INFLUENCE OF CRYSTALLIZATION TEMPERATURE ON PHASE TRANSFORMATION IN Ti-RICH NiTi THIN FILMS①

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ABSTRACT The effects of crystallization annealing temperature on phase transformation temperature and SME of Ti-rich NiTi thin films prepared by the magnetron-sputtering system were studied. The experimental results showed that the phase transformation sequence of Ti-rich NiTi thin films were $P \rightarrow R \rightarrow M$ for cooling transformation, and $R \rightarrow P$ and $M \rightarrow P$ for heating one, while increasing the annealing temperature from 823 K to 1 103 K, the R-phase transformation temperature T_{P-R} and T_{R-P} were nearly unchanged, the martensitic transformation temperatures, however, moved to higher temperature. A thin film with room temperature micro-structure consisting of almost whole R-phase can be obtained by annealing at appropriate temperature (e.g. at 923 K), which possesses a stable transformation temperature, narrow hysteresis and a good SME. It is suitable for the application to the micro-machine elements.

Key words NiTi alloy film crystallization phase transformation

1 INTRODUCTION

NiTi shape memory alloy thin films are promising candidates for application to actuators in micro-electron mechanical system (MEMS) and biomedical devices, owing to the great advantages such as large deformation and recovery force. Besides, even an intrinsic disadvantage of the bulk shape memory alloy, i.e. the slow response due to the limitation of cooling rate can be greatly improved in thin films[1]. Most of investigations were concerned with equiatomic or Ni-rich composition NiTi thin films[2-4], however, the control of the phase transformation temperature is somewhat difficult in these thin films because of the fluctuation of the composition in alloy matrix induced by the precipitation of the second phase[5]. Therefore, the study of Ti-rich NiTi thin films is increasingly interesting. The effect of heat treatment on shape memory behavious of Ti-rich NiTi films has been reported[6], however, the influence factors and the mechanism of phase transformation are not yet clear. In this work, the effect of crystallization annealing temperature on phase transformation temperature and SME are presented.

2 EXPERIMENTAL

The Ti-rich NiTi thin films were prepared by magnetron-sputtering system using NiTi target with equiatomic composition. Some pieces of Ti were pasted on the target in order to increase the titanium content in NiTi films. The argon pressure during the deposition was maintained at 0.67 Pa, the voltage applied was ~ 3 kV, and the power ~ 300 W. The deposition time was 90 min. The film thickness was approximately 7 μm. The free-films stripped from glass substrates were crystallized at various temperatures from 823 to 1 103 K in argon atmosphere for 20 min followed by furnace cooling. The composition of

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films determined by EDAX and the crystallization temperature are listed in Table 1. The transformation temperatures, the phase constitutes and the micro-morphology were determined by DSC, X-ray diffraction and TEM, respectively. The shape memory effect of films was estimated by a bending test, such that the thin film with a size of 5 mm × 25 mm was first bended to an angle α of 140° in an ice water, then heated in hot water, and the bending angle α' was determined. Thus the shape recovery rate η was calculated according to the following equation:

$$\eta = \frac{(\alpha - \alpha')}{\alpha} \times 100\% \quad (1)$$

3 EXPERIMENTAL RESULTS

3.1 Phase transformation sequence of Ti-rich NiTi films in cooling and heating

Fig. 1 shows the DSC curves for various crystallization annealing treatments. It is indicated that, the two separate peaks on cooling curves of films annealed at 1 103 K and 1 023 K correspond the transformations from the parent phase P to R-phase(at higher temperature) and from R-phase to the martensite M (at lower temperature), respectively (see Fig. 1 (a) and (b)). The DSC results can be identified by X-ray diffraction spectrums at room temperature as shown in Fig. 2 (a) and (b), in which all diffraction peaks are belong to the martensite phase. However, when the crystallization annealing temperatures decrease to 923 K and 823 K, a stronger peak and two weaker peaks appear on the cooling curves, corresponding to $P \rightarrow R$ and $R \rightarrow M1$, $R \rightarrow M2$ transformations, as shown in Fig. 1(c) and 1(d). It is consistent with the experimental results of X-ray diffraction analysis, that the structure at room temperature consists of a large number of R-phase and a few amount of martensite.

Therefore the transformation sequence on cooling of Ti-rich NiTi thin films is the same as that in bulk materials, i.e. $P \rightarrow R \rightarrow M$. However, while decreasing crystallization temperature to 923 K and 823 K, the martensitic transformation $R \rightarrow M$ can not be completed and the double peaks of martensitic transformation appear. It can be seen from heating curves of DSC (Fig. 1) that, a strong heat flow peak corresponding to $M \rightarrow P$ transformation appear on the films crystallized at 1 103 K and 1 023 K, though the peak corresponding to $R \rightarrow P$ is very weak (for specimen J1) or does not appear (for J2). On the contrary, in the films crystallized at 923 K and 823 K, the peak of $R \rightarrow P$ reverse transformation is very strong though the peak of $M \rightarrow P$ is weak (J4) or does not appear, and all the $M \rightarrow P$ peaks move to higher temperature than the $R \rightarrow P$ peaks. It is thus obvious that, the reverse transformation in Ti-rich NiTi films is separated as $R \rightarrow P$ and $M \rightarrow P$ which is different from that in bulk materials, namely $M \rightarrow R \rightarrow P$.

3.2 Effects of crystallization annealing on transformation temperature

Briefly, we take the peak temperature on DSC curves as phase transformation temperature, for example, T_{P-M}, T_{M-P} and T_{P-R}, T_{R-P} in Fig. 1. The relationship between the crystallization temperature and phase transformation temperature is shown in Table 1 and

Table 1 Composition, crystallization temperature and transformation temperature of films

No.	Mole fraction of Ni/%	Crystallization temp./K	R-transformation temp./K			M-transformation temp./K			
			T_{P-R}	T_{R-P}	ΔT_R	T_{R-M1}	T_{R-M2}	T_{M-P}	ΔT_M
J1	46.47	1 103	332.9	334.8	1.9	324.5	–	357.9	33.4
J2	47.21	1 023	334.3	–	–	323.0	–	357.3	34.3
J3	47.16	923	331.9	334.3	2.4	301.0	286.7	–	–
J4	47.86	823	332.6	335.3	2.7	306.1	291.1	345.4	39.3

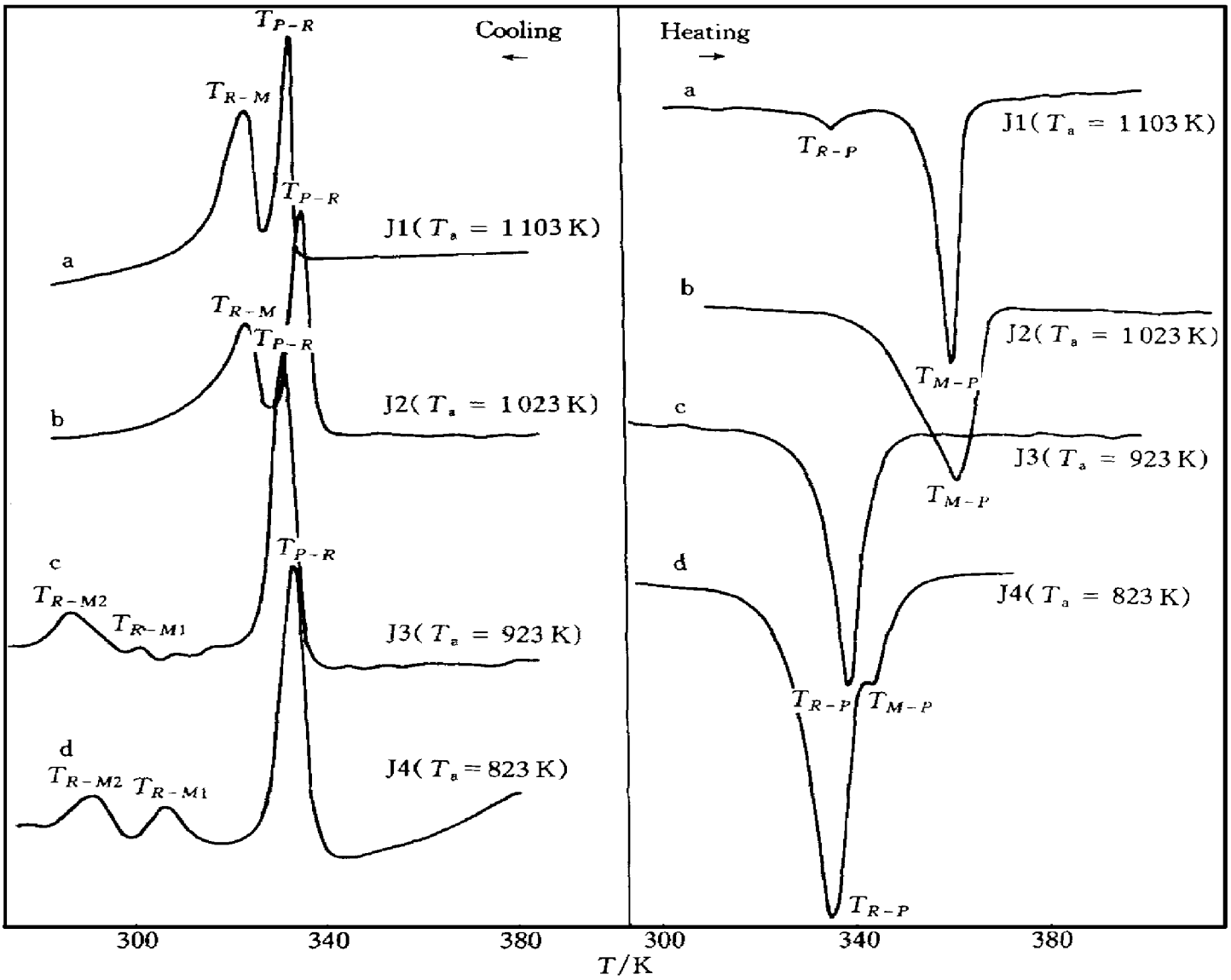

Fig. 1 DSC curves of samples J1~ J4

(cooling and heating rate are 10 K/min; T_a—annealing temperature)

Fig. 3.

Fig. 3 shows that, the R phase transformation temperatures are almost independent on the crystallization temperature. For example, while lowering the annealing temperature from 1 103 K to 823 K, the R-phase transformation temperatures T_{P-R} and T_{R-P} fluctuate within 331. 9~ 334. 3 K and 334. 3~ 335. 3 K, respectively. The hysteresis of R-phase transformation is very small. However, the martensitic transformation temperatures are affected obviously by the annealing temperature. While increasing the annealing temperature from 823 K to 1 023 K, the martensitic transformation temperature T_{R-M} and T_{M-P} rise by 16. 9 K and 12 K, respectively. Further increasing the crystallization temperature will not affect the T_{R-M} and T_{M-P}. The hysteresis of martensitic transformation is more than 30 K, and it slightly increases with lowering the crystallization temperature.

3.3 Deformation recovery properties of films

The recovery curves of bending strain of the thin films are shown in Fig. 4.

It is indicated that the recovery temperatures T_r and its variation tendancy are consistent with the results of DSC experiments. The T_r of films crystallized at 1 023 K and 1 123 K are ap-

proximate to their T_{M-P} (357.3 K and 357.9 K). The film crystallized at 823 K starts to recover at ~ 345 K, which correspond to the reversemartensitic transformation. The recovery temperature T_r(~ 335 K) for the specimen crystallized at 923 K with a room temperature structure consisted mainly of R-phase is in accordance with the R-phase reverse transformation temperature T_{R-P} (334.3 K). The shape recovery rate (η) for films crystallized below 1 023 K almost reaches 100%, but that for 1 103 K is slightly lower.

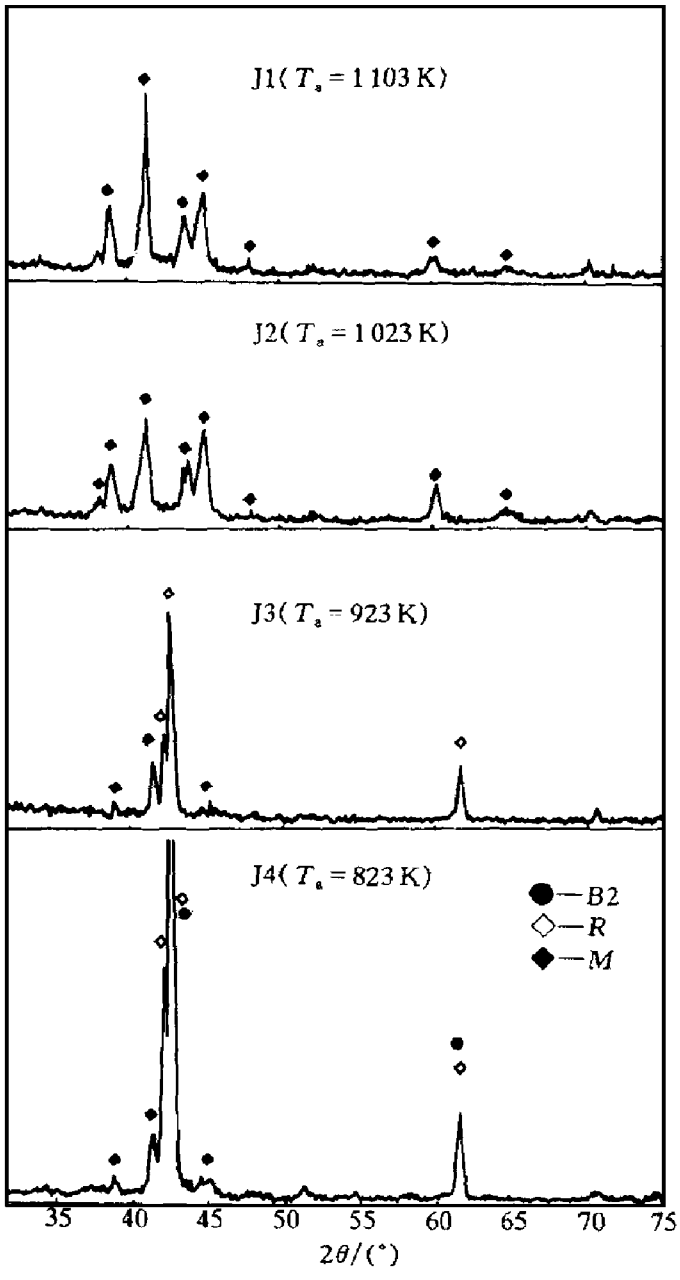

Fig. 2 X-ray diffraction spectrums of samples J1~ J4
(CuK_α monochromator, at room temperature)

4 DISCUSSION

4.1 Thermodynamics consideration about phase transformation in Ti-rich NiTi thin films

The phase transformation sequence and the effects of crystallization temperature on the phase transformation can be explained by thermodynamic analysis. According to Liu and McCromick[7], the free energy of martensitic phase in the cooling transformation, G^{M+}, is G^{M+} =

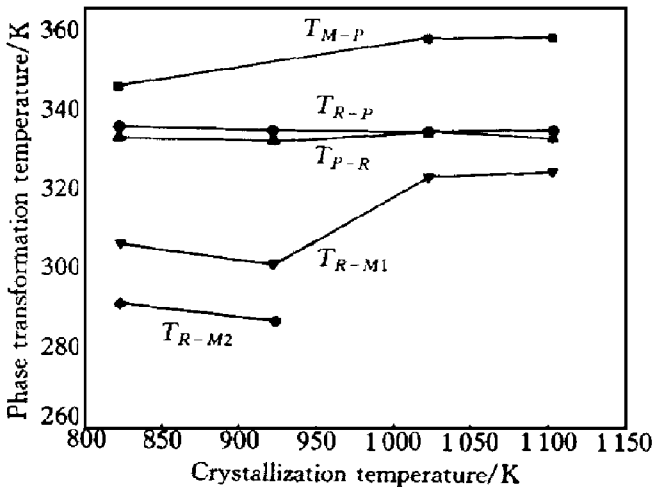

Fig. 3 Effect of crystallization annealing temperature on phase transformation temperature

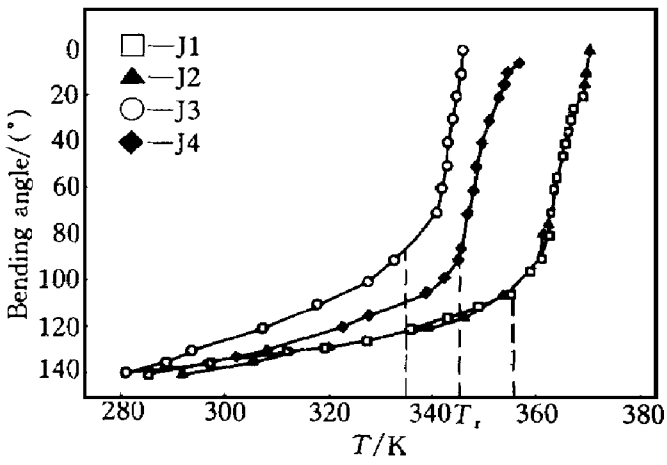

Fig. 4 Recovery curves of bending strain of thin films

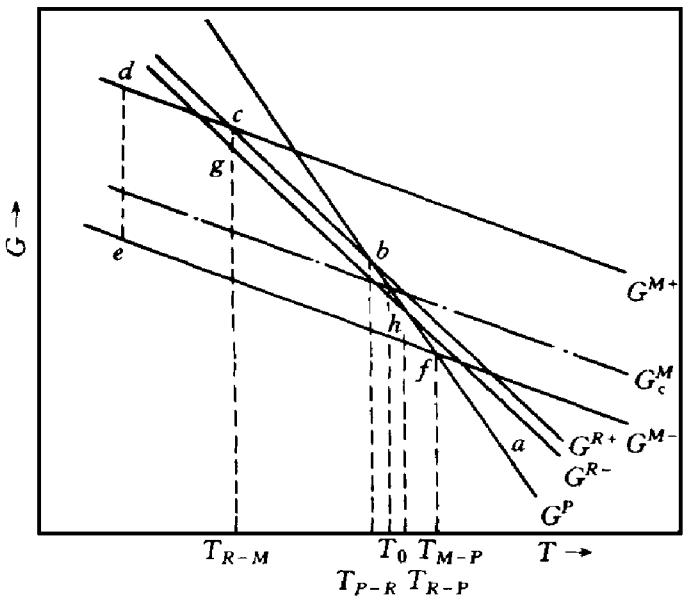

Fig. 5 Schematic diagram of free energy vs temperature

$G_c^M + \Delta E_e + \Delta E_i$ and that in reversed transformation, G^{M-}, is $G^{M-} = G_c^M + \Delta E_e - \Delta E_i$ as shown in Fig. 5, where G_c represents the chemical free energy of the martensite phase, ΔE_e is the reversible elastic storage energy resulted from transformation which is a resistance to the cooling transformation, however it becomes a part of driving force to the heating transformation, ΔE_i is the irreversible energy consumed during the transformation process, including the shear strain energy, the generation of heat and the emission of acoustic waves, which is an energy barrier needed to overcome in both of forward and reverse transformation. These energy barriers shift the transformation temperature to either sides of the equilibrium point, leaving a thermal hysteresis between the forward and reverse transformation, as shown in Fig. 5. The *R*-phase transformation is also plotted in the figure as two separate lines, as marked as G^{R+} and G^{R-}, respectively. G^P represents the free energy of the parent phase. A large hysteresis lies in the martensite transformation process and a small one in *R*-phase transformation because the difference of the structure between the martensite and the parent phase is larger than that between the *R*-phase and the parent phase. The transformation sequence determined by the path of lowest free energy is shown in Fig. 5, namely, a double stage transformation $P \rightarrow R \rightarrow M$ is on cooling (*abcd*), and two single stage transformations $M \rightarrow P$ and $R \rightarrow P$ are on heating (*efa* and *gha*). The martensitic transformation temperatures are easily affected by the strength of the parent. The shear strain energy involved in ΔE_i can be expressed as $(1/2)\ \tau_C \gamma_T$ [8], where τ_C is the required critical shear stress for transformation, γ_T is the transformation strain. On the basis of the Hall-Petch equation, τ_C may be represented as $\tau_C = \tau_0 + kd^{-1/2}$, in which τ_0 is the critical shear stress of the single crystal, k is a positive constant related to the material, d is the grain size of the parent phase. Therefore the smaller the grain size of the parent, the higher the shear strength of the parent, the larger the ΔE_i, so that the T_{R-M} temperature decreases; conversely, the higher the crystallization temperature, the coarser the grain size, so that the T_{R-M} increases. The TEM observation shows that, the mean grain size of thin films crystallized at 1 023 K and 823 K are about 2.0 μm and 1.5 μm, correspondingly the martensitic transformation temperatures T_{R-M} are 323 K and 306 K. However, the enhancement of crystallization temperature can not increase the transformation temperature T_{P-M} unlimitedly, because of the reduction of some crystal defects distributed at grain boundaries during crystallization at higher temperature, which are benefit to the nucleation of martensite[9]. Therefore, in this work, T_{R-M}, T_{M-P} for crystallized at 1 023 K and 1 123 K are nearly the same.

4.2 Double peaks of martensitic transformation

There appear two peaks on the DSC cooling curves in thin films crystallized at 923 K and 823 K. There are different approaches to explain the phenomenon, for example, the introduction by an incomplete order of the vacancies in the whole sample[10], or, the inhomogeneity in the dislocation configuration[11] etc. But we prefer to suggest that the main factor for the double peaks of

martensitic transformation may be the difference of Ti content between regions around precipitates of Ti_2Ni and matrix that causes the $R \rightarrow M$ transformation temperature early or late in different micro regions.

4.3 SME of Ti-rich NiTi films

A good shape recovery rate η in Ti-rich NiTi thin films crystallized at various temperatures is obtained by a bending method as shown in Fig. 4. The bending strain ε can be calculated by the equation $\varepsilon = t/r(\%)$, where t is the thickness of films, r is the bending radius of curvature. As $t \approx 5 \sim 7\ \mu m$, $r \approx 2$ mm, then $\varepsilon \approx 0.25\% \sim 0.35\%$. As known to all, the amount of recovery deformation of R phase is smaller than that of the martensite in bulk materials, but it is no problem for thin films. Therefore, the Ti-rich NiTi thin films consisting of nearly whole R phase obtained by a proper crystallization annealing, which possesses a stable phase transformation temperature and small hysteresis, are suitable for the application to the micro-machine elements.

5 CONCLUSIONS

(1) The phase transformation sequences in Ti-rich NiTi thin films magnetron-sputtered are $P \rightarrow R \rightarrow M$ for cooling and $R \rightarrow P$, $M \rightarrow P$ for heating.

(2) The crystallization annealing temperature obviously affects the martensitic transformation temperature, T_{R-M}, which is raised with increasing crystallization temperatures; but it has no obvious influence on R phase transformation.

(3) A micro-structure consisting of almost whole R phase can be easily obtained in the Ti-rich NiTi SMA thin films through appropriate crystallization treatment, which has a good SME and narrow hysteresis.

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