Influences of solution treatment on compressive properties of porous NiTi shape memory alloy with the porosity of 53.4 vol% fabricated by combustion synthesis

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Combustion synthesis or self-propagating high-temperature synthesis (SHS) has been proven to be an ideal alternative, with the advantages of time and energy saving, to fabricate porous NiTi shape memory alloy (SMA) by igniting a compressed powder mixture of Ti + Ni and producing a self-sustaining chemical reaction with sufficient heat released [1–3]. Moreover, C. L. Chu and co-workers recently prepared porous NiTi shape memory alloys with high strength and three-dimensionally interconnected pores successfully, by an improved SHS method [4, 5]. The porous NiTi SMAs with high compressive strength and low Young's modulus are very promising biomaterials for heavy load-bearing hard tissue implants.

Unfortunately, the presence of second phases is the common feature for the products 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 [6]. In the case of the porous NiTi SMAs with B2(NiTi) and B19′(NiTi) as the predominant phases, the SHS process often results in the formation of second phases, such as Ti_2Ni, $TiNi_3$, or Ni_4Ti_3 [2–5]. The amount of second phases could be changed by post-SHS solution treatment, which may have very important influences on compressive properties of porous NiTi SMAs fabricated by SHS. However, few literatures have been reported to date to study the influences of solution treatment on compressive properties of porous NiTi SMAs fabricated by SHS. It is the motivation of this paper to study the influences of solution treatment at 1050 °C on compressive properties of porous NiTi SMA with the general porosity of 53.4 vol% fabricated by SHS method.

The raw materials for 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 0.35, 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 hr firstly, 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. A small hole was drilled in the side of the compact to accommodate the W-5%Re/W-26%Re thermocouple. The temperature–time profile was recorded during the furnace heating of the sample using a strip chart recorder. The preheating temperature was 350–450 °C. The preheated pellet was ignited at one end by a special ignition reagent (4 g in weight) composed of Ti and C powders in the SHS equipment under an atmospheric 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, then porous NiTi SMA was synthesized.

The pore characteristics of the product were analyzed with an optical microscope. The general porosity of the product was calculated by the following formula,

$$\varepsilon = \left(1 - \frac{\rho}{\rho_0}\right) \times 100 \qquad (1)$$

in which ρ and ρ_0 are the density of the specimen and its corresponding theoretical density respectively. The density of the specimen was determined by measuring its weight and dimension. The theoretical density of Ti–51 at.% Ni alloy is 6.5 g/cm^3. The general porosity is composed of open porosity and closed porosity. The open porosity of the specimen was determined by

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the liquid weighing method, and the open porosity ratio is defined as the ratio of the open porosity to the general porosity.

The porous NiTi SMAs were solution treated at 1050 °C for 2, 4, and 10 hr respectively. A flowing argon environment was used in the furnace to protect the sample from oxidizing. The phase constituent of the specimen was determined by X-ray diffraction (XRD) analysis. The compressive samples were cut to a size of about 6 mm in width, 5 mm in thickness and 15 mm in height. Uniaxial compression test was carried out at a constant rate of 0.1 mm/min on Instron testing machine (4400 type) to investigate the compressive properties of porous NiTi SMA. The compressive strength was defined as the maximum value in the stress–strain curve, and the compressive strain is the value corresponding to the compressive strength in the stress–strain curve.

The porous NiTi SMA fabricated by SHS with a combustion temperature up to 1310 °C has an average porosity of 53.4 vol% with the deviation of ±1%. Its open porosity ratio is about 76%, which indicates that most pores in the specimen are three-dimensionally interconnected. Optical micrograph of the porous NiTi SMA was shown in Fig. 1. It could be found that porous NiTi SMA has the pore structure with the isotropic microstructure in pore morphology and pore distribution, and the size of most pores is about 200–600 μm. Such a porous NiTi SMA is a very promising biomaterial for use as hard tissue implants [7].

The relationship between ultimate compressive strength and solution time for porous NiTi SMA with the porosity of 53.4 vol% treated at 1050 °C is shown in Fig. 2. It could be found clearly that the compressive strength of porous NiTi SMA decreased remarkably at first, then increased with the rise of the time of solution treatment at 1050 °C again. The compressive strength of porous NiTi SMA non-treated is about 479 MPa, while the one of the sample treated at 1050 °C for 2 hr decreases to 460 MPa. After the solution was treated for 4 hr, the porous NiTi SMA had a lower compressive strength of about 453 MPa. However, when the porous NiTi SMA was treated at 1050 °C for longer time 10 hr, its compressive strength increased again to 474 MPa.

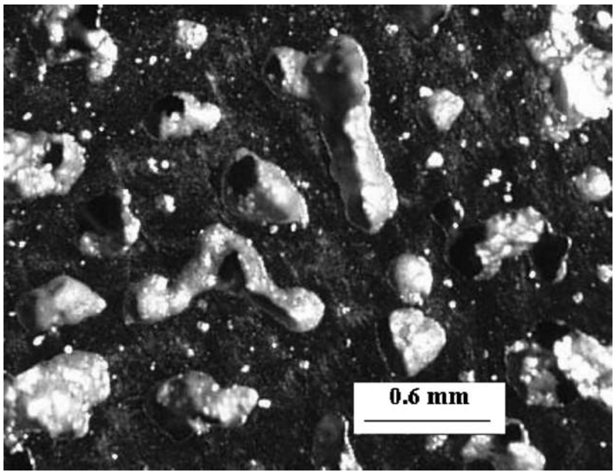

Figure 1 Pore characteristics of porous NiTi SMA with the porosity of 53.4 vol% prepared by SHS.

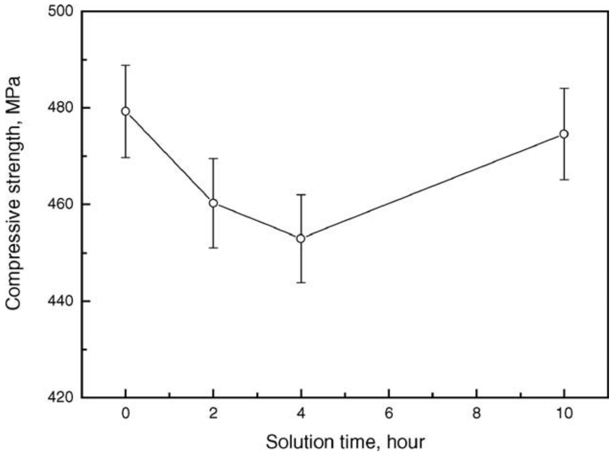

Figure 2 Relationship between ultimate compressive strength and solution time for porous NiTi SMA with the porosity of 53.4 vol% treated at 1050 °C.

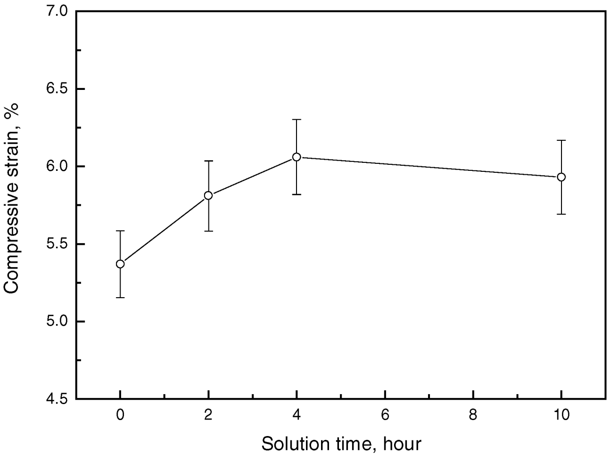

Figure 3 Relationship between compressive strain and solution time for porous NiTi SMA with the porosity of 53.4 vol% treated at 1050 °C.

The relationship between compressive strain and solution time for porous NiTi SMA with the porosity of 53.4 vol% treated at 1050 °C is shown in Fig. 3. It could be seen that the compressive strain of porous NiTi SMA increased dramatically at first, then decreased slightly with increasing solution time again. The compressive strain of porous NiTi SMA non-treated is about 5.37%, while the one of the sample treated at 1050 °C for 2 hr increases to 5.81%. After the solution was treated for 4 hr, the porous NiTi SMA had a higher compressive strain of about 6.06%. However, when the porous NiTi SMA was treated at 1050 °C for longer time 10 hr, its compressive strain decreased slightly to 5.93%.

The above-mentioned influences of solution treatment on compressive properties are relative to the effects of solution treatment on the microstructure of porous NiTi SMA. Fig. 4 shows the XRD patterns of the SHS-synthesized porous NiTi SMAs non-treated and treated at 1050 °C for 4 hr. It could be found that besides the predominant phases B2(NiTi) and B19′(NiTi), there are two second phases in porous NiTi SMA non-treated, such as Ni_4Ti_3 and Ti_2Ni. It is well known that Ni_4Ti_3 particles affect the features of the martensitic transformation in supporting the formation of the R-phase and affecting the Ni-content of the matrix [8, 9]. The porous

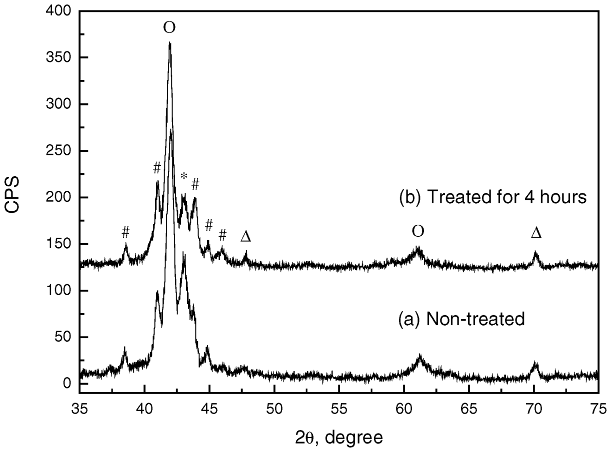

Figure 4 XRD patterns of the SHS-synthesized porous NiTi SMAs: (a) non-treated and (b) treated at 1050 °C for 4 hr. (○) B2(NiTi), (#) B19′(NiTi), (*) Ni_4Ti_3, (Δ) Ti_2Ni.

NiTi SMA in this work is Ni-rich (51 at% Ni), and the presence of Ti_2Ni phase could make the parent NiTi phase more Ni-rich. As a result, the solubility of the NiTi range is exceeded and the extra nickel then forms the Ni-rich Ni_4Ti_3 phase.

The existence of second phases can increase the brittleness of porous NiTi SMA, especially when they are in coarse dendritic form [10]. The amount and morphological character of second phases in porous NiTi SMA can be changed by post-SHS solution treatment. As shown in Fig. 4(b), it could be found that the amount of Ni_4Ti_3 phase in porous NiTi SMA decreased sharply after the solution heat treatment at 1050 °C for 4 hr, while the solution heat treatment had little effect on the amount of Ti_2Ni phase. That is to say, Ni_4Ti_3 phase is metastable and could disappear after solution treatment, while the undesired Ti_2Ni phase is very stable and difficult to remove by solid-state diffusion. However, the solution treatment can improve the morphological character of Ti_2Ni phase in NiTi SMA fabricated by SHS. The studies by Yi and Moore [10] indicated that the solution treatment could modify the Ti_2Ni dendrite arms in the dense NiTi SMA fabricated by SHS into the discrete precipitates, which is beneficial for the ductility of NiTi SMA.

As a result of the decrease in the amount and the improvement in the morphological character of second phases, the compressive strain of porous NiTi SMA prepared by SHS can be improved by solution treatment at a high temperature for a suitable time, while the compressive strength will decrease correspondingly. It should be pointed out that the ductility of porous NiTi SMA will be impaired due to the coarseness of NiTi matrix grains in porous NiTi SMA treated at a high temperature for a long time, which was indicated by the experimental results in this work. More detailed work on the influences of post-SHS heat treatment on the microstructure and properties of porous NiTi SMAs will be made in the future.

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References

1. C. L. CHU, B. LI, S. D. WANG, S. G. ZHANG, X. X. YANG and Z. D. YIN, *Tans. Nonferrous Met. Soc. China* **7**(4) (1997) 84.
2. B. Y. LI, L. J. RONG, Y. Y. LI and V. E. GJUNTER, *Acta Mater.* **48** (2000) 3895.
3. B. Y. LI, Ph.D. thesis, Institute of Metal Research, Shenyang, 2000.
4. C. L. CHU, C. Y. CHUNG, P. H. LIN and S. D. WANG, *Mater. Sci. Eng.* A **366** (2004) 114.
5. C. Y. CHUNG, C. L. CHU and S. D. WANG, *Mater. Lett.* (in press). Corrected Proof available online.
6. H. C. YI, J. J. MOORE and A. PETRIC, *Metall. Trans.* A **23** (1992) 59.
7. V. I. ITIN, V. E. GJUNTER, S. A. SHABALOVSKAYA and R. L. SACHDEVA, *Mater. Charact.* **32** (1994) 179.
8. T. SABURI, in edited by "Shape Memory Materials" K. Otsuka and C. M. Wayman (Cambridge University Press, Cambridge, 1998) p. 49.
9. J. KHALIL-ALLAFI, A. DLOUHY and G. EGGELER, *Acta Materialia* **50** (2002) 4255.
10. H. C. YI and J. J. MOORE, *J. Mater. Sci.* **27** (1992) 5067.

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