Stress–strain behavior of porous Ni–Ti shape memory intermetallics synthesized from powder sintering

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Abstract

The microstructure and stress–strain behavior of porous Ni–Ti intermetallics fabricated by powder sintering of Ni, Ti and/or TiH$_2$ are investigated. The pores are small and well distributed in the present porous Ni–Ti alloys and the phase constituent and stress–strain behavior of porous Ni–Ti alloys are significantly influenced by the sintering conditions (sintering temperature and sintering time) and TiH$_2$ additions. With increasing sintering temperature, the pseudoelasticity (PE) increases while the hysteretic width decreases. A second compression also leads to an increase of PE, elastic modulus and related deformation resistance. Further, the stress–strain behavior of porous Ni–Ti alloys is different in some way from that of bulk Ni–Ti alloys and other porous materials. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ti–Ni alloy has been extensively studied and applied in the medical field [1–2] since the initial discovery of its shape memory behavior and PE. Porous Ni–Ti shape memory intermetallic has recently become a central item of attention. It is usually used as hard tissue implants (such as artificial bone) because of its porous structure, good mechanical properties, high biocompatibility, shape memory effect (SME) and excellent PE [1,3]. The porous structure and related compressibility allow the transport of body fluids, and they are beneficial for the ingrowth of new-born bone tissue, making the fixation of implant more natural and reliable. Moreover, it is found that the mechanical deformation behavior of biological materials, which each has a high recovery of strain ($\geqslant 2\%$) after deformation, is very different from that of common metallic materials [4]. In this sense, only the PE of shape memory alloys, especially that of Ni–Ti alloys, can satisfy this medical-mechanical requirement. As far as the authors know, the deformation behavior of porous Ni–Ti alloys, which is different from that of bulk Ni–Ti alloys, has not been studied although porous Ni–Ti alloy has been synthesized by a few authors [5–7]. Thus, the lack of compressive reports on the deformation behavior of porous Ni–Ti alloys is the main motivation of this paper.

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2. Experimental procedure

Elemental Ti and Ni powders, both −74 μm in diameter, were used in the present study. TiH$_2$ (−44 μm) was originally expected to act as a pore-forming agent. Four kinds of equiatomic Ni/Ti blended powders with different TiH$_2$ additions were designed (Table 1). The ball-milled powder mixture was cold pressed at a pressure of 70 MPa. Then the powder compacts were sintered at various temperatures for 1 h or for various times at 950°C in a vacuum furnace (1.33×10^{-2} Pa). Specimens were sectioned along a diameter for microstructure examination and X-ray diffraction (XRD). Uniaxial compression tests were carried out at a constant rate of 8.8×10^{-4}/s on DCS-10t Instron testing machine to investigate the stress–strain behavior of the porous Ni–Ti alloys. After compression, the specimens were raised to 200°C for 30 min, and then subjected to a second compression.

3. Results and discussion

3.1. Microstructure

3.1.1. Pore distribution

In this study, porous Ni–Ti alloys with 30–40 vol% porosity have been successfully developed. The pore morphology and pore distribution of the final product

are shown in Fig. 1. Here, it can be seen that the pores are small and well distributed. Moreover, the pores become smaller, the pore number increases and the pore distribution becomes more homogeneous with increasing TiH_2 additions. This is mainly due to the small size of TiH_2 powder, which greatly increases the pore number and the homogeneity of pore distribution and results in relatively small pores in the powder compacts.

3.1.2. X-ray diffraction

The phases of the products of powder compacts after sintering are listed in Tables 2 and 3. As expected, the following are reactions which occur during sintering of the powder compacts of Table 1:
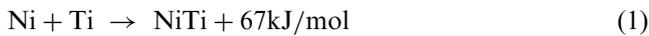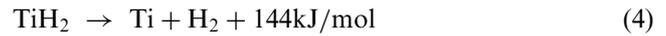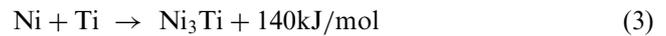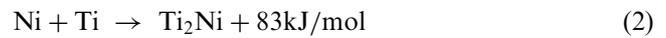
$$Ni + Ti \rightarrow NiTi + 67kJ/mol \tag{1}$$

Table 1
The nominal chemical composition of experimental blended powders

Sample No.	Chemical composition (wt %)		
	Ti	TiH_2	Ni
1	44.9	0.0	bal.
2	35.8	9.3	bal.
3	17.8	27.8	bal.
4	0.0	45.9	bal.

$$Ni + Ti \rightarrow Ti_2Ni + 83kJ/mol \tag{2}$$

$$Ni + Ti \rightarrow Ni_3Ti + 140kJ/mol \tag{3}$$

$$TiH_2 \rightarrow Ti + H_2 + 144kJ/mol \tag{4}$$

All of these four reactions are exothermic in nature with the heats as indicated. From the XRD results shown in Tables 2 and 3, it can be seen that NiTi, Ni_3Ti and Ti_2Ni always exist. This can be explained by looking at

Table 2
XRD results of sample No. 4 after sintering at different conditions

Sintering condition	NiTi	Ni_3Ti	Ti_2Ni	Ni	Ti
750°C-1 h	m	M[a]	m	S[b]	S
800°C-1 h	S	M	m	m[c]	m
850°C-1 h	M	S	m	m	m
900°C-1 h	M	S	m	m	m
950°C-1 h	M	S	m	⋯	⋯
950°C-3 h	M	S	m	⋯	⋯
950°C-5 h	M	S	m	⋯	⋯
950°C-7 h	M	S	m	⋯	⋯
950°C-9 h	M	m	m	⋯	⋯

[a] M, major phase.
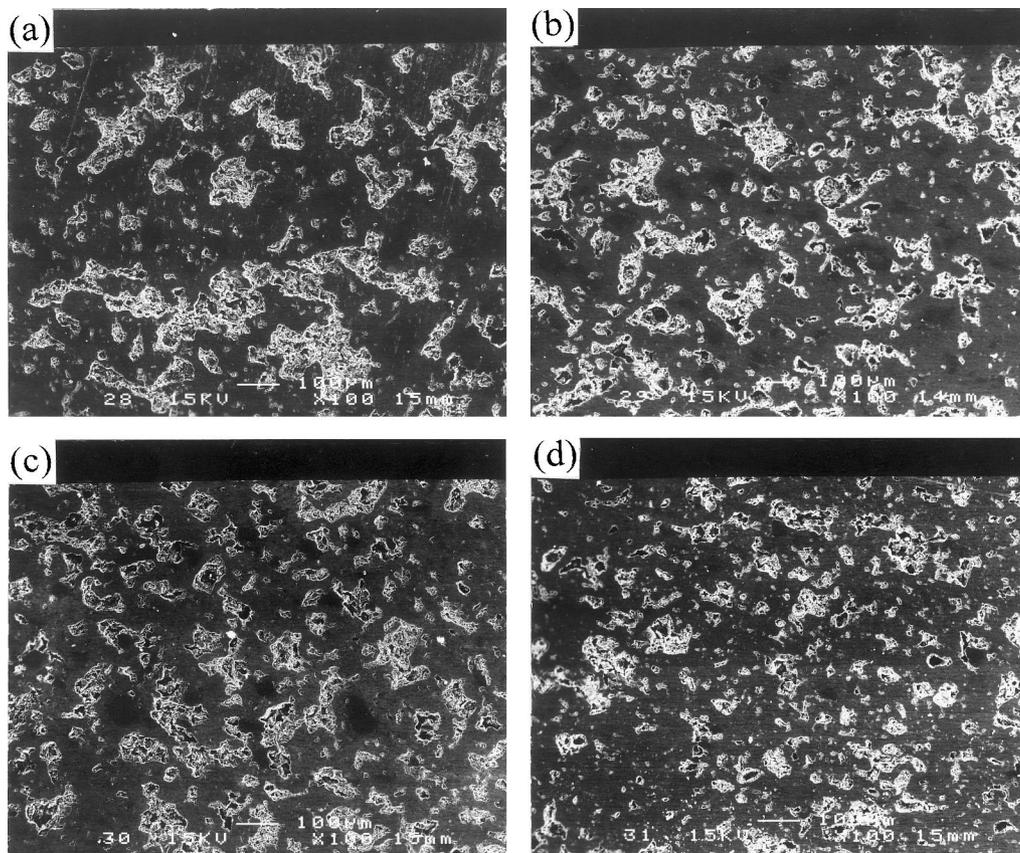[b] S, secondary phase.
[c] m, minor phase.

Fig. 1. The micrographs of porous Ni–Ti alloys after sintering at 850°C for 1 h. (a) Sample No. 1; (b) Sample No. 2; (c) Sample No. 3; (d) Sample No. 4.

Table 3
XRD results for porous Ni–Ti alloys sintered at 950°C for 9 h

Sample No.	NiTi	Ni₃Ti	Ti₂Ni	Ni	Ti
1	M[a]	S[b]	m[c]	...	...
2	M	S	m	...	...
3	M	m	m	...	...
4	M	m	m	...	...

[a] M, major phase.
[b] S, secondary phase.
[c] m, minor phase.

the phase diagram of Ni–Ti and noting that these three phases are stable. Moreover, reactions (2) and (3) are more thermodynamically favored than reaction (1). Thus, Ni₃Ti and Ti₂Ni are difficult to remove completely just by changing the sintering conditions. XRD experiments also show that the content of different phases in the porous Ni–Ti alloy is significantly influenced by sintering conditions as well as TiH₂ additions. At lower sintering temperatures, e.g. 750°C, Ni₃Ti is the dominate phase in the experimental alloy and pure Ni as well as pure Ti exists. With increasing sintering temperature, sintering time, and TiH₂ addition, NiTi phase increases greatly in contrast to the decrease of Ni₃Ti. This is because the self- and inter-diffusion of Ni and Ti are improved by increasing sintering temperature, sintering time and TiH₂ addition, and more NiTi phase forms due to the Ni/Ti equiatomic stoicheomitric relationship of all four powder compacts. The contribution of TiH₂ additions is attributed to the great exothermicity of reaction (4), which is favorable for the formation of NiTi phase, and the better reactivity of new-born Ti that decomposed from reaction (4).

Fig. 2 shows the XRD of sample No. 4 sintered at 950°C for 1 h before and after a compression of 8%. Expectedly, martensite B19'(NiTi) is induced by stress during compression by means of dissipating austenite B2(NiTi). As a result, B19'(NiTi) instead of B2(NiTi) becomes the main phase after compression.

3.2. Stress–strain behavior of porous Ni–Ti shape memory intermetallics

Unlike most other well known intermetallic compounds which are brittle at ambient temperature, the Ni–Ti alloy is ductile and can sustain large deformations. The influence of sintering conditions and TiH₂ additions on the stress–strain behavior of porous Ni–Ti alloys is studied and the results are shown in Fig. 3. In the curves, the PE associated with the stress-induced martensitic transformation appears in each sample. As can be seen, with increasing sintering temperature, the PE increases while the width of stress–strain hysteretic loop decreases. This is because the content of NiTi phase, which exhibits SME, increases with increasing
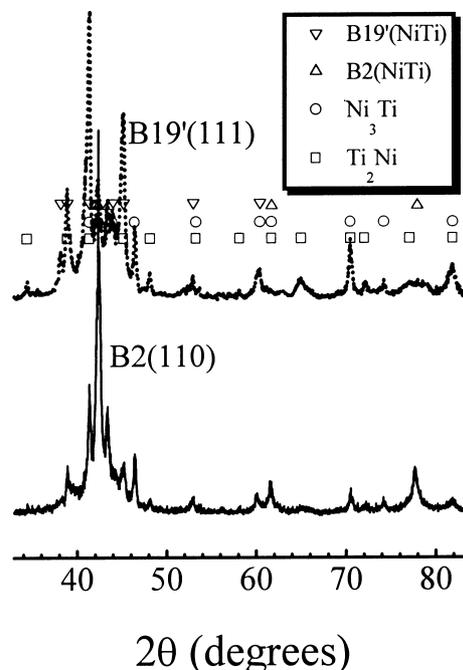

Fig. 2. XRD before and after a compression of 8% of sample No. 4 sintered at 950°C for 1 h. ——— before compression – – – after compression.
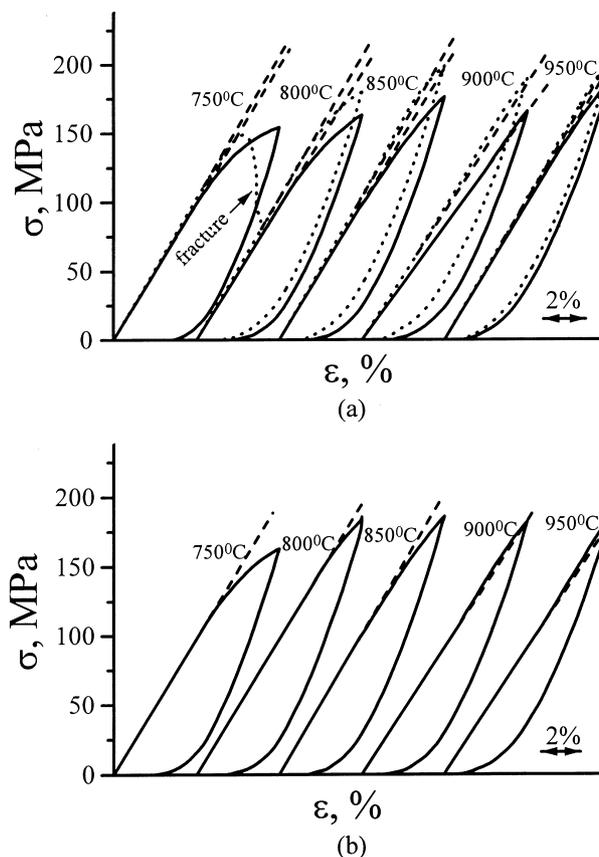

Fig. 3. The stress versus strain diagrams of porous Ni–Ti alloys sintered at various temperatures. The dotted line in (a) is after a second compression of 8%. Dashed direct line indicates the elastic modulus of the linear elastic deformation stage. (a) Sample No. 1; (b) Sample No. 2.
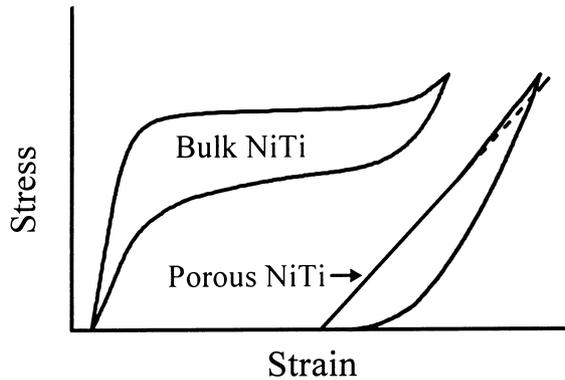
Fig. 4. The typical stress–strain curves of porous and bulk Ni–Ti alloys.

sintering temperature. In addition, the width of the hysteretic loop of the stress–strain curve is determined by the dissipation of energy. The more pronounced the PE is, the narrower the loop becomes. These trends weaken with increasing TiH$_2$ additions (comparing Fig. 3a to b) as the phase constituent changes little.

Moreover, it is found that a second compression cycle can greatly improve the SME of porous Ni–Ti alloys [6]. The stress–strain curves of porous Ni–Ti alloys after a second compression are shown in Fig. 3a. It is found that the PE and elastic modulus as well as its related deformation resistance increase after the second compression. This is possible because compression increases the defect concentration (such as dislocation, dislocation intertwine and voids) [8], which improves the matrix strength and constrains the plastic deformation.

3.3. Comparison of stress–strain behavior between porous and bulk Ni–Ti alloys

Fig. 4 shows the typical stress–strain behavior of porous and bulk Ni–Ti alloys which exhibit PE. As can be seen, both porous and bulk Ni–Ti alloy have good PE although there is no stress plateau in the porous one. Moreover, comparing to normal porous materials, the porous Ni–Ti alloys have high strain recovery and their deformation resistance increases dramatically with further strain after the elastic deformation stage during compression.

4. Conclusions

The effects of sintering conditions and TiH$_2$ additions on the microstructure and stress–strain behavior of porous Ni–Ti shape memory intermetallics were investigated. Results obtained are summarized as follows:

1. The pores are small and well distributed in the porous Ni–Ti alloys and the pore distribution becomes more homogeneous with increasing TiH$_2$ additions.
2. In porous Ni–Ti shape memory alloys sintered at lower temperatures, Ni$_3$Ti is the dominate phase; while in alloys sintered above 850°C, NiTi is the main phase. From the thermodynamic standpoint, it seems impossible to remove the Ni$_3$Ti and Ti$_2$Ni completely.
3. With increasing sintering temperature, the PE of the porous Ni–Ti alloy increases. A second compression cycle also enhances the PE as well as the deformation resistance of porous Ni–Ti alloys.
4. Like bulk Ni–Ti alloys, porous Ni–Ti alloys have excellent PE but there is no stress plateau. Moreover, comparing to normal porous materials, which have very low strain recovery, the deformation resistance of porous Ni–Ti alloys increases dramatically with further strain after the elastic deformation stage during compression.

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