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Two-Way Shape Memory Effect in Ni-Rich Ti-Ni Foils Produced From Ultrafine Laminate

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Using the ultrafine laminate method, thin foils (50 μm) of Ni-rich TiNi shape memory alloys were produced. Overall composition of the Ti/Ni laminate is Ti-50.7%Ni. TiNi (B2) phase was obtained after diffusion treatment at 1073 K for 36 ks. The constrained aging at 773 K was also done. Multiple step martensitic transformation was observed for aged samples. The shape memory strain was 5.5×10^{-2} and two-way shape memory strain was 4×10^{-3} in the sample after constrained aging at 773 K for 36 ks.

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

1. INTRODUCTION

Nearly equiatomic Ti-Ni alloys are well-known as the most excellent shape memory alloys for their outstanding shape memory characteristics. Application of Ti-Ni alloy has been limited by their low plastic workability due to a high work hardening rate. Production of thin sheets or foil by conventional rolling requires complex annealing procedures that lead to high cost of materials.

The production of multilayered structure composed of pure Ti and Ni layers can be accomplished by rolling a stack of elemental sheets of metals [1]. Sasaki *et al.* have successfully produced the Fe/Cu multilayered foils of 5 tons using conventional rolling facility by ultrafine laminates method [2]. In the present study, we have applied the ultrafine laminates method to produce thin foils of Ni-rich TiNi shape memory alloy. This paper will describe the microstructure, phase transformation and two-way shape memory behavior of obtained Ni-rich TiNi foils.

2. EXPERIMENTS

In our previous article we introduced the production method of ultrafine laminates [3]. The thickness of 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 Ti/Ni laminate foils were subjected to a diffusion treatment at 1073 K for 36 ks. The foils were then aged at 773 K for different periods of times as illustrated in Fig. 1.

Microstructures of as-rolled foils and those after the diffusion treatment were observed in a JSM-6300 scanning electron microscope (SEM).

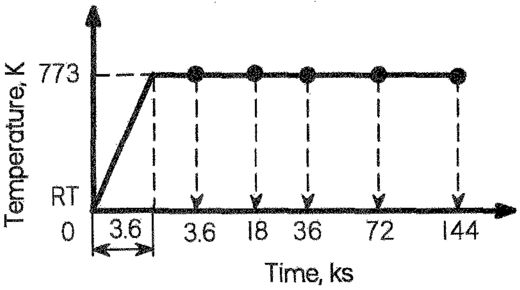

Fig.1 Aging treatment diagrams.

Transmission electron microscopy (TEM) observations were made using Hitachi H-800 operated at 200 kV. The specimens were electropolished using a Tenupol-3 at 253 K with H_2SO_4:methanol = 2:8 electrolyte at 40 V. Samples were taken at the different stages of aging treatment denoted by the circles in Fig. 1.

Transformation temperatures were measured by differential scanning calorimetry (DSC) using Rigaku DSC-8230L 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}.

3. RESULTS AND DISCUSSIONS

Fig. 2 shows a SEM micrograph of a longitudinal section of the Ti/Ni ultrafine laminates. Intermetallic compounds, possibly Ti_2Ni, TiNi and $TiNi_3$ were occasionally observed at the interface between the Ti and Ni layers.

A homogeneous TiNi phase was obtained after the diffusion treatment at 1073 k for 36 ks. In Fig. 3 is shown the SEM micrograph of sample after this diffusion treatment. The Kirkendall voids are occasionally seen.

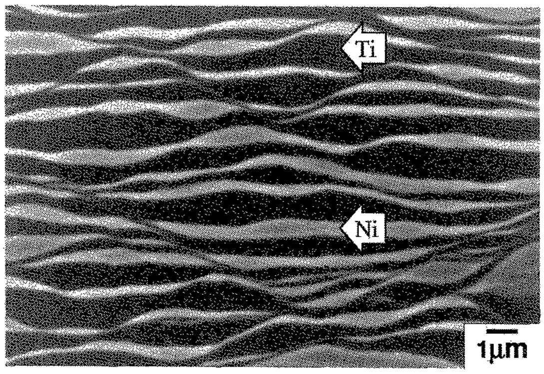

Fig. 2 SEM micrograph of longitudinal section of the Ti/Ni ultrafine laminate.

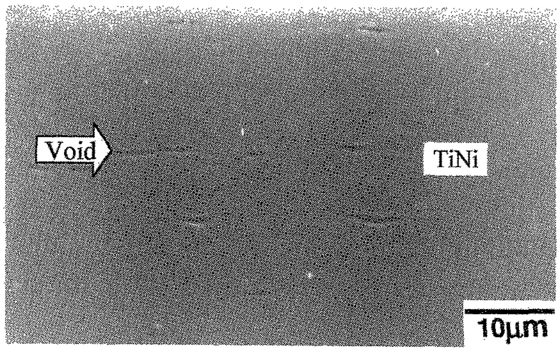

Fig.3 SEM micrograph of Ni-rich TiNi foils diffusion treated at 1073 K for 36 ks.

The DSC curves of the TiNi foils with and without aging are presented in Fig. 4. There are three characteristic features that change with aging: (1) the type of transformation changes from three steps (after 3.6, 18 and 36 ks) to two steps (after 72 and 144 ks); (2) there is an additional transformation, marked in Fig. 4 with triangles, at about 345 K which is M_S temperature in Ti-rich alloys [4]; (3) there are shifts in the transformation temperature.

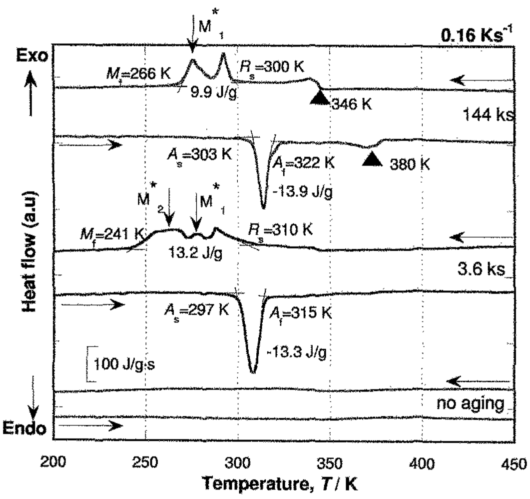

Fig.4 DSC curves of Ni-rich TiNi foils aged for 773 K for different times.

Khalil-Allafi *et al.* also found a similar evolution in DSC analysis of bulk TiNi [5]. It is known that three distinct DSC peaks on cooling always correspond to the formation of R-phase (R_s = 310 K, B2 to R-phase, first distinct DSC peak) followed by a transformation from R-phase to B19' (M_f = 241 K, second distinct peak). The one step reverse transformation was recorded on heating from B19' to B2 phase (A_f = 315 K). The reasons of this evolution were explained by Khalil-Allafi as follows: (1) the composition inhomogeneity that evolves during aging as Ti_3Ni_4 precipitates grow. (2) The difference between nucleation barriers for R-phase (small) and B19' (large). Based on these two elements they were able to rationalize the evolution of DSC charts; but they did not consider the features of the reverse transformation on heating [6].

Fig. 5 is a summary of aging time dependence of transformation temperature R_s, M_f, A_s, A_f and temperature peaks M^*_1 and M^*_2 marked in Fig. 4 with arrows. The A_s, A_f and M_f temperatures increase with increasing aging time. The R_s temperature increases for a short time aging and then decrease with increasing the aging time. The peaks M^*_1 and M^*_2 merge after 144 ks aging. The phase transformation occurs within 80 K temperature range upon cooling and 17 K upon heating.

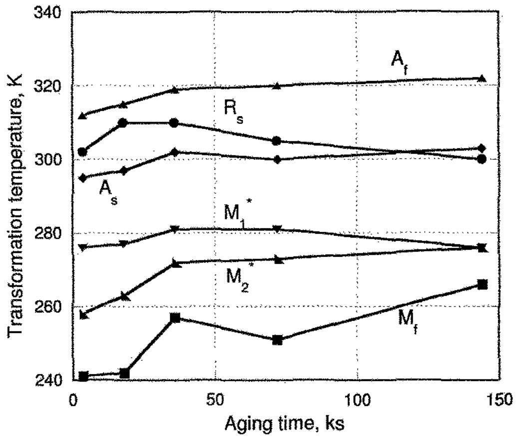

Fig.5 Variation of transformation temperatures as a function of aging time.

In Fig. 6 the microstructures are shown after aging treatment at 773 K. TEM observation of specimen without aging revealed that the B2 grain size is about 1μm as shown in Fig. 6 (a). In Fig. 6 (b) it can be seen that the lenticular Ti_3Ni_4 precipitates are uniformly distributed and aligned along two directions. The average size of these precipitates is less than 100 nm. Fig. 6 (c) corresponds to the sample aged for 18 ks. In the sample aged for 144 ks average size of the precipitates is larger than 500 nm as shown in Fig. 6 (d).

Kaimura *et al.* reported "all-round" shape memory behavior in Ni-rich TiNi alloys after constrained aging [8]. They have concluded that the stress field around the lenticular Ti_3Ni_4 precipitates is responsible for regaining the same variant arrangement as before reverting to the parent phase. In the present investigation sample does not exhibit "all-round" shape memory effect although some shape change toward flat shape on cooling was observed.

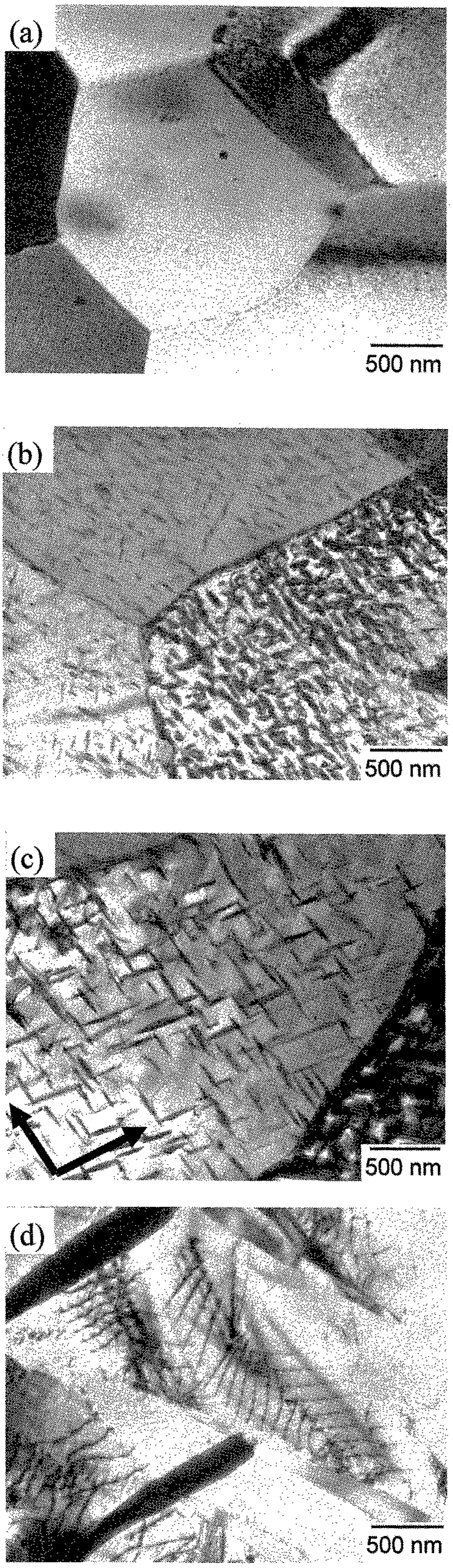

Fig.6 TEM photographs of the specimens (a) without aging, aged for (b) 3.6 ks, (c) 18 ks, and (d) 144 ks.

In stead, it was found that the deformation in martensite significantly enhances the two-way memory in the constrain aged sample, as show in Fig.7.

First, the aged foil was bent to a reverse curvature at LN_2 temperature (Fig. 7(a)). Upon heating the sample regain the original curvature (Fig. 7 (b)). Upon cooling (Fig. 7 (c)) the foil tends to change the shape to the deformed shape in Fig. 7(a) again. The detail of this enhancement of two-way memory by deformation is in progress.

The maximum shape memory effect for specimen aged for 36 ks was 5.5×10^{-2}. This value is comparable with that obtained for Ni-rich TiNi bulk sample [7]. The value for two-way shape memory effect was 4×10^{-3} in the sample aged for 36 ks.

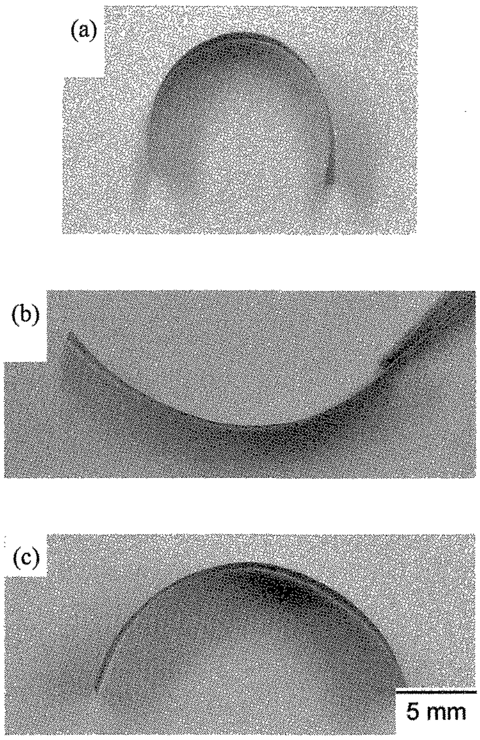

Fig. 7 Shape change in Ti-50.7at%Ni aged for 36 ks at 773 K. a) bent at 173 K, b) heated to 373 K and c) cooled to 173 K.

In order to prove the possibility of fabrication of three dimensional (3D) actuator, a sample was constrained in the shape of flower and aged. The results of this experiment are shown in Fig. 8. In Fig. 8 (a) the foil was flat at temperature below 273 K in martensite phase. By heating the sample to 373 K, the "flower" like shape was regained (Fig. 8 (b) and (c)). After cooling to below 273 K the foils tend to open toward the flat shape. (Fig. 8 (d) and (e)). Based on this experiment we can draw the conclusion that shape memory effect is isotropic and the curvatures with different radii can be recovered.

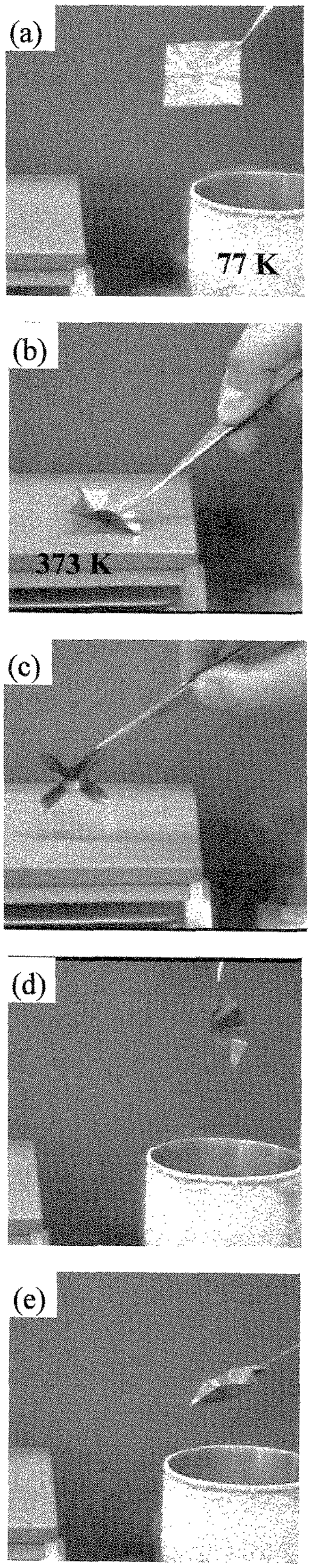

Fig. 8. Two-way shape memory effect in Ni-rich TiNi foils after aging treatment at 773 K for 36 ks: (a) flattened below 273 K, (b) during heating, (c) after heating at 373 K, (d) during cooling and (e) cooling below 273 K.

4. CONCLUSIONS

Using ultrafine laminates method 50 μm foils of Ti-50.7at%Ni were produced. After diffusion treatment at 1073 K for 36 ks TiNi B2 phase was obtained. The diffusion treatment was followed by aging treatment at 773 K in order to produce Ti_3Ni_4 precipitates.

In this study it was revealed that these TiNi foils have a shape memory response comparable to that in TiNi bulk materials. Two-way shape memory strain of $4x10^{-3}$ was realized. This type of processing method can produce a large quantity of TiNi alloy foils at much lower cost than that for the conventional method of rolling bulk ingots.

Designing an actuator with large displacement and 3D response is now possible using these TiNi foils.

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