of 99.98% pure argon flowing. Once ignited, 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 pore characteristics of the product were analyzed with optical microscope. The general porosity was determined by weight and dimensional measurements. The porous NiTi SMA in this work has an average porosity about 55 vol%. Optical micrograph shows that porous NiTi SMA has the isotropic pore structure in pore morphology and distribution, and the size of the pores is about 200–600 μm . Most pores are three dimensionally interconnected.

The porous NiTi SMA was solution treated in the flowing argon environment at 1050 °C for 10 h and then quenched into water at room temperature. The subsequent aging treatment was performed at different temperatures for 1 or 2 h. From the aged materials, specimens were cut out in one region for DSC measurements. The martensitic transformation behavior during cooling was investigated using a differential scanning calorimeter (DSC) of type 2910 from TA Instruments. The cooling rate was kept at 5 °/min. DSC specimens with masses between 20–50 mg were heated up to 60 °C where they were held for three minutes to established thermal equilibrium. Then the DSC measurement started by cooling down to –60 °C. The phase constituent was determined by X-ray diffraction (XRD) analysis.

Fig. 1 shows XRD patterns of porous Ni-rich NiTi SMAs after different heat treatments. There are two

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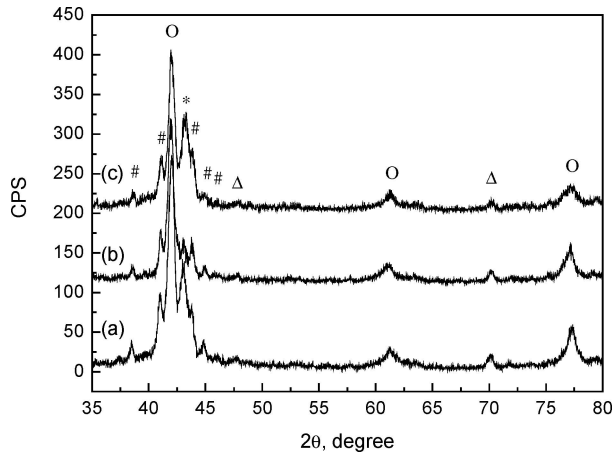


Figure 1 XRD patterns of porous Ni-rich NiTi SMAs: (a) Non-treated; (b) Solution treated at 1050 °C for 10 h; (c) Aged at 450 °C for 1 h after solution treatment at 1050 °C for 10 h. (O) B2(NiTi), (#) B19'(NiTi), (*) Ni₄Ti₃, (Δ) Ti₂Ni

second phases including Ni₄Ti₃ and Ti₂Ni in the SHS-synthesized porous NiTi SMA with B2(NiTi) and B19'(NiTi) as the predominant phases as indicated by Fig. 1a. Fig. 1b shows XRD pattern of porous NiTi SMA after solution treated at 1050 °C for 10 h. Obviously the amount of metastable Ni₄Ti₃ phase in porous NiTi SMA decreased after solution treatment, while solution treatment had little effects on stable Ti₂Ni phase.

The DSC charts on cooling of the samples aged at different temperatures for one or two hours are shown in Figs 2 and 3, respectively. In general, the martensitic transformation in dense Ni-rich NiTi SMAs on cooling shows a complex dependence on thermo-mechanical treatments and can usually occur in one-step transformation (after solution treated) from B2 to B19' directly, or two-step transformation (after subsequent aged) from B2 to R-phase (first DSC peak) and then R-phase to B19' (second DSC peak), or multiple-step behavior (under certain aging conditions) [3, 4, 10]. As shown by Figs 2 and 3, the similar martensitic transformation behaviors occur in porous Ni-rich NiTi SMA fabricated by SHS after solution and aging treatment. However, the multiple-step behavior (three- or more-step) could not be found in the samples under the given aging conditions.

From Fig. 2 corresponding to the samples aged at different temperatures for 1 h, four features in the martensitic transformation behaviors of porous Ni-rich NiTi SMA during cooling that change with the aging temperature can be found:

1. The type of martensitic transformation changes from one-step (after solution treated) to two-step (after aged at different temperatures).
2. The width of the overall transformation temperature range changes from small (after solution treated) through large (after aged at 400, 450 and 475 °C) back to small (after aged at 500 °C).
3. There are shifts in peak positions, and of the temperatures where the transformations begin for the aged porous Ni-rich NiTi SMA. Both R-phase start temperature (R_s) and the peak temperature corresponding to

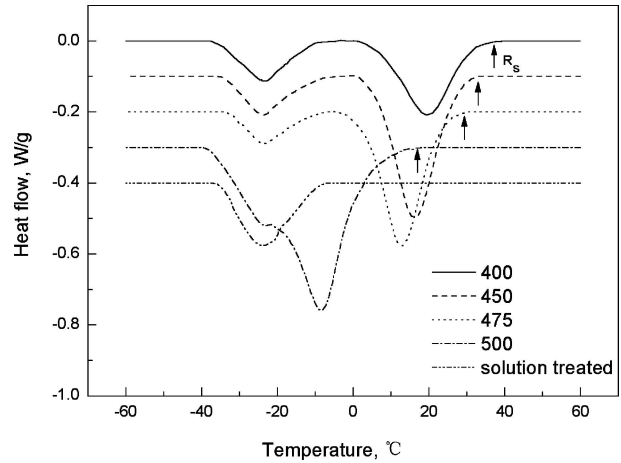


Figure 2 DSC charts on cooling of porous Ni-rich NiTi SMA fabricated by SHS after solution treated at 1050 °C for 10 h and subsequently aged at different temperatures for 1 h. For the aged samples, the vertical arrows indicate the R-phase start temperature (R_s).

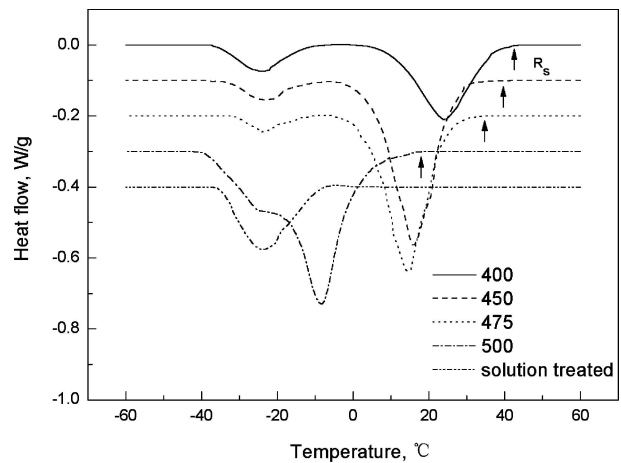


Figure 3 DSC charts on cooling of porous Ni-rich NiTi SMA fabricated by SHS after solution treated at 1050 °C for 10 h and subsequently aged at different temperatures for 2 h. For the aged samples, the vertical arrows indicate the R-phase start temperature (R_s).

the transformation of B2→R decrease with the rise of the aging temperature.

4. The positions of the last peaks on DSC charts of the aged samples correspond to the position of the single DSC peak obtained for the solution treated materials.

It should be pointed out that the above-mentioned features in the martensitic transformation behaviors are also present in Fig. 3 corresponding to porous Ni-rich NiTi SMA aged at different temperatures for two hours.

It is generally accepted that the coherency stress field due to the presence of Ni₄Ti₃ precipitates in B2 matrix can act as a strong resistance to large lattice variant deformations associated with the formation of B19' (about 10%) and has smaller effect on the formation of R-phase with a small transformation strain about 1/10 of B19' martensitic transformation. Thus the initial martensitic formation from B2 to R-phase can reduce the overall energy of the system [11]. The precipitate of Ni₄Ti₃ particles from B2 matrix in porous Ni-rich SMA during the aging process is shown in Fig. 1c. The amount of Ni₄Ti₃ particles in porous NiTi SMA

increased after aging treatment. The overall Ni_4Ti_3 particles in aged porous NiTi SMA are composed of the ones that formed during the SHS processing and the ones that precipitated from B2 matrix during the aging treatment. Only the later can favor the formation of R-phase, which can also be indicated by one-step transformation behavior of solution treated porous Ni-rich NiTi SMAs.

The phenomenon in porous Ni-rich NiTi SMA after aged at different temperatures for 1 or 2 h that the positions of the last peaks on DSC charts of the aged samples during cooling correspond to the one of the single DSC peak obtained for the solution treated materials was also found in the dense Ni-rich NiTi SMA after aged at 500 °C for short (1 h) or intermediate (10 h) time by Khalil-Allafi *et al.* [10]. Their studies showed the short term (1 h) or intermediate term (10 h) aging at 500 °C could result in heterogeneous microstructures where coherent Ni_4Ti_3 precipitates are mainly found within 2 μm wide regions around grain boundaries while grain interiors exhibit precipitate-free zones, and the above-mentioned phenomenon was associated with the heterogeneous microstructures in the aged samples [10]. For porous Ni-rich NiTi SMA fabricated by SHS, there are more preferential nucleation sites besides grain boundaries for coherent Ni_4Ti_3 particles in solid-state precipitation processes. Both grain boundaries and Ti_2Ni particles existing in porous NiTi SMA can act as the precipitate locations for heterogeneous nucleation of Ni_4Ti_3 particles. As a result, the microstructure in porous Ni-rich NiTi SMA after aged at the temperatures between 400 and 500 °C for short time (1–2 h) generally consists of Ni_4Ti_3 precipitate-rich regions near grain boundaries or Ti_2Ni particles and Ni_4Ti_3 precipitate-free regions in grain interiors. Thus it is reasonable that the above-mentioned phenomenon also presents in aged porous Ni-rich NiTi SMA with such heterogeneous microstructures.

The Ni_4Ti_3 is the only precipitate present during aging as indicated by Fig. 1, thus the effect of aging temperature on the martensitic transformation temperature of porous Ni-rich NiTi SMA can be explained by considering the metastable equilibrium between NiTi matrix and Ni-rich Ni_4Ti_3 precipitates at different aging temperatures as discussed by Zhang *et al.* [2]. Ni-content of NiTi matrix strongly affect phase transformation temperatures, e.g. 0.1% increase in Ni-content can lower the transformation temperatures by about 18.5 °C [12]. When the aging temperature in-

creases, the solubility limit of Ni in matrix will increase and the Ni_4Ti_3 precipitates have to partially dissolve into NiTi matrix. As a consequence, the Ni-content in NiTi matrix increases and the transformation temperatures (R_s) decrease as shown in Figs 2 and 3. The positions of the first peaks on the DSC charts of the aged porous Ni-rich NiTi SMA shift to lower temperatures with increasing aging temperatures, which can result in the overlap of the two thermal peaks corresponding to two-step martensitic transformation and the decrease of the overall transformation temperature range. Further work is required to describe the microscopic details of martensitic transformation behaviors in porous Ni-rich NiTi SMA fabricated by combustion synthesis.

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