RAPID PUBLICATION

Martensitic Transformation in Thin Foil Specimen of a Shape Memory TiNi Alloy

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Since shape memory alloys are applied in various fields, especially in the micro-machine field, and the dependence of size effect on shape memory phenomena of the alloys has been reported, it should be important for using the alloys actually to clarify the quantitative relationship between the thickness and the occurrence of martensitic transformation of the alloys. In the present paper, the relationship for TiNi (its M_s temperature is 248 K) thin film specimens suitable for TEM observation was investigated by *in-situ* TEM and SEM methods using cooling stages, and a convergent beam electron diffraction method. The results obtained are as follows: (1) At 98 K, martensitic transformation does not occur in areas thinner than about 100 nm; (2) The M_s temperature of the thin film is considerably lower than that of the alloy in the bulk-state; and (3) The interval between A_s and A_f temperatures decreases with decreasing specimen thickness, and in the case of a thin film specimen suitable for TEM observation, the interval becomes almost zero.

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Keywords: shape memory alloy, thickness dependence of martensitic transformation, critical thickness, *in-situ* transmission electron microscopy observation, convergent beam electron diffraction method

I. Introduction

A shape memory alloy has such a characteristic property that a shape formed by an external stress is recovered to the original one by heating at an appropriate temperature. Because of this property, shape memory alloys have been gradually tested for application in various fields such as industrial products, aerospace industry, medical and dental treatments, and household goods. On the other hand, some kinds of machines are becoming smaller and smaller, and especially in the micro-machines field, shape memory alloys are thought of useful materials for a micro-actuator. Therefore, shape memory behaviours of sputtered thin films and rapid solidified ribbons have been investigated⁽¹⁾⁽²⁾. Also, it has been reported by many authors that shape memory phenomena did not appear in an extremely thin foil of a shape memory alloy⁽³⁾ and that M_s temperatures in some alloy systems were varied as the thickness of specimens were varied⁽⁴⁾⁻⁽¹⁰⁾. Recently, the effect of specimen dimension on the phenomena of some alloy systems has been investigated and it has been reported that as the size of a shape memory alloy decreases, M_s temperatures drop and the interval between the onset and finish temperatures of a martensitic transformation becomes smaller⁽¹⁰⁾.

Therefore, in order to use shape memory alloys in the thin film-state, it is important to clarify the quantitative relationship between the thickness and the occurrence of

shape memory behaviour of the alloys, and this is also interesting from a viewpoint of materials science.

In the present study, a TiNi alloy, the nominal martensitic transformation temperature (M_s) of which is 248 K, was chosen as a specimen and the critical thickness for the occurrence of the martensitic transformation was investigated by *in-situ* transmission electron microscopy (TEM) and *in-situ* scanning electron microscopy (SEM) using cooling stages, and a convergent beam electron diffraction (CBED).

II. Experimental Procedures

A Ti-50.2 at%Ni shape memory alloy was supplied from Furukawa Electric Company for the specimen material and the foil sheet was cut into disks of 3 mm in diameter using a spark erosion machine. The disks were solution-treated in a vacuum at 1223 K for 3.6 ks and quenched into an oil bath. The solution treatment was carried out by Furukawa Electric Company. Specimens for transmission electron microscope observation were prepared by a twin jet electro-polishing method and the adopted conditions were reported elsewhere⁽¹¹⁾. Surface relief effects due to the occurrence of martensitic transformation were observed on some thick specimens, which were unsuitable for TEM observation. *In-situ* TEM observation was carried out using a JEM 2000EX electron microscope equipped with a cooling stage, and all phenomena in cooling and heating processes were recorded by a TV-VTR system. *In-situ* SEM observation was also carried out using a JSM 35 scanning electron microscope with a cooling stage and a TV-VTR system. The

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specimen thickness was measured by a convergent beam electron diffraction method using a JEM 2010F electron microscope.

III. Results and Discussion

1. Surface morphology observed using an *in-situ* scanning electron microscope method

Figure 1 shows results for a specimen cooled to 193 K. Figure 1(O) shows a whole view of the specimen, and a hole denoted by a white arrow can be seen. Because the specimen was prepared using a twin-jet electro-polishing machine as mentioned in Section II, the cross-section is wedge-shaped. Therefore, it is assumed that the specimen thickness increases with increasing distance from the hole edge; points A and C were observed as representative of thin and thick areas respectively, and a point B was also observed. At these areas, A, B and C, surface relief effects due to the occurrence of martensitic transformation were recognized at about 231 K. As seen from Figs. 1(A), (B) and (C), surface relief effects become clearer as the specimen thickness increases. It is thought that the features of surface relief effects depend on the amount of bending of the thin foil specimen. The distances at B and C from the hole edge are over $350\text{ }\mu\text{m}$, so that it is assumed that the amounts of the bending at B and C are negligibly small. Therefore, it seems that surface relief effects due to martensitic transformation appear easily in thicker areas. The same observation was carried out again and almost the same phenomenon was observed. During a heating process from 153 K to room temperature, the A_s and A_f temperatures, at which surface relief started to disappear and disappeared completely, respectively, were obtained at the points A and C. The A_s tem-

peratures at the points A and C were 243 K and 227 K respectively, and the A_f temperatures at points A and C were 248 K and 250 K respectively. Therefore, the intervals between A_s and A_f at the points A and C were 5 K and 23 K respectively. The results on intervals are consistent with those of an investigation about the effect of specimen size on the martensitic transformation⁽¹⁰⁾: the interval for a small specimen is shorter than that for a large specimen.

2. *In-situ* and conventional TEM observations

Figure 2 shows a result for *in-situ* TEM observation of the appearance and growth of martensite plates in a grain of a specimen cooled down to 187 K. The white arrow denotes a marker, which is thought to be a precipitate or an inclusion. The lapse of time (s) from the onset of the transformation is indicated in the top-left of each image. It can be seen that martensite plates grew from a thinner area (the left-hand side of each image), but not from the specimen edge and the growth was stopped at a grain boundary. As time progressed, some martensite plates grew quickly and some ones grew jerkily. It was also found in a picture after 9 s that the growth of a martensite plate was stopped at the marker. Each image of Fig. 2 was taken while the specimen was kept at 187 K. It was found that M_s temperature in a thin film specimen is lower than that estimated by SEM observation, and because SEM observations were carried out using specimens unsuitable for TEM observation, the specimen is thought to be thicker than that of a specimen used for TEM observation. Upon heating to $239\text{ K}^\dagger$, these martensite plates instantaneously disappeared. Therefore in this case the A_s and A_f temperatures were almost the same, and it seems that the interval was nearly zero. In Section III.1, it was recorded that the intervals between A_s and A_f in thin and

Fig. 1 Surface morphology in three areas with different thickness at 193 K. (O) A whole view of a specimen, which was prepared by a twin-jet electro-polishing machine. SEM observations were carried out at the three points denoted by A, B and C. Pictures (A), (B) and (C) correspond to thin and thick areas, A, B and C in (O), respectively.

Fig. 2 *In-situ* TEM observation of the growth process of martensite plates at 187 K. The lapse of time (s) from the beginning of the transformation is indicated on the top-left of each image.

[†] Temperature calibration of the cooling stages for both TEM and SEM was not carried out. Therefore, it is not possible to compare precisely the absolute values measured by both stages.

thick areas were 5 and 23 K, respectively. On the other hand, in the case of a thin film specimen with a composition of Ti-50Ni prepared by sputtering, and of 5 μm in thickness, the interval was reported to be about 4.5 K⁽¹⁰⁾. Therefore, it seems that the interval becomes shorter with decreasing specimen thickness, and that the interval becomes almost zero at a thickness suitable for TEM observation. This will be discussed later in Section III.2. This specimen was again cooled down to 187 K, however, martensite plates did not appear. It is known that microstructure reversibility of this alloy in a bulk-state is not so good, and the present result indicates that the reversibility in a thin foil of this alloy is not so good either.

Figures 3(a) and (b) show bright field images of an identical area in a grain, taken at room temperature and at 98 K respectively. Short white arrows in the two images indicate the same marker. In Fig. 3(a) a homogeneous feature can be seen. However, in Fig. 3(b) it is seen that the martensites consisting of finely striated structures appear in the right-hand and upper sides of the image. Figures 4(a) and (b) show the selected area diffraction patterns from the region shown in Fig. 3(a) and the area denoted by a star C shown in Fig. 3(b) respectively. Figure 4(a) indicates that the region is the austenitic phase, while Fig. 4(b) indicates that the region is the martensitic phase. It is seen in Fig. 3(b) that near the specimen edge, there is no

martensitic phase. A long white arrow in Fig. 3(b) indicates a boundary between the austenitic and martensitic phases. Because the cross-section of this thin foil specimen is thought to be wedge-shaped as described in Section III.1, it is concluded that the martensitic phase does not appear in a thin area near the specimen edge even at 98 K. This result suggests that the occurrence of the martensitic transformation depends on the specimen thickness, as reported already for the same alloy system⁽³⁾.

3. The critical thickness for the occurrence of martensitic transformation

In order to determine the thickness limit for the occurrence of martensitic transformation, the measurement of specimen thickness at points A, B, C and D denoted in Fig. 3(b) was carried out using the convergent beam electron diffraction method⁽¹²⁾. The thickness at the each point was plotted against each distance from the specimen edge. The results are shown in Fig. 5. As judged from Fig. 3(b), the boundary indicated by the white arrow is about 1.82 μm away from the edge. Using a straight line through points A to D in Fig. 5, the thickness at the point of 1.82 μm is estimated as 106 nm. Therefore, it is concluded that the martensitic transformation does not occur in a film thinner than about 100 nm at 98 K. To explain this two possibilities have been considered. One is that with decreasing specimen thickness, the M_s temperature decreases continuously, so that in the case of a thickness of 100 nm, the M_s temperature is lower than 98 K. However, on the same alloy system, it was found that even at 77 K, the martensitic transformation is not observed⁽³⁾. The other possibility is that there is a critical thickness for the occurrence of the martensitic transformation. In order to distinguish these two possibilities, it seems that further experimental studies, in which specimens are cooled down to much lower temperature, and theoretical studies are necessary. In addition, it is

Fig. 3 Bright field images of the same area of a specimen. (a) at 300 K and (b) at 98 K. In (b), martensite plates appear in the areas denoted by B and C. An arrow X shows the boundary between the martensitic and austenitic regions.

Fig. 4 (a) A diffraction pattern from Fig. 3(a), which indicates the austenite phase. (b) A diffraction patterns from an area denoted by C in Fig. 3(b). The pattern shows the occurrence of martensitic transformation.

Fig. 5 Relationship between distance l at A, B, C and D from the hole edge in Fig. 3(b) and specimen thickness t . An arrow X corresponds to the distance from the hole edge to the boundary between martensitic and austenitic regions. The thickness at the point X is estimated as 106 nm.

considered that although the thickness 100 nm was estimated from Fig. 5, the actual value depends on the surface normal of the grain, because while the thicknesses of the other grains around the grain shown in Fig. 2 seems to be almost the same, no martensitic transformation is observed in those grains.

The non-occurrence of martensitic transformation in a thin film as described in Section III.2 might be a characteristic phenomenon of a thin film, and the phenomenon is also considered to be the same as the lowering of the M_s temperature in small size crystals. To understand this phenomenon, quantitative considerations including the strain energy of the nucleation and growth of martensite⁽¹⁰⁾ and the effect of surface orientation of specimens, and further investigations described above seem to be necessary. In the present study this phenomenon was observed under the electron beam irradiation, and therefore it is also necessary to consider the influence of the irradiation on this phenomenon. To this end a test was carried out, and Fig. 6 shows the result. The white arrow in Fig. 6(a) indicates the appearance of the martensitic phase in a specimen cooled to 123 K. After this picture was taken, the illumination of the electron beam was turned off for 3.6 ks while the specimen temperature was kept at 123 K. Then the illumination was turned on again, and Fig. 6(b) was taken from the same place. It is noted that no martensite plate is observed in other places excepting the places in which martensite plates were observed in Fig. 6(a). Therefore, it seems that the electron beam irradiation does not affect the non-occurrence of martensitic transformation described in Fig. 3(b).

IV. Conclusion

Since shape memory alloys have been considered to have applications in the micro-machine field, it seems to be important to evaluate the quantitative relationship between the thickness and the occurrence of shape memory phenomena of the alloys. The relationship for a Ti-50.2 at%Ni shape memory alloy has been investigated by *in-situ* transmission and scanning electron microscope methods using cooling stages, and by a convergent beam

electron diffraction method. The results obtained are summarized as follows:

(1) The results of the *in-situ* SEM investigation suggest that the M_s temperatures in thin and thick areas of a specimen were almost the same, but, it seems that surface relief effects due to the martensitic transformation appear easily in the thicker area.

(2) *In-situ* TEM investigation indicates that the M_s temperature of a thin film, the thickness of which is suitable for observation in a transmission electron microscope operated at 200 kV, is considerably lower than that of a specimen in the bulk-state.

(3) The interval between the A_s and A_f temperatures for a thin film was smaller than that for a thick one. This result agrees with those reported in some alloy systems for the effect of specimen size on martensitic transformation⁽¹⁰⁾. In the case of thin films as described in (2), the interval becomes almost zero.

(4) It is clarified that the occurrence of martensitic transformation depends on the specimen thickness. In the present case, the martensitic transformation does not occur in areas thinner than about 100 nm.

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REFERENCES

- (1) A. Ishida, M. Sato, A. Takei and S. Miyazaki: *Mater. Trans., JIM*, **36** (1995), 1349.
- (2) Y. Furuya, M. Matsumoto, H. Kimura, K. Aoki and T. Masumoto: *Mater. Trans., JIM*, **32** (1990), 504.
- (3) K. Otsuka, T. Sawamura and K. Shimizu: *Phys. Stat. Sol.*, (a) **5** (1971), 457.
- (4) H. Warlimont: *Metall., Trans.*, **2** (1971), 1847.
- (5) S. Nagakura, M. Kikuchi, Y. Kaneko and S. Oketani: *Japanese J. Appl. Phys.*, **2** (1963), 201.
- (6) E. Grunbaum and G. Kremer: *J. Appl. Phys.*, **39** (1968), 347.
- (7) S. Miyazaki and A. Ishida: *Mater. Trans., JIM*, **35** (1994), 14.
- (8) J. D. Busch, A. D. Johnson, D. E. Hodgson, C. H. Lee and D. A. Stevenson: *Materials Science Forum*, **56-58** (1990), 729.
- (9) K. Nomura, S. Miyazaki and A. Takei: *Trans. Met. Res. Soc. Jpn.*, **18B** (1993), 1049.
- (10) H. Sakamoto, K. Meguro, A. Tanaka and A. Imai: in press in the Proceedings of "ICOMAT" 1995.
- (11) H. Ohgi, I. Itai, M. Nishida, A. Chiba and K. Yamauchi: *Collected Abstracts of 1993 Fall Meeting of Japan Inst. Metals*, (1993), p. 276.
- (12) M. H. Loretto: *Electron Beam Analysis of Materials*, Chapman and Hall, (1984), p. 80.

Fig. 6 The effect of electron beam irradiation on the appearance of martensitic phase. (a) martensitic phases denoted by an arrow appeared at 123 K. (b) after taking (a), the illumination of electron beam was turned off and the specimen was kept at 123 K for 3.6 ks. Then, the illumination was turned on again and only the same martensitic phases were observed.