

Effect of Heat Treatments on Microstructures and Shape Memory Effect in TiNi Foils Produced from Ultrafine Laminates

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The effect of aging on transformation temperatures, shape memory behavior, multi-stage martensitic transformation and precipitation process was studied on Ni-rich TiNi foils with 50 μm thickness produced from ultrafine laminates. Overall composition of the Ti/Ni laminate was Ti-50.7%Ni. TiNi (B2) phase was obtained after diffusion treatment at 1073 K for 36, 259.2 and 518.4 ks. Aging treatments at 773 K for 3.6, 18, 36, 72 and 144 ks were also performed. Multiple step martensitic transformation was observed for aged samples. The martensite transformation temperature showed a marked increase for short-term aging, no increase for medium-term aging and a slight increase for long-term aging. The shape memory strain was 3.69×10^{-2} in the sample aged at 773 K for 18 ks.

Key words: shape memory alloys, multilayer, martensitic transformation.

1. INTRODUCTION

The functional property of the equiatomic TiNi shape memory alloy is based on the superior shape memory property that make it used in a wide range of applications. However, the high working hardening rate induces a low plastic workability especially in Ni-rich TiNi alloys and all mechanical processing including rolling are difficult to apply. Using a complex annealing procedures, the TiNi thin sheets can be obtain but with a high cost of production.

Other possible method to produce TiNi thin sheets is to use multilayers of pure Ti and Ni. Production of Ti/Ni multilayers by rolling has been done starting from the elemental powders [1] or from the foils of pure metals [2]. Crone *et al.* have shown that TiNi obtained by the heat treatment of multilayered Ti/Ni exhibits a composite behavior of superelastic and shape memory effect [2]. This method can be extended to produce the multilayered materials in a large quantity. Sasaki *et al.* have successfully produced the Fe/Cu multilayered foils in a large quantity using conventional rolling by ultrafine laminates method [3].

The shape memory characteristic of nearly equiatomic Ti-Ni alloys can be improved by aging treatments. The reason of this resides in the formation of Ti_3Ni_4 precipitates. Thus, many investigations have been focused on the influence of aging on shape memory properties of TiNi alloys. However, the effect of aging is complicated and further investigation should be engaged for a complete understanding of this phenomenon especially for the multiple step martensitic and R-phase transformation.

In the present study, the effect of aging on transformation temperatures, shape memory behavior, multiple step martensitic and R-phase transformation and precipitation process was studied on Ni-rich TiNi foils with 50 μm thickness produced *via* ultrafine laminates method.

2. EXPERIMENTS

Details of production method of Ti/Ni ultrafine laminates can be found in our previous article [4]. The thickness of the laminate foils used in this study was 50 μm . The overall composition of the laminates was Ti-50.7at%Ni.

In order to obtain the TiNi phase, the as-rolled Ti/Ni laminate foils were subjected to a slow diffusion treatment to 1073 K and kept for 36, 259.2 and 518.4 ks in a vacuum furnace. The slow heating was adopted to prevent the sample from irregular bending due to the difference in thermal expansion coefficients of Ti and Ni. Separated groups of the foils were further aged at 773 K for 3.6, 18, 36, 72 and 144 ks.

Microstructures of the as-rolled foils and those after the diffusion treatment were observed in a JEOL JSM-6500F field emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) observations were made using Hitachi H-800 operated at 200 kV. Disc specimens of 3 mm diameter were cut and electropolished using Struer Tenupol-3 at 253 K with H_2SO_4 :methanol (2:8 in volume) electrolyte with an applied voltage of 10 V. A Rigaku DSC-8230L differential scanning calorimeter (DSC) was used to determine transformation temperatures for the aged samples under a flow of argon gas in the temperature range from 123 K to 473 K with heating/cooling rate of 0.16 Ks^{-1} . Transformation temperatures were determined by an intersecting slopes method on transformation peaks.

The shape memory effect of the foils was measured by bending test. Heat treated foils (0.05 x 5 x 30 mm) were bended to give 5 % surface strain and in a fully martensitic state (at liquid nitrogen temperature) recovery strain was measured after heating to 373 K. The sample curvatures at different temperatures were recorded by a digital camera in order to measure the radii and to calculate the recovery strain.

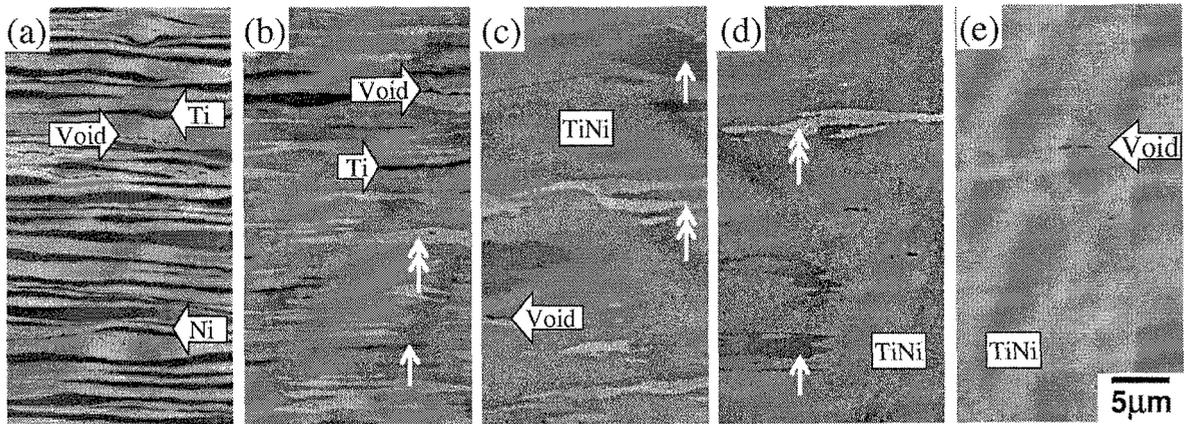


Fig. 1 SEM micrographs of cross section of the Ti/Ni ultrafine laminates at various stages of diffusion treatments: (a) 773 K, (b) 873 K, (c) 973 K, (d) 1073 K and (e) 1073 K for 36 ks; (Ti₂Ni marked by white single-headed arrows, TiNi₃ marked by white double-headed arrows).

3. RESULTS AND DISCUSSIONS

Shown in Fig. 1 are SEM micrographs of Ti/Ni laminate at the various stages of the diffusion treatments. We observed the onset of changes in the microstructure after heating up to 773 K (Fig. 1 (a)). The EDX analysis revealed that the formation of Ti₂Ni indicated by the white single-headed arrows, TiNi₃ indicated by the white double-headed arrows and TiNi phase after heating to 873 K (Fig. 1 (b) and (c)). In Fig. 1 (a) and (b), voids are seen around the Ni layers or in the TiNi₃ phase. Our previous investigation of the diffusion process using a sample with Ti and Ni layers of 10 µm thick clearly indicated that the voids form in the Ni side of the Ni/Ti interface [5]. The diffusion coefficient data [6] for Ni in α-Ti is several orders of magnitude higher than that of Ti in Ni. Thus, the observed voids are most likely the Kirkendall voids. The longer diffusion treatment caused an increase in the volume fraction of TiNi phase (Fig. 1 (c) and (d)). A homogeneous structure with TiNi phase was obtained after 36 ks at 1073 K (Fig. 1 (e)).

The DSC curves of the TiNi foils before and after aging at 773 K for various aging times are presented in Fig. 2. The sample diffusion treated at 1073 K for 259.2 ks did not show any characteristic of phase transformations as can be seen in the DSC traces shown at the bottom. For the samples after short (3.6 ks and 18 ks) and long (144 ks) time aging treatments the DSC curves on cooling show the first peak (marked as R* at around 288 K, which corresponds to the transformation of the austenite into the R-phase. On further cooling this phase is transformed into the B19' martensite as is shown by the appearance of the second peak (marked as M₁*). The curves obtained on heating are characterized by a single peak which corresponds to a reverse transformation from the martensite to austenite. We will refer to this type of behavior as two steps transformation. For the sample after intermediate time (36 ks) aging treatments, the DSC curve exhibits different transformation behavior. The first peak corresponds to the appearance of the R-phase, and on further cooling two peaks, marked as M₁* and M₂*, appear. The curves obtained on heating are also characterized by a single peak which corresponds to the

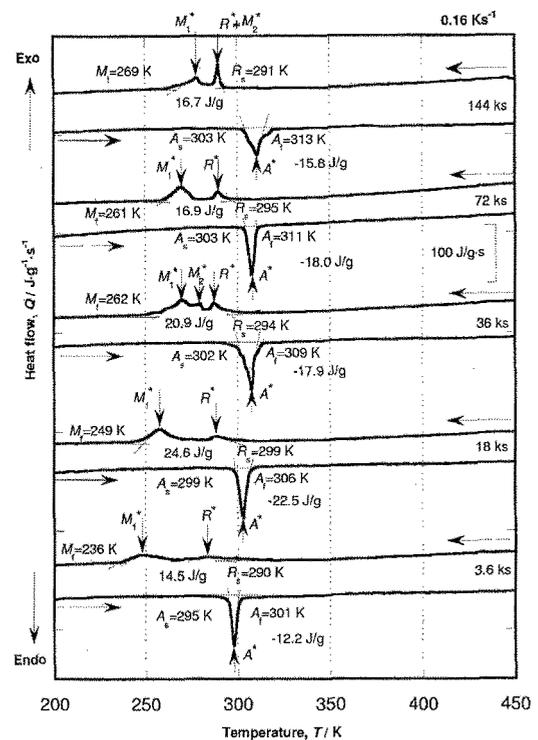


Fig. 2 DSC curves of Ni-rich TiNi foils diffusion treated at 1073 K for 259.2 ks and aged at 773 K for various times.

reverse transformation from the martensite to austenite. We will refer to this as three steps transformation behavior. Fig. 3 is the summary of transformation temperatures M_f, A_s, A_f, A*, R* and M₁* (marked in Fig. 2 with arrows) as a function of aging time. The A_s, A_f, A*, M₁* and M_f temperatures increase with aging time but the increase was less pronounced for A*, A_s and A_f. The R* peak temperature is almost constant irrespective of the aging time. This tendency is similar to the one obtained by Honma [7] and data for 673 K aging by Khalil Allafi *et al.* [8] but is different from the data for 773 K aging [9]. In the latter, M₁*, R* and A* increased parallelly, and more than one peak was observed on

heating. The temperature difference between M_1^* and R^* decreases with aging time. Longer aging times resulted in about a 30 K increase in the M_1^* temperature.

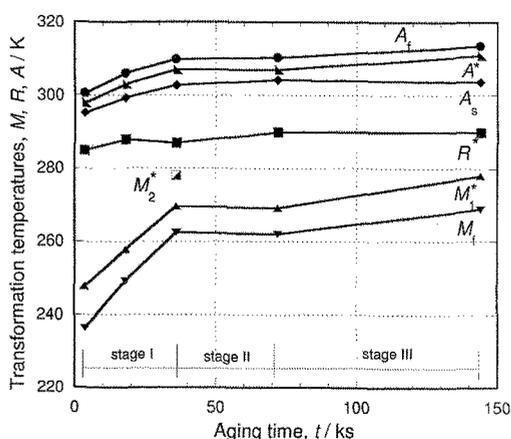


Fig. 3 Variation of transformation temperatures as a function of aging time.

The TEM observations of the foils after the diffusion treatment at 1073 K for 259.2 ks revealed that the B2 grain size is about 10 μm as shown in Fig. 4 (a).

In Fig. 4 (b) it can be seen that Ti_3Ni_4 lenticular precipitates are uniformly distributed with the average size of 100 nm. The precipitates were distributed uniformly throughout the interior of the grains, and the preferential distribution at the grain boundaries [10] was not observed. In Fig. 4 (c) the precipitates increased their size to about 200 nm and exhibit a tendency to align along the traces of three planes, $(\bar{1}11)$, $(1\bar{1}1)$ and $(11\bar{1})$. The aging treatment for 144 ks produced precipitates with the size bigger than 400 nm (Fig. 4 (f)).

Evolution of DSC profiles during aging of Ni-rich TiNi alloys has been subjected to many investigations. Origin of multi step transformation has been discussed with respect to the coherency stress field [11, 12] around Ti_3Ni_4 precipitates and to the development of Ni concentration gradient due to the precipitation [9]. Peculiar three steps transformation was also observed in the present investigation after aging at 773 K for 36 ks. In the following the origin of this evolution will be assessed with reference to the results of the previous investigations. In Fig. 3 the M_f and M_1^* temperatures have three stages evolution with the aging time. In the first stage there is a marked increase in the martensitic transformation temperature for sample aged for 3.6 ks to 36 ks. In this stage of aging, Ti_3Ni_4 precipitates are fine (100 ~ 200 nm) and are coherent with the B2 matrix. Thus they produce the coherency stress field around them. Previous investigations on the effect of Ti_3Ni_4 precipitates on phase transformation [13], and on the two way shape memory effect [7, 14] seem to point that Ti_3Ni_4 precipitates have the most significant effects when the samples are aged at about 780 K for 1-2 hours, leading to the precipitates size of about 100 ~ 200 nm. The observed increase in M_1^* and M_f in the first stage was about 25 K.

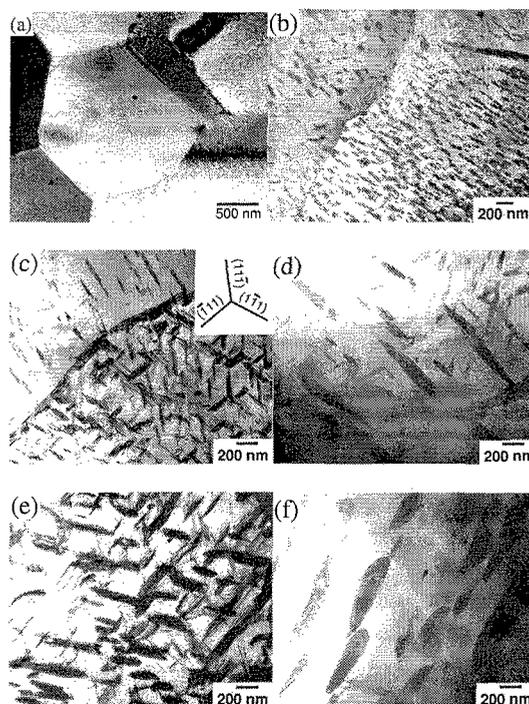


Fig. 4 TEM photographs of the foils (a) without aging, aged for (b) 3.6 ks, (c) 18 ks, (d) 36 ks, (e) 72 ks and (f) 144 ks.

Following the analysis based on the Clausius - Clapeyron equation by Bataillard *et al.* [12], the stress field required to cause the observed M^* increase is about 96 MPa, which seems to be reasonable value to explain the M_1^* increase. Thus the significant part of the observed M_1^* and M_f increase in the first stage is due to the stress field caused by the Ti_3Ni_4 precipitation. Although there may be some contribution from the decrease in Ni content in the matrix due to the precipitation, the contribution must be very small since the R^* temperature is almost constant, which is less sensitive to the stress field and obeys the similar dependence on Ni concentration to that for M_s [15]. Another characteristic of the DSC profiles in the stage I is that the transformation peaks for forward transformation is broader than that for the reverse transformation. Particularly the onset of the first peak (assigned to R phase transformation) is not very clear but seems to be very high. This may be due to the inhomogeneous size distribution of the precipitates and also interaction of stress field of the neighboring precipitates since they are very closely spaced in the first stage of aging. The maximum transformation heat was observed for the sample aged for 18 ks. This indicates that the transforming volume increases during aging up to 18 ks due to the increase of the volume affected by the internal stress of the precipitates, and decreases after 18 ks due to the increase in the volume fraction of precipitates.

At the end of the first stage (36 ks aging), three steps transformation was observed on cooling and a single peak with some indication of shoulders on heating. The size of the larger precipitates is about 600 nm (Fig. 4 (d)). Thus the effect of coherency stress field becomes less significant and more dominant effect can be

expected from the gradient in Ni concentration around the precipitates. Thus the multi step transformation may be attributed to the steep concentration gradient around the precipitates as proposed by Khalil Allafi *et al.* [9].

In order to understand the two steps transformation evolution for short and long time aging treatment and three steps transformation for intermediate time aging treatment on cooling Khalil Allafi *et al.* [9] have taken two factors into consideration. The first factor is the inhomogeneous Ni distribution evolution during aging which affect the local phase transformation temperature. The second is the different transformation barriers for R-phase and B19'.

More recent explanation by Khalil-Allafi *et al.* [10] attributes the two peaks to the different transforming region in the sample, that is, the higher temperature one to the region near the grain boundary where a high density of Ti_3Ni_4 was observed and the lower one to the grain interior where less precipitates were found. Contrary to the results of their TEM observation, the present results did not reveal such heterogeneous distribution of the particle. This may be due to the smaller grain size, 5 μm in the present material unlike 35 μm in [10].

In the end of the second stage the transformation again become two step. A slight increase in the R^* can be seen. In the third stage, M_1^* increased for about 9 K. At the end of the third stage (144 ks) the first peak on cooling was more pronounced than the second one, and the reverse transformation peak is somewhat broader and exhibits a shoulder in the higher temperature side. This indicates the first peak on cooling is not only from the R-phase but may also include some B19' transformation and suggests that some region with higher transformation temperature formed. Nishida *et al.* studied the process of phase decomposition process of non-equilibrium B2 TiNi into the equilibrium state of TiNi and $TiNi_3$ [16]. The decomposition path was characterized as: β (B2) \rightarrow β_1 (B2) + $Ti_{11}Ni_{14}$ (Ti_3Ni_4) \rightarrow β_2 (B2) + Ti_2Ni_3 \rightarrow β_3 (B2) + $TiNi_3$. Thus the increase in M_1^* might be due to the formation of Ni depleted region by the evolution of precipitates from Ti_3Ni_4 toward Ti_2Ni_3 . Further investigation is necessary to fully understand this complex evolution of DSC profiles during aging.

In order to quantify the shape memory effect we measured the diameters of the foils bent in the martensitic state at the liquid nitrogen temperature and after heating at 373 K. Based on these experimental results the highest value of recovered strain was measured for sample diffusion treated to 1073 K for 259.2 ks and aged to 773 K for 18 ks and was 3.69 %. The transformation heat of this sample is 24.6 J/g which is comparable with those of bulk TiNi alloys [17].

4. CONCLUSIONS

Using ultrafine laminates method 50 μm foils of Ti-50.7at%Ni were successfully produced. After diffusion treatment at 1073 K and 1173 K for 36 and 259.2 ks TiNi B2 phase was obtained. The diffusion treatment was followed by aging treatment at 773 K for different times in order to study the Ti_3Ni_4 precipitates process and to analyze their influence on transformation temperature and shape memory effect.

The R-phase transformation temperature was found to be almost constant irrespective of the aging time. The martensite transformation temperature has a noticeable increase for short-term aging, a constant evolution for medium-term aging and a slight increase for long-term aging.

Two steps transformation in the samples after short and long time aging treatment and three steps transformation after intermediate time aging treatment was observed in aged Ni-rich TiNi ultrafine laminates foils.

The value of transformation heat 24.6 J/g of aged sample at 773 K for 18 ks is comparable with those of bulk TiNi alloys. The average size of the Ti_3Ni_4 precipitates for the foil with the highest recovery strain was 100 nm.

The largest recovered strain of the sample diffusion treated to 1073 K for 259.2 ks and aged at 773 K for 18 ks was 3.69 %.

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