Effect of Heat Treatment on Shape Memory Behavior of Ti-rich Ti-Ni Thin Films

Akira Ishida*, Morio Sato*, Atsushi Takei*
and Shuichi Miyazaki**

*National Research Institute for Metals, 1-2-1, Sengen, Tsukuba, Ibaraki 305, Japan

**Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Thin films of Ti-rich Ti-Ni were prepared by sputtering. The sputter-deposited films were annealed at three different temperatures of 773, 873 and 973 K for three different times of 1, 10 and 100 h in order to crystallize them. After the heat treatment, the shape memory behavior was examined with a thermomechanical tester. The shape memory behavior was found to be very sensitive to the annealing conditions, being different from that in bulk specimens. The martensitic and reverse martensitic transformation temperatures increased with increasing annealing temperature and time. The film annealed at 973 K for 100 h showed a single-stage shape change associated with the martensitic transformation, while the other annealed films showed a two-stage shape change associated with both the martensitic and R-phase transformations. It was found from transmission electron microscopy that the difference in the shape memory behavior between thin films and bulk specimens comes from a difference in the distribution of Ti_2Ni particles. That is, fine Ti_2Ni particles distribute inside the TiNi grain in the annealed films except the one annealed at 973 K for 100 h. On the other hand, the structure of the film annealed at 973 K for 100 h is similar to that normally observed in bulk specimens, where Ti_2Ni particles distribute along the grain boundaries.

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I. Introduction

Shape memory thin films formed by sputtering are considered to be an attractive candidate for a microactuator owing to their large deformation and strong recovery force⁽¹⁾⁻⁽⁴⁾. In previous papers⁽⁵⁾⁽⁶⁾, the present authors demonstrated that Ti-Ni thin films sputter-deposited under the optimum conditions exhibited a perfect shape memory effect comparable to that in a bulk Ti-Ni. However, the shape memory behavior of Ti-Ni thin films is affected not only by sputtering conditions⁽⁵⁾, but also by heat treatment conditions after the sputtering⁽⁷⁾⁻⁽⁹⁾. Especially, in the films deposited at low temperatures, heat treatment is necessary to crystallize them. Therefore, the effect of heat treatment on the shape memory behavior of Ti-Ni thin films has been systematically investigated by varying film composition⁽⁹⁾, annealing temperature and annealing time. In this paper, the heat treatment effect on the shape memory behavior of Ti-rich Ti-Ni thin films will be discussed.

II. Experimental Procedures

Thin films of Ti-rich Ti-Ni were deposited on glass substrates by r.f. magnetron sputtering. The sputtering conditions used in this study were as follows: substrate temperature, 523 K; Ar gas pressure, 0.3 Pa; r.f. power, 600 W; substrate-to-target distance, 80 mm; deposition time, 2 h. In order to obtain the Ti-rich composition, several discs of pure titanium 10 mm in diameter were placed on

a 6 in. diameter target of Ti-50 at.%Ni alloy. The film thickness ranged from 6 to 7 μm . The film composition was determined with an EPMA apparatus to be Ti-48.2 at.%Ni. After the sputtering, they were removed from the glass substrates and then annealed at three different temperatures, 773, 873 and 973 K for three different times of 1, 10 and 100 h to produce crystallization of Ti-Ni. These heat treatments were carried out in evacuated quartz capsules, followed by quenching them into water. X-ray diffractometry was carried out to identify the phase formed in the films. The microstructure of the films was observed with a transmission electron microscope. Thin foils for the transmission electron microscopy were prepared by double-jet electropolishing in an electrolyte consisting of 95% acetic acid and 5% perchloric acid by volume. These X-ray diffractometry and transmission electron microscopy studies were carried out at 423 K to avoid the formation of the martensitic phase and R-phase. The shape memory behavior of the annealed films was measured with a small tensile tester equipped with an automatically controlled heater. The size of the sample used for this test was $1 \times 5 \text{ mm}^2$ (gauge portion) and the thickness was from 6 to 7 μm . This test involved loading the sample at a high temperature, cooling it down to 143 K at the rate of -10 K min^{-1} and heating it back to the original temperature at the rate of 10 K min^{-1} . A series of strain-temperature measurements under various constant stresses was carried out with one sample by varying the stress from 20 to 120 MPa in steps of 20 MPa and then from 120 to 600 MPa in steps of 40 MPa. The transformation temperatures were defined as

the averages of their transformation start and finish temperatures which were measured in the strain-temperature curves by the tangential extrapolation method.

III. Results and Discussion

1. X-ray diffraction

Figure 1 shows X-ray diffraction patterns of annealed thin films. For all the films, several peaks of a Ti_2Ni structure are detected in addition to those of a B2 structure. It has been pointed out that the diffraction pattern of Ti_2Ni is similar to that of $\text{Ti}_4\text{Ni}_2\text{O}$ so that it is difficult to distin-

Fig. 1 X-ray diffraction patterns taken at 423 K for annealed thin films of Ti-48.2 at.%Ni. (a) 973 K, 1 h, (b) 873 K, 1 h, (c) 773 K, 1 h, (d) 973 K, 100 h and (e) 773 K, 100 h (♦: Ti_2Ni).

guish them⁽¹⁰⁾. However, we did not find similar peaks for diffraction patterns obtained from Ni-rich Ti-Ni thin films and hence it is believed that the peaks in Fig. 2 belong to Ti_2Ni .

2. Transmission electron microscopy

Figure 2 shows transmission electron photomicrographs of annealed thin films. The grain size of the films is almost the same, about $3\ \mu\text{m}$, except for the film annealed for 1 h at 773 K where the grain size is smaller and the size distribution is inhomogeneous. It should be noticed that the precipitate distribution in the film annealed at 973 K for 100 h is different from that in the other annealed films. That is, in the former film, Ti_2Ni particles are formed along the grain boundaries, while they are distributed inside the grain in the latter films. The Ti_2Ni particles formed along the grain boundaries seem to suppress the growth of the TiNi grains as shown in Figs. 2(c) and (e).

Enlarged transmission electron photomicrographs of the films in Fig. 2 are shown in Fig. 3, where the precipitates inside the grains can be seen clearly. The size of the precipitates is about 10 nm after annealing at 773 K for 1 h and becomes large after annealing for 100 h at the same temperature. On the other hand, after annealing at 973 K, the precipitates grew, but the amount appeared to decrease with annealing time. Figure 3(e) shows a photomicrograph taken at a lower magnification so that grain boundaries are included in the visual field. It was found that the precipitate size is small near the grain boundaries compared with in the core of the grain. This means that Ti_2Ni precipitates inside the grain were consumed for the growth of the precipitates along the grain boundaries. This change in precipitate distribution indi-

Fig. 2 Transmission electron photomicrographs of annealed thin films of Ti-48.2 at.%Ni. These photographs were taken at 423 K. (a) 773 K, 1 h, (b) 873 K, 1 h, (c) 973 K, 1 h, (d) 773 K, 100 h and (e) 973 K, 100 h.

Fig. 3 Transmission electron photomicrographs of precipitates inside a TiNi grain in annealed thin films of Ti-48.2 at.%Ni. These photographs were taken at 423 K. (a) 773 K, 1 h, (b) 873 K, 1 h, (c) 973 K, 1 h, (d) 773 K, 100 h, (e) 973 K, 100 h (at a low magnification) and (f) 973 K, 100 h.

Fig. 4 Strain-temperature curves under constant stresses for Ti-48.2 at.%Ni thin films annealed at 773 K for (a) 1 h, (b) 10 h and (c) 100 h.

cates that the precipitates inside the grain are not stable. In the bulk specimens, Ti_2Ni precipitates have been reported to form at grain boundaries, like in the film annealed at 973 K for 100 h⁽¹¹⁾. Therefore, the microstructure shown in Figs. 2(a) to (d) is characteristic of the films annealed at low temperatures or for a short time and is considered to be unstable.

3. Shape memory behavior

(1) Thin films annealed at 773 K

Figure 4 shows strain-temperature curves under constant stresses for thin films annealed at 773 K for different times of 1, 10 and 100 h. Under low stresses a two-stage elongation is seen in the cooling curve of each annealed film, while it shows a single-stage elongation under high stresses. The two-stage elongation was at-

tributed to the martensitic and R-phase transformations and the single-stage elongation to the martensitic transformation alone. On the other hand, in the heating curve, a two-stage contraction is seen for the film annealed for 1 h, while the other films annealed for more than 10 h show a single-stage contraction. The two-stage contraction was attributed to the reverse martensitic and reverse R-phase transformations and the single-stage contraction to the reverse martensitic transformation.

The dependence of each transformation temperature on stress is shown in Fig. 5. The martensitic and reverse martensitic transformation temperatures are more sensitive to stress than the R-phase and reverse R-phase transformation temperatures. They increased with increasing stress and eventually exceeded the R-phase or reverse R-phase transformation temperature. This leads to the single-stage shape change in the strain-temperature curve under high stresses. Also, both the martensitic and reverse martensitic transformation temperatures are affected by heat treatment, as shown in Figs. 5(a) to (c). These transformation temperatures increased significantly with increasing annealing time, while the R-phase and reverse R-phase transformation temperatures increased slightly. Therefore, the stress range where the two-stage elongation is observed becomes narrow with increasing annealing time and the two-stage contraction disappears in the films annealed for more than 10 h as shown in Fig.

4. Such increases in the martensitic and reverse martensitic transformation temperatures can be caused by precipitate coarsening and/or grain growth as shown in Figs. 2 and 3. The composition of a TiNi matrix is also an important factor which should be taken into account. However, the effect of the matrix composition is not clear in the present study. Most researchers have reported that Ti-rich Ti-Ni alloy bulk specimens have slightly higher martensitic transformation temperatures than that of an equiatomic composition alloy⁽¹²⁾. In bulk specimens, the TiNi matrix composition was considered to be close to the equilibrium one. However, in the case of the films, there is a probability that the TiNi matrix contains titanium in excess. Thus, in order to clarify the effect of the TiNi matrix composition on the martensitic transformation temperature, further work including analysis of the matrix composition is needed.

The transformation strains and plastic strain measured in Fig. 4 are plotted as a function of stress in Fig. 6. The martensitic transformation strain at 600 MPa decreased from 4.9 to 3.9% with increasing annealing time and a slight increase in the plastic strain was observed. The increase in the plastic strain is caused by precipitate coarsening as shown in Fig. 3. The reason why the martensitic transformation strain decreases in spite of the precipitate coarsening might be a decrease in the TiNi phase volume fraction as a result of formation of a Ti_2Ni phase. There

Fig. 5 Transformation temperatures vs. stress for the Ti-48.2 at.%Ni thin films annealed at 773 K for (a) 1 h, (b) 10 h and (c) 100 h.

Fig. 6 Transformation strains and plastic strain as a function of stress for the Ti-48.2 at.%Ni thin films annealed at 773 K for (a) 1 h, (b) 10 h and (c) 100 h.

is another interesting point with regard to the dependence of the plastic strain on stress in Fig. 6. The plastic strain was very small in the stress range where the two-stage elongation was observed, but it suddenly became large at the stress where the single-stage elongation appeared. This implies that the R-phase is effective to reduce the introduction of dislocations associated with the martensitic transformation. When the R-phase transformation occurs, the martensitic transformation strain can be reduced by the amount of the R-phase transformation strain, that is, nearly 10% of the martensitic transformation strain. However, it does not seem to be enough to explain the effect of the R-phase described above. Another explanation for this effect could be twin deformation in some R-phase transformation products. Such deformation might accommodate the local stress concentration introduced by the martensitic transformation, since, in this study, the plastic strain is not so large in comparison with the R-phase transformation strain. Furthermore, the twin deformation occurs by changing one variant to another variant and hence the shape change caused by this type of deformation is reversible during a thermal cycle. This coincidence between the appearance of the plastic strain and the disappearance of the R-phase transformation was commonly observed in the films annealed at 873 K and at 973 K, as shown in Figs. 7(c) and 10(a).

(2) Thin films annealed at 873 K

Figure 7(a) shows strain-temperature curves under constant stresses for a thin film annealed at 873 K for 1 h. The dependence of the transformation temperatures on

stress obtained in Fig. 7(a) is shown in Fig. 7(b). Figure 7(c) shows the transformation strains and plastic strain measured as a function of stress in Fig. 7(a). The strain-temperature curve for this film is almost the same as that for the film annealed at 773 K for 100 h, reflecting the observation that their microstructures are almost the same (see Figs. 2 and 3). In Fig. 7(c), it is interesting to note that both the martensitic transformation strain and plastic strain at 480 MPa are slightly large compared with the other ones. The specimen was kept at 523 K accidentally for 20 min before this cycle by a simple mistake. Thus the specimen could recover while it was held at the high temperature for 20 min. This causes the plastic strain at 480 MPa to be higher than the other ones. Furthermore, it should be noted that the increase in the martensitic transformation strain is exactly the same as the increase in the plastic strain. This means that the plastic strain was introduced largely during the forward transformation at least under this stress. This seems to support that the R-phase is effective to reduce the plastic strain introduced by the martensitic transformation in the cooling process as described in the previous section.

(3) Thin films annealed at 973 K

Figure 8 shows strain-temperature curves under constant stresses for thin films annealed at 973 K for different times of 1, 10 and 100 h. It should be noted that shape change associated with the R-phase transformation is absent in the film annealed for 100 h even under a small stress of 40 MPa.

Figure 9 shows the dependence of the transformation temperatures on stress. The martensitic transformation

Fig. 7 (a) strain-temperature curves, (b) transformation temperatures vs. stress, and (c) transformation strains and plastic strain as a function of stress, for a Ti-48.2 at.%Ni thin film annealed at 873 K for 1 h.

Fig. 8 Strain-temperature curves under constant stresses for Ti-48.2 at.%Ni thin films annealed at 973 K for (a) 1 h, (b) 10 h and (c) 100 h.

Fig. 9 Transformation temperatures vs. stress for the Ti-48.2 at.%Ni thin films annealed at 973 K for (a) 1 h, (b) 10 h and (c) 100 h.

temperatures slightly increased with increasing annealing time, resulting in the absence of R-phase transformation in the film annealed for 100 h. As described earlier, dras-

tic change in precipitate distribution took place during annealing at 973 K. This change in the microstructure is considered to cause the change in the transformation behavior.

According to a previous paper⁽¹¹⁾, the R-phase transformation is not produced in bulk specimens only by heat treatment. Further, the transformation temperatures are almost constant irrespective of heat treatment. These results are quite different from those obtained in the present study; in the case of films, the transformation temperatures were sensitive to the annealing conditions and the R-phase transformation occurred, as discussed in the section 3.1, 3.2 and 3.3. This difference in the transformation behavior between the thin films and the bulk specimens seems to come from the difference in the microstructure described in Section II. In the case of sputter-deposited films, annealing at low temperatures or for a short time produces fine Ti_2Ni particles inside the TiNi grain. These precipitates seem to depress the martensitic transformation temperature and thus make the R-phase transformation appear. Further, such precipitate distribution is not stable against heat treatment and changed by annealing. Consequently, the martensitic transformation temperatures increase either by coarsening of Ti_2Ni precipitates inside the grain at 773 K or by the disappearance of the precipitates at 973 K.

Figure 10 shows the transformation strains and plastic strain as a function of stress. The transformation strain is seen to increase with increasing annealing time. However, the plastic strain also increases with increasing annealing time, and hence the recoverable strain is almost constant. This increase in plastic strain seems to be attributed to the change in precipitate distribution. With increasing annealing time, the amount of Ti_2Ni in-

Fig. 10 Transformation strains and plastic strain as a function of stress for the Ti-48.2 at.%Ni thin films annealed at 973 K for (a) 1 h, (b) 10 h and (c) 100 h.

side the TiNi grain decreases. This introduces the plastic deformation in the TiNi matrix. It is also interesting to note that, in the intermediate stress region of 100 to 200 MPa, the martensitic transformation strain decreases with annealing time, as shown in Figs. 10(b) and (c). During annealing at 973 K, Ti_2Ni particles grew at the grain boundaries. They seem to suppress the deformation of each grain. The transformation strain decrease in the intermediate stress region suggests that there is the threshold stress to deform the TiNi grain surrounded by the Ti_2Ni precipitates. Such grain deformation is probably accompanied by plastic deformation, since the Ti_2Ni phase is difficult to deform. This phenomenon can be seen in Figs. 10(b) and (c), in which the plastic strain appears at the threshold stress of around 160 MPa where the transformation strain starts to increase.

IV. Conclusions

The shape memory behavior of Ti-48.2 at.%Ni thin

films annealed at 773, 873 and 973 K for 1, 10 and 100 h was investigated. The results obtained in the present study are as follows.

(1) All the annealed films showed a two-stage shape change associated with the martensitic and R-phase transformations except the film annealed at 973 K for 100 h.

(2) Both the martensitic and reverse martensitic transformation temperatures increased with increasing annealing temperature and time.

(3) The transformation strain decreased with increasing annealing time for the films annealed at 773 K. On the other hand, for the films annealed at 973 K, the transformation strain decreased with increasing annealing time in an intermediate stress region.

(4) The plastic strain increased with increasing annealing temperature and time.

(5) The fine precipitates of Ti_2Ni were observed inside the TiNi grain for all the annealed films except for the film annealed for 100 h at 973 K, in which the Ti_2Ni precipitates grew at the grain boundaries rather than inside the grain.

(6) The shape memory characteristics of the Ti-rich Ti-Ni thin films were significantly different from those reported in bulk specimens. This comes from the difference in the distribution of Ti_2Ni particles.

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