Influence of Heat Treatment on Phase Transformation of Ni-rich TiNi Foils Produced via Ultrafine Laminates

Dacian Tomus¹, Koichi Tsuchiya¹, Takeshi Nagano¹, Akihide Hosokawa¹, Toshiki Ohmori², Masahiro Sasaki¹, Yoshikazu Todaka¹ and Minoru Umemoto¹

¹Tohohashi University of Technology, Dept. Production Systems Engineering, Tohohashi 441-8580, Japan
²Nippon Metal Industry, Co., Ltd., Sagamihara 229-1184, Japan

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 at% Ni. TiNi (B2) phase was obtained after different diffusion treatments at 1073 K for 36 and 259.2 ks and 1173 K for 259.2 ks and 259.2 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 shape memory strain was \(3.69 \times 10^{-3}\) in the sample aged at 773 K for 18 ks.

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1. Introduction

Near equiatomic Ti-Ni alloys are well-known as the most excellent shape memory alloys for their shape memory characteristics. One of the disadvantages of TiNi alloys is their low plastic workability due to a high work hardening rate. Production of thin sheets or foils by conventional rolling requires several times of intermittent annealing that lead to a high cost of materials.

Other possible methods 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 or from the foils of pure metals. 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. 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.

In our previous investigations we have applied this method to produce foils of Ti-48.5 mol% Ni alloy. However, in general, we can obtain better shape memory effect or superelastic characteristics in Ni-rich TiNi alloys. It is also possible to obtain two-way-shape memory effect caused by the stress field around the Ti₃Ni₄ precipitates. Practically, the cold working of TiNi shape memory alloys become increasingly difficult with increasing Ni-content. Therefore, in the present investigation, foils of 50 µm thick were produced via the Ti/Ni ultrafine laminates. Effect of diffusion treatments and aging on the phase transformation and shape memory effect was investigated.

2. Experimental

Details of production method of Ti/Ni ultrafine laminates can be found in our previous article. The thickness of the laminate foils used in this study was 50 µm. The overall composition of the laminates was Ti-50.7 at% 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 and 259.2 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 H₂SO₄: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 to 473 K with heating/cooling rate of 0.16 K s⁻¹, Transformation temperatures were determined by an intersecting slopes method on transformation peaks.

The shape memory effect of the foils was measured by bending heat treated foils (0.05 mm × 5 mm × 30 mm), in which 5% strain were induced in a fully martensitic state (at liquid nitrogen temperature) and 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.

3. Results and Discussions

Figure 1 shows SEM micrograph of a cross section of the Ti/Ni ultrafine laminates. The average thickness of Ti and Ni layers are 0.7 µm and 0.2 µm, respectively. Intermetallic compounds, possibly Ti₃Ni, TiNi and TiNi₃ were occasionally observed at the interface between the Ti and Ni layers, as shown by the arrows.

Shown in Fig. 2 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. 2(a)). The EDX analysis revealed that the formation of Ti$_2$Ni indicated by the white single-headed arrows, TiNi$_3$ indicated by the white double-headed arrows and TiNi phase after heating to 873 K (Figs. 2(b) and (c)). In Figs. 2(a) and (b), voids are seen around the Ni layers or in the TiNi$_3$ 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.\textsuperscript{6}) The diffusion coefficient data\textsuperscript{7)} for Ni in Ti$_3$Ni$_2$ 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 (Figs. 2(c) and (d)). A homogeneous structure with TiNi phase was obtained after 36 ks at 1073 K (Fig. 2(e)). Cross section of TiNi foil after the diffusion treatment at 1073 K for 259.2 ks is shown in Fig. 3. The volume fraction of the Kirkendall voids was reduced from 1% (36 ks) to 0.31% (259.2 ks) by applying a longer diffusion treatment. The voids are indicated by the white arrows in the figure.

The DSC curves of the TiNi foils before and after aging at
773 K for various aging times are presented in Fig. 4. The sample diffusion treated at 1073 K for 259.2 ks did not show any characteristic of phase transformation 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 $M_f^*$). The curves obtained on heating are characterized by a single peak which correspond to a reverse transformation from the martensite to austenite. We will refer to this type of single peak which correspond 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 curves exhibit different transformation behavior. The curves obtained on heating are characterized by a 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 curves exhibit different transformation behavior. The first peak corresponds to the appearance of the R-phase, and on further cooling two peaks, marked as $M^*_1$ and $M^*_2$, appear. The curves obtained on heating are also characterized by a single peak which corresponds to the reverse transformation from the martensite to austenite. We will refer to this as three steps transformation behavior. Figure 5 is the summary of transformation temperatures $M_t$, $A_t$, $A_R$, $A^*$, $R^*$ and $M^*_t$ (marked in Fig. 4 with arrows) as a function of aging time. The $A_t$, $A_R$, $A^*$, $M^*_t$ and $M_t$ temperatures increase with aging time but the increase was less pronounced for $A^*$, $A_t$ and $A_R$. The $R^*$ peak temperature is almost constant irrespective of the aging time. This tendency is similar to the one obtained by Honma et al. but is different from the results obtained by Khalil Allafi et al. In the latter, $M^*_t$, $R^*$ and $A^*$ increased parallelly, and more than one peak was observed on heating. The temperature difference between $M^*_t$ and $R^*$ decreases with aging time. Longer aging times resulted in about a 30 K increase in the $M^*_t$ temperature.

The evolution of transformation heat as a function of aging time on cooling (the sum of $R^*$, $M^*_1$ and $M^*_2$ peaks) and on heating is plotted in Fig. 6. The transformation heat on cooling increased from 14.5 to 24.6 J/g for the sample aged for 18 ks and then decreased to 16.7 J/g for longer aging treatment of 144 ks. 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 5 µm as shown in Fig. 7(a). In Fig. 7(b) it can be seen that Ti₃Ni₄ 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 was not observed. In Fig. 7(c) the precipitates increased their size to about 200 nm and exhibit a tendency to align along the traces of three planes, (111), (11) and
The aging treatment for 144 ks produced precipitates with the size bigger than 400 nm (Fig. 7(f)). Fig. 8(b) is the diffraction pattern corresponding to the bright field image in Fig. 8(a) of the foil aged at 773 K for 3.6 ks. The electron beam was parallel to the [111]B2.

It can be seen that there are 7 superlattice diffraction spots between the transmitted beam spot 000 and the 321(B2) and 3 superlattice diffraction spots between 000 and 110(B2) indicating the presence of the Ti₃Ni₄ precipitates and R-phase, respectively. This TEM observation is consistent with the DSC analysis, in which the R°C is just above the room temperature.

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 field¹¹,¹² around Ti₃Ni₄ 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. 5 the Mr and Mf 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, Ti₃Ni₄ 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 Ti₃Ni₄ precipitates on phase transformation,¹³ and on the two way shape memory effect,⁸,¹⁴ seem to point that Ti₃Ni₄ 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 Mf°C and Mr in the first stage was about 25 K. Following the analysis based on the Clausius-Clapeyron equation by Bataillard et al.,¹² the stress field required to cause the observed Mf increase is about 96 MPa, which seems to be within the reasonable range of value.¹² Thus the significant part of the observed M°C increase in the first stage is due to the stress field caused by the Ti₃Ni₄ 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°C temperature is almost constant, which is less sensitive to the stress field and obeys the similar dependence on Ni concentration to that for Ms.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 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 step 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. 7(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.\textsuperscript{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.\textsuperscript{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\textsuperscript{7}.

More recent explanation by Khalil-Allafi et al.\textsuperscript{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\textsubscript{3}Ni\textsubscript{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 in the present material. 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, \(M^*_r\) 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\textsuperscript{7} 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\textsubscript{3}.\textsuperscript{16} The decomposition path was characterized as: \(\beta (B2) \rightarrow \beta_1 (B2) + Ti_3Ni_4\ \rightarrow \beta_2 (B2) + Ti_2Ni_3 \rightarrow \beta_3 (B2) + TiNi_3\). Thus the increase in \(M^*_r\) might be due to the formation of Ni depleted region by the evolution of precipitates from Ti\textsubscript{3}Ni\textsubscript{4} toward Ti\textsubscript{2}Ni\textsubscript{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 (Fig. 9(a)) and after heating at 373 K (Fig. 9(b)). 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 3.7\%. The transformation heat of this sample is 24.6 J/g which is comparable with those of bulk TiNi alloys.\textsuperscript{17}

A practical demonstration of foil usability for a three dimensional (3D) actuator was done by constraining a foil into a flower-shape and apply the aging treatment at 773 K for 36 ks. The results of this experiment are shown in Fig. 10. In Fig. 10(a) the foil was flatted at martensite state temperature. By heating the sample to 373 K, the “flower” like shape was regained (Fig. 10(b) and (c)). After cooling to below 273 K the foils tend to open toward the flat shape. (Fig. 10(d)). Based on this experiment we can draw the conclusion that shape memory effect is isotropic and the curvatures with different radii can be recovered.
The TiNi foil is also useful for various medical devices. Recently, Kuribayashi et al. developed the design for a self-deployable tubular stent. The application of the TiNi foil to this new type stent is currently under investigation.

4. Conclusion

Using ultrafine laminates method 50 μm foils of Ti-50.7 at%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 Ti3Ni4 precipitates process and to analyzes their influence on transformation temperature and shape memory effect.

The evolution of transformation temperature can be explained by means of the nickel content in matrix and internal stress field which surround the Ti3Ni4 precipitates. These two elements can be controlled by aging time which changing of the precipitates size. 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 Ti3Ni4 precipitates for the foil with the highest recovery strain was 100 nm. These values where achieved on sample which exhibited the largest shape memory effect.

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 3.7%.

In this study it was revealed that these Ni-rich TiNi foils have a shape memory response comparable to that in Ni-rich bulk TiNi alloys. Designing an actuator with large displacement and 3D response is now possible using these TiNi foils.

REFERENCES