Transformation Behavior of Sintered Porous NiTi Alloys

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TiH_2 powder is added as a reactant and pore-forming agent to produce porous NiTi shape-memory alloys (SMAs). The transformation behavior of porous NiTi alloys is investigated as it is relevant to the engineering and medical applications of SMAs. It is found that the transformation behavior of porous NiTi alloys is different from that of cast NiTi alloys. It is demonstrated for the first time, by *in situ* X-ray diffraction (XRD), that there is no R-phase transformation in porous NiTi alloys, and a broadened, two-peak phenomenon observed with a differential scanning calorimeter (DSC) is not associated with R-phase transformation. The characteristic transformation temperatures of porous NiTi alloys are independent of sintering temperature, sintering time, TiH_2 content, and the heating/cooling rate during thermal cycling between +123 and +423 K. Further, the latent heats of transformation are associated with the TiH_2 content and the sintering conditions.

I. INTRODUCTION

THE properties of cast SMAs are well known and exploited for many applications in different technological fields. Recently, as a promising biomedical material for application in bone implant surgery and in the substitution for cranial-facial defects, porous NiTi alloy has become a central item of attention because of its shape memory effect, its compatibility with biological tissues, and its porous structure, which is favorable for implant fixation and the transport of body fluids.

There have been several publications on powder sintering consolidation of NiTi alloys.[1-6] These studies, however, laid emphasis on the method of obtaining dense alloys of a desired composition, and the transformation behavior of porous NiTi alloys has not yet been reported. As the transformation behavior of SMAs is important for their engineering and medical applications, the purpose of the present study is to investigate the transformation behavior of porous NiTi alloys prepared with different contents of TiH_2, which is added as a reactant and pore-forming agent.

II. EXPERIMENTAL

Elemental Ti (-74μm), Ni (-74μm), and TiH_2 (-44μm) powders were mixed in the ratio 50Ti/50Ni at.% by ball-milling in a steel chamber for 2h in an argon atmosphere. Table I shows the nominal composition of blended powders. The blended powders were then uniaxially compacted for 2min at a pressure of 70MPa. The compacts were sintered in vacuum (1.33×10^{-2}Pa) for 1h at temperatures ranging from 1023 to 1223 K, or at 1223 K for times between 1 and 9h. The change of phase amount was determined by X-ray diffraction (XRD). The transformation related latent heats and temperatures were determined using a Rigaku PTC-10A differential scanning calorimeter (DSC). ΔH_A and ΔH_M, indicated as the hatched areas in Figure 1, were defined as the latent heats of transformation as usual. They are absolute values of the total heat measured in a forward or a reverse martensitic transformation. The thermal cycling experiments were carried out between +123 - +423 K using different heating/cooling rates.

III. RESULTS AND DISCCUSION

Figure 1 represents the typical DSC curve of porous NiTi alloys. One can easily recognize that the thermal peaks are much broader than the peaks obtained for cast alloys. Two peaks, whose shape and size are found to experimentally change with different sintering conditions, overlap under both heating and cooling conditions. The reason for such behavior is thought due to the microcompositional difference existing within individual sintered grains. Since the sintering is based on elemental materials, slight concentration differences may exist within the newly

Table I. Chemical Composition of the Experimental Blended Powders (Weight Percent)

Sample No.	TiH_2	Ti	Ni
1#	0	44.9	bal
2#	9.3	35.8	bal
3#	27.8	17.8	bal
4#	45.9	0	bal

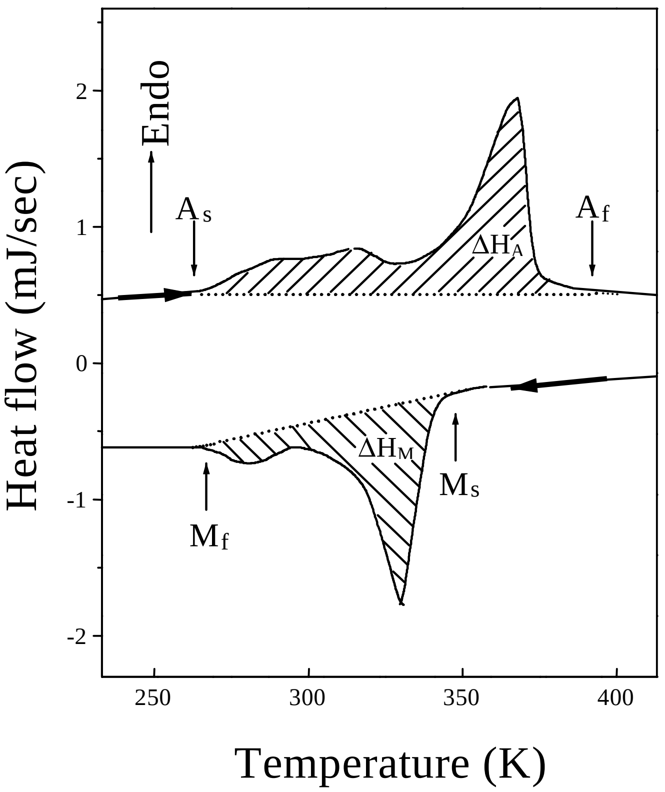

Fig. 1—Schematic DSC curve of porous NiTi alloys.

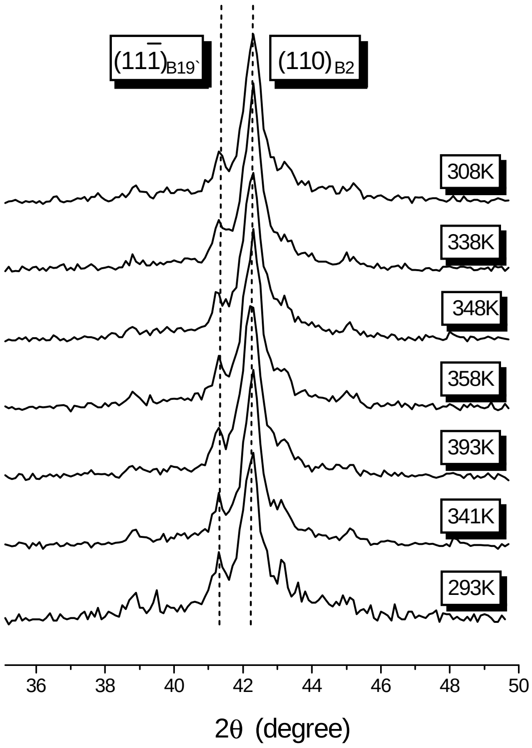

Fig. 2—*In situ* XRD spectra of sample 4$^\#$ sintered at 1223 K for 9h during heating and cooling.

formed grains upon completion of a specific sintering process, corresponding to the equilibrium composition range of NiTi phase. As the transformation temperatures are very sensitive to composition, the broadened DSC peaks result from this effect. In addition, a lot of experiments found that the characteristic transformation temperatures are insensitive to the sintering conditions since each of them is almost the same in an allowable deviation (±5 K), respectively. This is due to the same nominal composition of all the present alloys. The characteristic transformation temperatures (K) for sample 4$^\#$ sintered at 1223 K for 9h revealed by DSC are: A_s, 264.8 K; A_f, 378.3 K; M_s, 342.7 K; M_f, 267.2 K; and $|A_s\text{-}M_s|=77.9$ K. It is reported that the transformation temperatures of equiatomic NiTi cast alloys are between 73 and 384 K, their M_s (about 326 K) is less than A_s, and the corresponding transformation hysteresis is about 2 - 50 K.[7, 8] It is clear that the transformation temperatures of porous NiTi alloys are in the range of those of cast alloys, while the transformation hysteresis is much wider than that of cast alloys. Moreover, the A_s of porous NiTi alloys is much less than M_s. The latter phenomenon has been observed previously in the martensitic transformation of β-brass, and here is probably due to that, at the surface of pores, there are much defects (like voids, dislocation etc), which are good sites for martensite to nucleate. Thus, the existence of many pores enhances the martensitic nucleation, and raises Ms but leaves As unaffected,[9, 10] and the transformation hysteresis is also wide in porous NiTi alloys.

Table II. The Relative Diffraction Peak Strength of Sample 4$^\#$ Sintered at 1223 K for 9h

Temperature (K)	$I_{41.3}/I_{42.2}$
308	0.282
338	0.280
348	0.278
358	0.275
393	0.270
341	0.287
293	0.488

Table III. The Influence of Thermal Cycling on Transformation Temperatures of Sample 3$^\#$ Sintered at 1223 K for 1h (K)

Heating/Cooling Rate (K/min)	10	20	30	40
M_s	340.1	342	337.3	337.5
A_f	373.3	377.5	374.6	375.7

Figure 2 shows the in situ XRD spectra of sample 4$^\#$ sintered at 1223 K for 9h during heating and cooling after cooling to liquid nitrogen. The corresponding relative peak strength of the main peak of martensite

Table IV. The Latent Heats of Transformation of Porous NiTi Alloys (J/g)

Sintering Conditions	$1^{\#}$		$2^{\#}$		$3^{\#}$		$4^{\#}$	
	$-\Delta H_M$	ΔH_A	$-\Delta H_M$	ΔH_A	$-\Delta H_M$	ΔH_A	$-\Delta H_M$	ΔH_A
1023 K-1h	6.4	—	6.9	—	—	5.2	9.1	9.3
1073 K-1h	7.9	8.0	6.2	8.2	5.1	—	—	—
1123 K-1h	8.6	9.2	6.8	12.2	10.8	12.6	9.1	14.1
1173 K-1h	7.8	13.6	12.0	12.4	13.2	13.7	11.1	13.8
1223 K-1h	7.4	12.2	8.3	16.0	14.8	17.3	18.7	23.9
1223 K-3h	12.8	16.2	16.1	—	—	15.9	15.9	17.7
1223 K-5h	12.9	18.0	11.9	16.5	—	16.8	15.4	25.5
1223 K-7h	—	14.6	6.8	14.6	10.5	20.0	—	18.0
1223 K-9h	17.6	19.7	13.5	19.7	16.0	21.9	19.7	21.4

B19' at 2θ=41.3 and the main peak of autensite at 2θ=42.2, i.e., $I_{41.3}/I_{42.2}$, is listed in Table II. One can see that with increasing heating temperature from 308 to 393 K, the $(1\bar{1}1)_{B19'}$ peak at 2θ=41.3 decreases while correspondingly that of $(110)_{B2}$ peak at 2θ=42.2 increases slightly, which is also indicated by the decrease of $I_{41.3}/I_{42.2}$. This decrease is due to the reverse martensitic transformation, in which the B19' martensite transforms into B2 parent phase. In distinction, when cooled from 393 to 293 K, the $(1\bar{1}1)_{B19'}$ peak and $I_{41.3}/I_{42.2}$ increase as a result of the forward martensitic transformation. Since the appearance of a transitional R-phase is characterized by narrowing of lines of the B2-phase at temperatures above M_s and splitting in two near M_s, as well as an increase in the half-width of line $(110)_{B2}$ during cooling,[11, 12] it can be concluded from the XRD spectra that no R-phase transformation exists in the present alloys. This implies that the two-peak phenomenon in DSC curves cannot be attributed to the R-phase transformation even though a DSC trace of alloys exhibiting R-phase transformation also displays a two-peak phenomenon.[13]

It is known that the transformation temperatures of cast NiTi alloys are strongly affected by the heating and cooling rates during thermal cycling, which usually makes M_s decrease. In an allowable deviation range, however, it is found that the transformation and related transformation temperatures of the present alloys are independent of heating/cooling rates during thermal cycling between +123 - +423 K (see Table III). This independence is important for the engineering applications of SMAs, but the reason for this behavior is not known at this time.

Table IV reports the latent heats of transformation of porous NiTi alloys sintered for different conditions. The latent heats, ΔH_A and $-\Delta H_M$, increase with increasing sintering temperature, sintering time and TiH_2 content. This increase is because NiTi is the only phase responsible for the change of latent heats in NiTi SMAs and NiTi phase increases with increasing sintering temperature, sintering time, and TiH_2 content.[14] Further, the absolute latent heat value of reverse transformation is larger than that of the forward transformation, i.e., $|\Delta H_A| > |-\Delta H_M|$. This difference is associated with the porous structure of sintered alloys. The measured latent heat of transformation is the sum of three parts: (1) the chemical enthalpy change (the actual latent heat of transformation), (2) the stored elastic strain enthalpy change, and (3) the non-chemical free energy change in the energy balance, termed as work $E_{fr}^{P\to M}$.[15] In the forward transformation, part of the chemical enthalpy released ($-\Delta H_{ch}^{P\to M}$) is stored as elastic enthalpy $\Delta H_{el}^{P\to M}$ or spent as work $E_{fr}^{P\to M}$. The work $E_{fr}^{P\to M}$ includes (i) frictional work spent for interfacial motion, (ii) free energy changes related to imperfections induced by the transformation and (iii) partial plastic accommodation of the transformational shape and volume changes. The latent heat of transformation released during cooling is therefore

$$-\Delta H_M = -\Delta H_{ch}^{P\to M} + \Delta H_{el}^{P\to M} + E_{fr}^{P\to M} \qquad [1]$$

Correspondingly, in the reverse transformation, while the chemical enthalpy $\Delta H_{ch}^{M\to P}$ is absorbed by the specimen, the elastic enthalpy $\Delta H_{el}^{M\to P}$ is reversibly recovered; again, work $E_{fr}^{M\to P}$ has to be done to overcome the frictional barriers opposing reversion of the interfacial movement. Thus, the latent heat of transformation absorbed during heating is given by

$$\Delta H_A = \Delta H_{ch}^{M\rightarrow P} - \Delta H_{el}^{M\rightarrow P} + E_{fr}^{M\rightarrow P} \qquad [2]$$

In this treatment a sign convention is followed, in which heat given to the system is positive while work made on the system is negative, and vice versa.

From Eqs. [1] and [2],

$$\Delta H_A = \Delta H_M + (\Delta H_{ch}^{M\rightarrow P} - \Delta H_{ch}^{P\rightarrow M}) + (\Delta H_{el}^{P\rightarrow M} - \Delta H_{el}^{M\rightarrow P}) + E_{fr}^{P\rightarrow M} + E_{fr}^{M\rightarrow P}$$

With the assumption that the difference of specific heat between martensite and autensite is negligible, i.e., $\Delta H_{ch}^{P\rightarrow M} = \Delta H_{ch}^{M\rightarrow P}$, then

$$\Delta H_A = E_{fr}^{P\rightarrow M} + E_{fr}^{M\rightarrow P} + \Delta H_M \qquad [3]$$

From Eq. [3], we conclude that the latent heat of reverse transformation is larger than that of forward transformation. Normally, the difference of these two latent heats is very small for cast alloys. But for porous NiTi alloys, the difference is relatively large. This is because the free energy changes related to the accommodation of the transformational shape and volume changes perhaps increase due to the difficulties for martensite to self-accommodate at the aforementioned defects during the forward martensitic transformation.

IV. CONCLUSIONS

(1) The transformation behavior of porous NiTi alloys is different from that of cast NiTi alloys. The transformation hysteresis of porous NiTi alloys is much wider, and their A_s is much less than M_s.

(2) The characteristic transformation temperatures of porous NiTi alloys do not vary with sintering temperature, sintering time, TiH_2 content, and the heating/cooling rate during thermal cycling between +123 and +423 K.

(3) Although a broadened, two-peak phenomenon occurs under both heating and cooling conditions in DSC curves, there is no R-phase transformation in porous NiTi alloys. The broadened two-peak is thought to be due to the microcompositional difference existing within individual sintered grains.

(4) The latent heats of transformation increase with increasing sintering temperature, sintering time, and TiH_2 content as a result of the increase of NiTi phase.

(5) For porous NiTi alloys, the absolute latent heat of reverse martensitic transformation is relatively larger than that of the forward martensitic transformation.

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