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Differences of transformation behavior between Ni-rich TiNi shape memory films and alloys①

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[Abstract] The differences of transformation behavior between Ni-rich TiNi shape memory film (SMF) and shape memory alloy (SMA) age-treated at 773 K after solution-treatment at 973 K have been investigated, using Ti-51.5Ni thin film and Ti-51.5Ni bulk alloy as examples, by differential scanning calorimetry (DSC), SEM and EDX. It is found that the age-treated Ni-rich TiNi SMF and SMA are of the same types of transformation, i.e., $A \rightarrow R \rightarrow M$ (during cooling), and $M \rightarrow A$ (during heating) (A: parent phase; R: R-phase; M: martensite); the transformation temperature of the TiNi SMF is lower than that of the SMA, but the SMF's hysteresis is larger. The transformation heat of the TiNi SMF and SMA is nearly the same. The reason that TiNi SMF's strain is sensitive to temperature is not hysteresis, but its thickness is thinner, and the temperature is easy to distribute homogeneously.

[Key words] TiNi thin film; TiNi alloy; shape memory film; shape memory alloy; transformation temperature; transformation heat; temperature hysteresis

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1 INTRODUCTION

TiNi shape memory materials can be made into bulk (wire, ribbon etc) and thin film states based on their applications. The bulk alloys are prepared by vacuum induction melting method or an electron beam melting method, and used to make conventional heat-sensitive elements[1]. Thin films are prepared using a sputter-deposition technique, and used to fabricate microactuator and micro electro mechanical systems[2]. Both have excellent shape memory effect (SME) and superelasticity (SE)[1~4]. The phase transformations are the basis of the SME and SE. The effects of the Ni content and heat treatment on microstructure and transformation behavior of TiNi shape memory alloys (SMA)[5~9] and shape memory films (SMF)[3,10] have been investigated. The results show that the near equiatomic and Ni-rich TiNi SMF and SMA have similar properties of microstructure and SME[2]. The near equiatomic TiNi SMF and SMA have higher $A \rightarrow M$ transformation temperature (T_M) (A: parent phase B2, CsCl-type structure; M: martensite B19′, monoclinic distortion of B19 structure). The T_M of Ni-rich TiNi SMF and SMA decreases with increasing Ni content. The near equiatomic TiNi SMF and SMA are precipitate-free after aging, but in the Ni-rich ones the precipitates of Ti_3Ni_4 and Ti_2Ni_3 are observed[8]. After aging, or after deformation-medium temperature annealing, $A \rightarrow R$ transformation takes place in both of the TiNi SMF and SMA (R: intermediate phase, rhombohedral structure). There are some differences between TiNi SMF and SMA, especially for Ti-rich alloys. After annealing Ti-rich TiNi SMF shows different shape memory behavior from those of the SMA specimens[11,12].

The conclusions above, however, were got by indirect comparison of the results given by various specimens which probably are of different Ni contents, and the direct comparison study on differences of transformation behavior between Ni-rich TiNi SMF and SMA, in which both of them possess the same Ni content and heat treatment processes have not been reported. In the present paper, the comparison of the transformation behavior of Ti-51.5Ni SMF and SMA after aging will be discussed since the age-treatment is an effective process to produce the two-way and the all-round SME[13].

2 EXPERIMENTAL

TiNi SMF was prepared by a RF(radio frequency) magnetron sputtering method using a Ti-50.0Ni target of 4-inch diameter. The films were deposited on glass substrates, substrate-to-target distance, 80 mm, and the

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deposited rate was 1.2 nm/s, the film thickness ranged from 8 to 9 μm. Films with different alloy compositions were prepared by changing a number of small Ti plates put on the TiNi target sequentially, respectively.

TiNi SMA was prepared from 99.7% sponge Ti and 99.9% electrolytic Ni by arc melting in an argon atmosphere. The ingots were melted and remelted at least six times for homogenization. Pure titanium buttons were also melted and used as a getter.

The Ni-content of the SMF and SMA used in this study was 51.5% (mole fraction) by electron microprobe analysis, respectively. The SMF and SMA specimens were annealed at 973 K for 1 h (solution treatment) in evacuated quartz capsules and quenched into ice water by breaking the capsules, and the age-treatment was carried out in evacuated quartz capsules at 773 K for 1, 10, and 100 h, respectively, and then quenched into ice water without breaking the capsules. The differences of the transformation behaviors (the transformation temperature, temperature hysteresis, and transformation heat, etc) of the TiNi SMF and SMA were analyzed by differential scanning calorimetry (DSC) using a Shimadzu DSC-50, respectively. The sizes of DSC specimens for the SMF and SMA were 9 μm × 3 mm × 3 mm and 2 mm × 3 mm × 3 mm, respectively. The temperature range was 150~ 400 K with a heating/cooling rate of 10 K/min. Let DSC peak temperature T_R represent temperature of R-phase transformation, and T_M, and T_A represent temperatures of M-transformation temperature and reversion, respectively. The specimens for SEM were mechanically polished, etched with the solution of $V(\mathrm{HF}):V(\mathrm{HNO_3}):V(\mathrm{N_2O}) = 1:4:5$, and observed by SEM and EDX with S-2700.

3 RESULTS

3.1 DSC curves

After aging at 773 K for 1, 10, 100 h, respectively, the DSC curves of Ti-51.5Ni SMF and SMA are shown in Fig. 1. It can be seen that the age-treated Ni-rich TiNi SMF and SMA possess the same transformation type: $A \rightarrow R \rightarrow M$ (during cooling) and $M \rightarrow A$ (during heating), which reveals two stage transformation, i.e., the R-phase transformation for the first stage and the martensitic transformation for the second stage upon cooling, and reveals only the reverse martensitic transformation from the martensitic phase to the parent B2 phase upon heating. The shifting rate of the M and A peaks of the SMA towards higher temperature is larger than that of the SMF, and the peak size and shape are nearly not changed with increasing aging time (t_A). The characteristics of R-phase transformation peak for the Ti-Ni SMF and SMA are nearly the same.

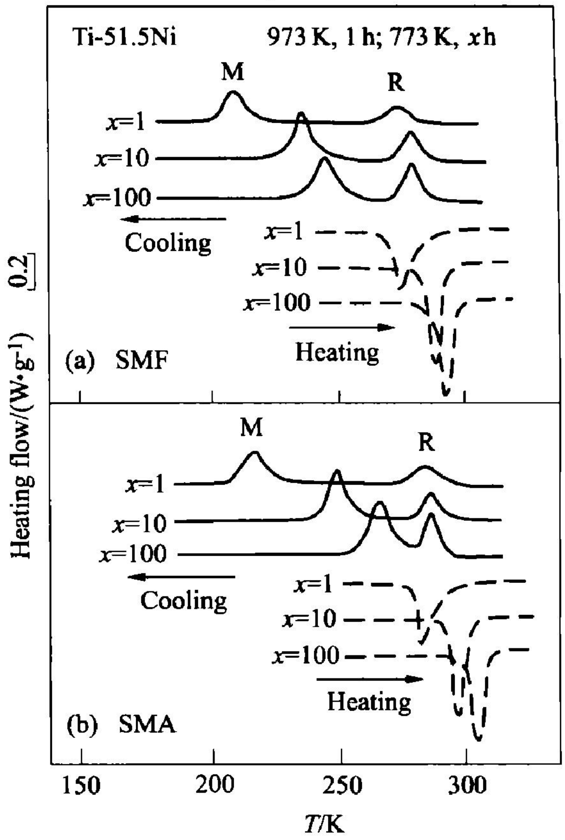

Fig. 1 DSC curves of age-treated Ti-51.5Ni SMF (a) and SMA (b)

3.2 Transformation temperature, temperature hysteresis and transformation heat

The effects of t_A on the transformation temperature, temperature hysteresis, and transformation heat of Ti-51.5Ni SMF and SMA are shown in Fig. 2. It can be seen in this Figure, 1) aging at 773 K, the T_R temperature increases slowly, and the T_M temperature increases rapidly with increasing t_A; 2) the transformation temperatures of the SMA specimens are higher than that of the SMF,

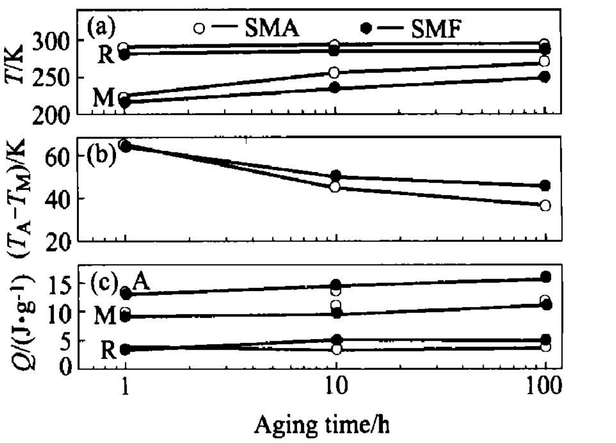

Fig. 2 Effect of aging time on transformation temperature (a), hysteresis (b) and transformation heat (c) of Ti-51.5Ni SMF and SMA

i. e. $T_R^a > T_R^f$, $T_M^a > T_M^f$, and $T_A^a > T_A^f$ (a—alloy, f—film), and the difference of the T_M temperature between the SMF and SMA increases with increasing t_A (Fig. 2(a)).

The dependence of the M-transformation hysteresis ($T_A - T_M$) on t_A for TiNi SMF and SMA is shown in Fig. 2(b). It can be seen that, 1) the temperature hysteresis decreases with increasing t_A; 2) as t_A = 1 h, the temperature hysteresis of TiNi SMF and SMA is the same, and as t_A > 1 h, the SMF's hysteresis is larger than that of the SMA. The difference of temperature hysteresis between Ti-51.5Ni SMF and SMA increases with increasing t_A.

The effect of t_A on the transformation heat of Ti-51.5Ni SMF and SMA is shown in Fig. 2(c). 1) The transformation heat, Q_R, Q_M, and Q_A, all increase with increasing t_A; 2) $Q_R^f > Q_R^a$, $Q_M^a > Q_M^f$, $Q_A^f \approx Q_A^a$; 3) as t_A = 1 h, the difference of transformation heat between the SMF and SMA specimens reaches the least.

3.3 Microstructure

The microstructure of Ni-rich TiNi SMF is similar to that of the SMA after aging treatment[8, 13]. The typical microstructure and EDX pattern for Ti-51.5Ni alloy after aging at 773 K for 1 h are shown in Fig. 3. It can be seen that the precipitates present within the grain or at the grain boundary. The morphology of the precipitates within the grain is needle, or point state, and the ones at the boundary are lump state. The needle and point precipitates are Ti_3Ni_4 (Fig. 3(b)), and the lump ones are Ti_2Ni_3 base on the EDX results (Fig. 3(c)).

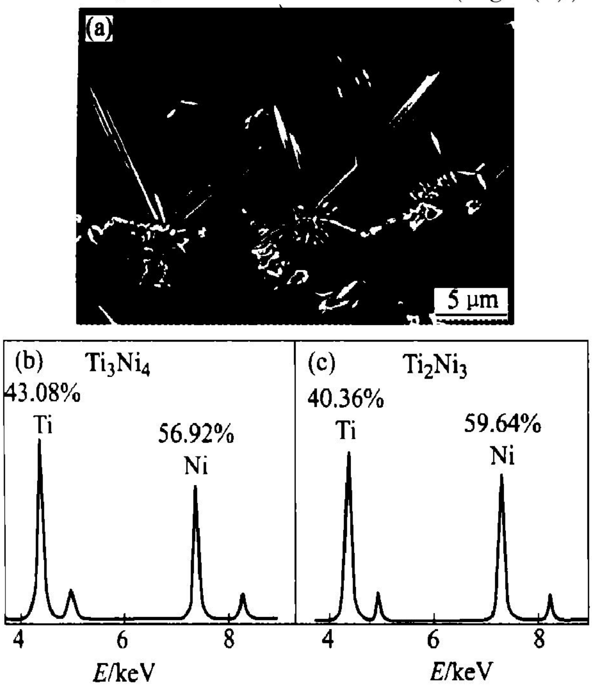

Fig. 3 Microstructure (a) and EDX patterns of Ti-51.5Ni SMF(a) and SMA(c) after aging at 773 K for 1 h

4 DISCUSSION

After the same processes of solution- and aging-treatment, Ni-rich TiNi SMF and SMA show the same transformation type. The transformation characteristics (i. e., the transformation temperature, temperature hysteresis, and transformation heat, etc) of Ni-rich TiNi SMF and SMA are sensitive to alloys' preparation methods and heat-treatment processes.

When TiNi SMFs are prepared using the sputter-deposition technique, the amorphous thin films will be got first, and the sputtering process is liable to introduce defects such as vacancies, voids, impurities, and need to be solution-treated to crystallize and to reduce or eliminate defects[14, 15]. The grain size of the thin film after solution-treatment is very small, i. e., about 1 μm, and the grain size of the solution-treated bulk TiNi SMA prepared by melting is larger than that of the SMF. Since the amount of grain boundaries of the SMF is more, and the boundary has a constrained action on the thermoelastic martensite transformation, so the transformation temperatures of the TiNi SMF are lower than those of the SMA.

After Ni-rich TiNi SMF and SMA were aging-treated at 773 K following the solution-treatment at 973 K, the $A \rightarrow R \rightarrow M$ (during cooling) and $M \rightarrow A$ (during heating) took place. R-phase transformation in TiNi SMF and SMA is very stable, and is not sensitive to microstructure and stress field, so the difference of the T_R temperature between the SMF and SMA is very small, and the T_R increases slightly with increasing t_A. The martensitic transformation is very sensitive to the composition, microstructure and stress field. After aging at 773 K for short time, the Ni-rich coherency precipitates appeared, which caused larger strain, and hindered the martensitic transformation, so that the T_M temperature is lower. With increasing aging time, the precipitates grow to a large size and lose coherency and cannot generate sufficient internal stress fields to control martensitic transformation, therefore the T_M temperature increases[16]. On the other hand, the precipitates on aging caused a depletion of nickel in the matrix, which also leads T_M to rise[5].

Furthermore, with increasing t_A the increment of the M-transformation temperature is larger than that of reverse, and the increased range of the T_M temperature for the SMA is larger than that of the SMF, so the temperature hysteresis of the SMA is smaller than that of the SMF. If only hysteresis is considered, the TiNi SMA should be more sensitive to temperature than the SMF, but, as for the response degree of TiNi the SMF to changing temperature is larger than that of the SMA. Therefore, the reason of the TiNi SMF's strain is more sensitive to the temperature than that of the SMA is not temperature hysteresis, but the effective thickness of the specimens. The thickness of the SMF's specimen is μm rank and the SMA's is mm. Since the thickness of the SMF is very thin, and the temperature is easy to contribute homogeneously as the temperature changes, so the shape-change of TiNi SMF is very sensitive to the temperature-change.

Transformation heat is a function of the phase-transformed fraction. Both the SMF and SMA have the same conditions of the composition, temperature, and pressure with which the phase transformation can be completed, so the transformation heat of Ti-51.5Ni SMF and SMA is almost the same.

5 CONCLUSIONS

1) Age-treated Ni-rich TiNi SMF and SMA possess the same transformation type: $A \rightarrow R \rightarrow M$ (during cooling), and $M \rightarrow A$ (during heating).

2) The transformation temperature of the SMF is lower than that of the SMA, but the SMF's temperature hysteresis is larger. The transformation heat of both materials is nearly the same.

3) The reason that TiNi SMF's strain is sensitive to temperature is not temperature hysteresis, but its thickness is thinner, and the temperature is easy to distribute homogeneously.

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