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ELECTRIC RESISTANCE PHENOMENA IN POROUS Ni-Ti SHAPE-MEMORY ALLOYS PRODUCED BY SHS

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1. Introduction

Porous Ni-Ti shape-memory alloys (SMAs) have promising applications in medical field (such as cranial-facial replacement and prosthesis, dental roots, and medical instruments) due to their good biocompatibility, unique shape-memory effect (SME) as well as superelasticity (SE), and good mechanical properties (1,2).

It is well known that Ni-Ti SMAs show a crystalline transition from parent phase to martensite phase and vice versa when they are subjected to cooling or heating processes, respectively. It is reported that porous Ni-Ti SMAs also show the SME when they are mechanically deformed at low temperature, in the martensitic phase, and successively heated up to the parent phase; and they present SE if deformed in the parent phase within a definite temperature range (3,4). That is to say, SME and SE of Ni-Ti SMAs are associated with transformation temperatures, and therefore the transformation temperatures are very important for the medical and engineering applications of Ni-Ti SMAs. However, the transformation temperatures of Ni-Ti SMAs are very sensitive to composition. For example, a 0.1at.% nickel change in composition or presence of 0.1at.% oxygen can result in about a 10°C change in transformation temperatures (5,6). The transformation behavior of cast Ni-Ti SMAs has been studied extensively (5,7–11). Nevertheless, to the authors' knowledge, there are very few reports about the transformation behavior of porous Ni-Ti SMAs. In the present study, the transformation behavior of porous Ni-Ti SMAs prepared by self-propagating high-temperature synthesis (SHS) is investigated in detail for the first time using electrical resistance versus temperature, differential scanning calorimetry (DSC) and thermal expansion.

2. Experimental

Porous Ni-Ti SMAs were produced by SHS, as described in the literature (12), using Ti (36.5 μ m) and Ni (18.0 μ m) powders at different preheating temperatures, at which the mixed powders were ignited. The porosity here refers to the general porosity, which is determined by weight and dimensional



Figure 1. DSC curves of porous Ni₅₀Ti₅₀ SMAs with different porosity (P) prepared by SHS.

measurements. The DSC sample ($\Phi 3.0 \times 0.55$ mm), electrical resistance sample ($\Phi 3.0 \times 80$ mm), and dilation sample ($\Phi 3.0 \times 50$ mm) were obtained by electric spark cutting. The electric resistance versus temperature curves were obtained by a standard four-probe potentiometric method in the temperature range of about -160° C to $+160^{\circ}$ C, and DSC was used to determine the transformation temperatures and latent heats at a heating/cooling rate of 10° C/min. The thermal expansion curve was measured in a sequence of $+150^{\circ}$ C $\rightarrow -50^{\circ}$ C $\rightarrow +150^{\circ}$ C by a DP-49 dilatometer equipped with a cryostat, and an electrolyzed copper rod was used as a temperature calibrator.

3. Results and Discussion

Figure 1 represents the typical DSC curves of porous Ni-Ti SMAs produced by SHS. Apart from the difference in the peak height, the transformation temperatures, thus the transformation hysteresis, are almost identical for porous Ni-Ti SMAs with different porosity. The transformation temperatures and related latent heats are shown in Table 1. As can be seen, the transformation temperatures of porous Ni-Ti SMAs with different porosity are almost identical, which can be attributed to the same nominal composition, and the transformation hysteresis (A_s - M_s) is very small. However, the latent heats of transformation increase greatly with increasing porosity. The porosity dependent latent heat in porous Ni-Ti SMAs produced by SHS is thought to be associated with the smaller elastic energy of porous Ni-Ti SMAs with higher porosity.

Figure 2 is the electric resistance versus temperature curves of porous Ni-Ti SMAs produced by SHS. The curves are very novel and are very different from those of cast Ni-Ti SMAs prepared by conventional arc-melting or those of dense Ni-Ti SMAs prepared by powder metallurgy (5,8). Comparing the DSC curves with the corresponding electric resistance-temperature ones (Fig. 3), one can see

Porosity, %	Transformation Temperature, °C					Latent Heats of Transformation, J/g	
	M _s	M _f	A _s	A _f	A _s -M _s	ΔH_A	ΔH_{M}
59.2	61.9	34.2	63.5	93.7	1.6	6.51	-8.45
65.6	60.5	42.1	62.4	95.4	1.9	9.77	-9.04
71.5	61.6	40.7	61.8	85.2	0.2	14.08	-14.95

 TABLE 1

 Transformation Temperatures and Latent Heats of Porous Ni₅₀ Ti₅₀ SMAs Prepared by SHS



Figure 2. Electrical resistance versus temperature curves of porous Ni-Ti SMAs prepared by SHS at different preheating temperatures (T_0). The open symbols represent the cooling process and the solid ones represent the heating process.

that the transformation temperature during cooling in DSC is in accordance with those in the first peak of electric resistance. Noted that the present M_s in the electric resistance-temperature curves is obtained using tangential method, and is different from the conventional method, which takes the peak temperature as M_s . Moreover, the electric resistance is abnormal during cooling from 0°C to -150°C, which shows another peak. This second peak in the two peaks during cooling may be associated with an unknown phase transformation. Meanwhile, there is no obvious peak during the heating process, and the martensitic transformation during heating can not be observed in the electric resistance versus



Figure 3. Compare of DSC and electrical resistance-temperature curves of porous Ni₅₀Ti₅₀ SMAs prepared by SHS.



Figure 4. Linear expansion between -50° C and $+150^{\circ}$ C of porous Ni₅₀Ti₅₀ SMAs prepared by SHS.

temperature curves. The reasons for these phenomena are not very clear now. To some degree, they may be related with the pores which lead to inhomogeneous distribution of stresses.

Figure 4 shows the thermal dilation curve of porous Ni-Ti SMAs produced by SHS. The corresponding linear expansion coefficients of the low- and high-temperature structures are $9.0 \times 10^{-6/\circ}$ C and $9.9 \times 10^{-6/\circ}$ C, respectively. That is to say, the linear expansion of porous Ni-Ti SMAs is small, due to the porous structure which leads to less bulk materials involved in the thermal expansion. The transformation temperatures determined by this method are in accordance with those by DSC. The thermal dilation shows that there exists a volume increase during martensitic transformation as those of cast Ni-Ti SMAs. Since the martensitic transformation accompanies a volume change, the constraints of the volume change should suppress the phase transition. In the present porous Ni-Ti SMAs, the adjacent grains and relatively much more Ti/Ni-rich phases (such as Ti₂Ni, Ni₃Ti and Ni₄Ti₃) should play a part in this effect and should be responsible for the relatively weak martensitic transformation and thermal expansion compared with cast Ni-Ti SMAs.

4. Conclusions

The transformation behavior, especially the electric resistance versus temperature, of porous Ni-Ti SMAs produced by SHS is studied comprehensively for the first time. It is found that the transformation temperatures of porous Ni-Ti SMAs with different porosity are almost identical, and the latent heats of transformation increase with increasing porosity. The electric resistance-temperature curves of porous Ni-Ti SMAs produced by SHS are very novel and different from those of cast Ni-Ti SMAs prepared by conventional arc-melting method or those of dense Ni-Ti SMAs prepared by powder metallurgy. There appear two peaks in the cooling process while no peak is observed in the heating process in the electric resistance-temperature curves. Furthermore, the expansion/shrinkage of porous Ni-Ti SMAs produced by SHS during cooling/heating is relatively small.

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- 1. V. E. Gjunter, Superelastic Shape Memory Implants in Maxillofacial Surgery, Traumatology, Orthopaedics and Neurosurgery, Tomsk University Publishing House (TUP), Tomsk, Russia (1995).
- 2. S. Rhalmi, M. Odin, M. Assad, M. Tabrizian, C. H. Rivard, and L'H Yahia, Biomed. Mater. Eng. 9, 151 (1999).
- 3. V. I. Itin, V. E. Gjunter, S. A. Shabalovskaya, and R. L. C. Sachdeva, Mater. Charact. 32, 179 (1994).
- 4. B. Y. Li, L. J. Rong, and Y. Y. Li, Sci. China (Series E). 42(1), 94 (1999).
- 5. H. Kato, T. Koyari, M. Tokizane, and S. Miura, Acta Metall. Mater. 42(4), 1351 (1994).
- 6. Y. Furuya, R. Watanabe, J. Chiba, and H. Shimada, J. Mater. Sci. Lett. 8, 1302 (1989).
- 7. K. Otsuka and X. B. Ren, Intermetallics. 7, 511 (1999).
- 8. F. E. Wang, B. F. DeSavage, and W. J. Buehler, J. Appl. Phys. 39(5), 2166 (1968).
- 9. K. Funami, Y. Sekiguchi, and H. Funakubo, J. Jpn. Inst. Metals. 48(11), 1113 (1984).
- 10. Y. C. Lo, S. K. Wu, and H. E. Horng, Acta. Metall. Mater., 41(3), 747 (1993).
- 11. M. Otake, K. Isobe, T. Kosugi, K. Tsuchiya, and M. Umemoto, J. Jpn. Soc. Powder and Powder Metall. 46(7), 746 (1999).
- 12. B. Y. Li, L. J. Rong, Y. Y. Li, and V. E. Gjunter, J. Mater. Res. 15(1), 10 (2000).