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PHASE TRANSFORMATIONS IN Ti50Ni50-xFeX ALLOYS

M. Nishida and T. Honma

Graduate School, Tohoku University, Japan
*Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Sendai, Japan

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Abstract.- The phase transformations in Ti50Ni50-xFeX alloys have been studied by means of electrical resistivity measurement, differential scanning calorimetry (DSC), dilatometry, observation of shape changes, optical microscopy, transmission electron microscopy (TEM) and electron diffraction. During cooling, the electrical resistivity rapidly increased at \( M_b \) (starting temperature for the parent to intermediate phase transformation) and then reached maximum at \( M_s \) (starting temperature for the intermediate to martensite phase transformation). \( M_b \) and \( M_s \) corresponded with temperatures of abrupt rising of two exothermic peaks and two breaks in DSC and thermal expansion curve on cooling, respectively. The shape changes during heating and cooling for Ti50Ni47.5Fe2.5 were divided into two steps. Correspondingly, two kinds of surface relief were distinctly observed. In the parent to intermediate phase transformation, its metallographic feature exhibited the thermoelastic nature. In electron diffraction, many extra reflections occurred close to one-third and one-half positions of the B2 reciprocal lattice on cooling. As an intermediate state, the needle shaped domains with \( 1/3B2 \) extra spots were observed in electron microscopy. Judging from morphology and temperature range of the structural change, these domains coincided with the surface relief of the parent to intermediate phase transformation in optical microscopy. The crystal structure, internal defects and morphology of martensites were also described. As an applied investigation for development of practical use of TiNi alloys, the drastic reversible shape memory (RSM) effect associated with the two-step transformation was found to be obtained by a constrained aging in Ni rich TiNi alloys.

Introduction.- Recently, the practical applications of shape memory effects have been developed not only in technological but also medical and dental fields. TiNi alloy is one of the most excellent shape memory materials. This alloy exhibits unique physical properties, depending on the composition and the heat treatment. By complete and incomplete thermal cycles, \( M_s \) falls and the intermediate phase with rhombohedral distortion appears between parent [B2] and martensite phase [monoclinic]. In this temperature range, the electrical resistivity remarkably increases on cooling. \( M_s \) is defined as the temperature at which electrical resistivity increases on cooling. These phenomena include diffuse scattering streaks, extra diffraction spots at 1/3 and 1/2 positions of the B2 reciprocal lattice, the intensities of which increase on cooling. When Ni atoms are substitution by Fe atoms, \( M_s \) and \( M_b \) are clearly separated [1]. Therefore it is suitable to use Ti50Ni50-xFeX for the synthesized investigation of phase transformation in the TiNi alloy, especially the parent to intermediate phase transformation. The principal purpose of the present work is to investigate the role of this transformation for the shape memory effect and its metallographic features, and to clarify the drastic RSM associated with two-step transformations.

Experimental procedure.- Sample preparation and specimens for optical and electron microscopy have been reported in our previous papers [1,2]. The determinations of
transformation temperatures were made by the electrical resistivity measurement and DSC. Thermal expansion was measured by a differential dilatometer using reference sample of quartz rod. Specimens for shape change experiments were initially formed into a U-shape in a stainless pipe and then memorized its shape for 1.8 ks at 77 K, finally quenched into ice water. To observe the shape change behaviour, the following method was accepted [3], the U-shaped specimen was nearly straightened by hand in the mixture of ethanol and dry ice at about 170 K, and then warmed up in the above mixture, while the shape change was monitored optically and electrical resistivity was measured. The electron microscopic observation was carried out with JSEMZ008 operating 200 KV and fitted a single tilting cooling device. Generating procedure of RSM will be described later.

Experimental results and discussion. Measurement of transformation temperature. In Figure 1 broken and solid lines represent electrical resistivity versus temperature and DSC curves, respectively, for Ti50Ni50-xFe2.5. We defined the indications of transformation temperature [1], as shown in Figure 1(b). The electrical resistivity decreases linearly, and then begins to increase at M's on cooling. At M's the electrical resistivity is maximum. Two abrupt risings of peaks are observed in DSC curves for Ti50Ni50-xFe1.5 and Ti50Ni50-xFe2.5 on cooling, corresponding with M's and M's in electrical resistivity curves. In Ti50Ni60Fe4, M's is 216 K, but M's is not observed until liquid nitrogen temperature. Electrical resistivity begins to abruptly increase at As (starting temperature for reverse transformation of martensite to intermediate phase), and decrease at A's (starting temperature for reverse transformation of intermediate to parent phase), in reverse transformation on heating. The temperature difference of As and A's is narrow in the specimen containing low concentrations of Fe atoms. Therefore, a single peak appears on heating in DSC curve for Ti50Ni50-xFe2.5. As Fe atoms increase, separation of A's and A's becomes clearer as shown in Figure 1(b). The thermal hysteresis in the parent to intermediate phase transformation (A's : 296 K - M's : 287 K) and that of intermediate to martensite (As : 264 K - Ms : 246 K) are 9 K and 18 K for Ti50Ni47.5Fe2.5, respectively. These results coincide with electrical resistivity data. The former transformation also has small thermal hysteresis, which is clear in DSC and electrical resistivity curve for Ti50Ni47Fe2.

Dilatometry and shape change behaviour. Figure 2 shows thermal expansion of Ti50Ni47.5Fe2.5. D1 is the difference of expansion or contraction between specimen and reference sample, and l is the length of a specimen. In Ti50Ni47.5Fe2.5, gradual contraction starts at Ms and then severe expansion occurs at Ms on cooling. It seems that these results correspond to the parent to intermediate phase transformation with rhombohedral distortion and martensitic transformation, respectively. The reversible changes occur during heating. Transformation temperatures coincide with electrical resistivity changes and DSC results. Figure 3 shows the shape change behaviour and corresponding electrical resistivity vs. temperature curve for Ti50Ni47.5Fe2.5. The electrical resistivity did not change during straightening specimen. It means that the specimen have been transformed to martensite. The ref-

Fig.1 DSC and electrical resistivity vs. temperature curve for Ti50Ni50-xFe2.5. (a) X=1.5, (b) X=2.5, (c) X=4.
coverage angle rapidly decreases near $A'$ and gradually begins to reach constant value above $A'$ during heating. During cooling, clear two-step shape change occurs. From these results, the parent to intermediate phase transformation contributes to shape change, especially in RSME, which are consistent with the another investigation [3].

Optical microscopy results.- The typical examples of optical micrographs observed for Ti$_{50}$Ni$_{47.5}$Fe$_{2.5}$ are shown in Figure 4. The surface is flat in parent phase at about 304K, except for etch pits and inclusions, as shown in Fig.4(a). As the temperature decreases, a straight-banded relief gradually appears. Starting temperature for this structural change coincides with $N'$. On further cooling, the banded regions expand in horizontal and longitudinal directions, and their contrasts become clearer. At near 285K corresponding to $A'$, the banded relief suspends growth, as shown in Fig.4(b). These bands consist of a pair of light and dark contrasts, and the light and dark bands are twin-related two variants of intermediate phase. Upon further cooling, the surface relief for martensite appears at $M_s$. Its morphology is similar to that of martensite in TiNi. Reverse transformation occurs on subsequent heating. First, martensite relief completely disappears at 296K, and then straight-banded relief disappears at 306K. On the second thermal cycle, straight banded relief has a complete microreversibility but martensite relief does not, as shown in Fig.4(d). These results suggest that the parent to intermediate phase transformation should be considered not as a premonitory but as an independent phenomenon.

Electron microscopy results. - The series of diffraction patterns taken from the three most densely recipro-
Fig. 5 Changes in diffraction patterns on cooling from 320K to 100K for Ti₅₀Ni₄₇.₅Fe₂.₅, corresponding to Ti₅₀Ni₄₇.₅Fe₂.₅, 50Ni₄₇.₅Fe₂.₅. Cal lattice planes for the B₂ structure in Ti₅₀Ni₄₇.₅Fe₂.₅ on cooling, are reproduced in Figure 5. Fig. 5(a) to (e), (f) to (j), and (k) to (o) are taken from [110]B₂, [111]B₂, and [001]B₂ zone axis, respectively. The diffraction patterns taken from parent phase are shown in Fig. 1(a), (f), and (k). The 1/3 110 extra spots come out at vicinity of room temperature, as shown in Fig. 5(b), (g), and (l). On cooling under M_s, the existing extra spots intensify, except for [110]B₂ zone axis, and new 1/3 extra spots make appearance, for example 1/3 111, 1/3 112, etc, as shown in Fig. 5(c), (h), and (g). Appearance and disappearance of the 1/3 extra spots are very complicated. It is due to domain effects, which will be described later. On further cooling just above M_s, the 1/2 extra spots emerge in [001]B₂ and [111]B₂ zone axis, as shown in Fig. 5(i) and (n), but these spots can not be observed in [110] B₂ zone axis. The all parts of specimen don't always transform in above sequence. Appearance of 1/2 extra spots is not frequent. At last, the martensite spots come out under the M_s temperature, as shown in Fig. 5(e), (j), and (o). These and some other diffraction patterns taken from martensite phase can be indexed using the lattice parameters given by Otsuka et al. [4]. The crystal structure is described as of distorted B₁₉ or modified 2H type with a monoclinic unit cell. Therefore the presence of intermediate state has little influence on the crystal structure of martensite. The internal defects also coincide with those of TiNi martensite [2,4]. The bright field images in Figure 6(a) to (e), correspond to the diffraction patterns taken from [110]B₂ zone axis in Fig. 5(a) to (e), respectively. Electron micrograph at about 320K proves that the specimen are single phase of B₂ structure as shown in Fig. 5(a) and 6(a). On cooling to room temperature, an obvious change is not observed in bright field image as shown in Fig. 6(b), but fine irregular domains are observed in dark field image using 1/3 110 extra spot. On further cooling, needle shaped domains are observed with 1/3 111 B₂ reflection, as shown in Fig. 6(c). It seems that these two phenomena correspond to the incommensurate and commensurate rhombohedral phase, respectively, which are reported by Wayman et al. [5]. An intermediate product appearing with 1/2 B₂ extra spots in [111]B₂ and [001]B₂ zone axis exists together with needle shaped domain in very few instances. Its morphology is indefinite shape and
Fig. 7 Spontaneous and reversible shape changes in Ti$_4$Ni$_5$. Scale: 50mm

Fig. 8 (a) Electron micrograph taken for Ti$_4$Ni$_5$ aging at 673K for 14.4ks. M: martensite
(b) electron diffraction pattern taken from (a).
microstructure is not clear in dark field image, using 1/2B2 extra spots. According to morphology and temperature range of appearance, needle shaped domains coincide with the straight banded relief in optical micrographs. As the temperature more decreases, the image of the needle shaped domains and intensity of 1/3[112] reflections become stronger, and then martensite phase appears across the needle shaped domains, as shown in Fig.6(e).

RSM in Ni rich TiNi obtained by constrained aging.- In Ni rich TiNi, it is known to precipitate second phase particles and exhibit two-step transformations behaviour by means of aging [6]. Several generating methods of RSM have common principles in respect of introducing internal stress field into parent phase. Therefore, it is very likely that above precipitations get internal stress field. Ribbon specimens (3×0.2~0.5×90mm³) of Ti₄₉Ni₅₁ (Ms=175K) were prepared by cold work, which were homogenized at 1073K for 7.2ks in an evacuated quartz and quenched into ice water. They are bent in a circular form and fixed by copper pipe as shown in Figure 7(b), and then which are heat treated at 573~873K. Fig.7(c) to (x) show spontaneous and reversible shape changes in Ti₄₉Ni₅₁ generated by constrained aging at 573~873K for 3.6ks. In the case of aging at 573K, RSM occurs, but it is reverse phenomenon in respect of one-way memory. On aging at 673K and 773K, the specimens reverse themselves between Ag' and Mg, i.e. the curvature turns upside down, as shown Fig.7 (i) to (n) and (o) to (t). It is noteworthy that a large amount of shape change takes place even in the parent to intermediate phase transformation. On aging at 873K, the RSM does not occur because of a single phase. The character and capacity of RSM are markedly varied by aging condition, initial constrained strain and composition. Figure 8 shows electron micrograph taken at 100K for Ti₄₉Ni₅₁ aging at 673K for 14.4ks. Banded contrasts show martensites and small irregular particles are second phase in Fig.8(a). Morphology of martensite is different from that of single phase, as shown in Fig.6(e). Fig.8(b) shows electron diffraction pattern taken from Fig.8(a). It indicates that the parent, intermediate and martensite phase coexist. The 1/3B2 extra spots derived from intermediate phase are observed along only one <110> direction. It means that the variant of intermediate phase are arranged along a preferential orientation by the interfacial strains between the matrix and the precipitations. These results suggest that the transformation behaviour and the morphology of intermediate and martensite phase in Ni rich TiNi are affected by second phase particles, which have enough internal strain fields to generate RSM.

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