Advanced transmission electron microscopy study on premartensitic state of Ti$_{50}$Ni$_{48}$Fe$_2$

D. Shindo*, Y. Murakami

Institute for Advanced Materials Processing, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan

Received 29 February 2000; accepted 8 March 2000

Abstract

Microstructure of the premartensitic state in Ti$_{50}$Ni$_{48}$Fe$_2$ is extensively analyzed by advanced transmission electron microscopy utilizing energy filtering and in situ dark-field imaging. From the energy-filtered electron diffraction study, microdomains less than 5 nm with transverse atomic displacement are clarified to extend preferably in the $\langle 110 \rangle$ directions. Careful energy-filtered dark-field electron microscopy reveals that each microdomain has a single transverse type of atomic displacement whose propagation and displacement directions are such as the $[011]$ and $[0\bar{1}1]$ directions, respectively. Furthermore, from in situ dark-field electron microscopy, the growth process of the microdomains is observed dynamically for the first time. Size limitation of the microdomains is discussed in terms of the lattice strain without the translational symmetry accompanying the transverse atomic displacement.

Keywords: Energy filtering; Diffuse scattering; TiNi; Martensite; R-phase; Dark-field image

1. Introduction

Recently, advanced transmission electron microscopy for materials science has been developed extensively. In addition to high-resolution electron microscopy [1], analytical electron microscopy such as electron energy-loss spectroscopy has now extensively progressed. Based on the improvement and modification of the spectrometers, various types of energy filters were developed and installed on conventional electron microscopes. Combining the energy filters with new recording systems such as imaging plates and a slow scan CCD camera, quantitative analysis of electron diffraction patterns can now be carried out. Actually, the structural modulation associated with diffuse scattering in an alloy semiconductor Al$_{12}$In$_{28}$P$_{50}$ was analyzed in detail with energy-filtered electron diffraction combined with high-resolution electron microscopy [2]. In a Cu$_3$Pd alloy, 2D short-range order parameters were accurately determined through quantitative energy-filtered electron diffraction [3]. Recently, we have also started to apply this technique to the structural study of martensitic transformation in alloys [4], especially in the Ti–Ni–Fe system [5,6].

In Ti$_{50}$Ni$_{50}$–Fe$_x$ alloys, two successive martensitic transformations occur upon cooling, i.e. cubic (parent phase) $\rightarrow$ trigonal (R-phase) $\rightarrow$ monoclinic (B19’ phase). Anomalies in some physical properties, such as elastic constant and phonon, are observed in the parent phase just before the transformation to the R-phase, and the state exhibiting these behaviors are sometimes called “premartensite” or “precursor”. Since the addition of a small amount of Fe markedly suppresses the subsequent trigonal $\rightarrow$ monoclinic transformation [7], while the cubic $\rightarrow$ trigonal transformation is less affected, the R-phase is observed in a much wider temperature range compared with the case of the TiNi binary system. Thus, Ti$_{50}$Ni$_{50}$–Fe$_x$ alloys are ideal to investigate the R-phase transformation and its precursor effects; actually, a lot of studies with X-ray diffraction [8–10], inelastic neutron scattering [11] and electron microscopy [12–14] have been reported in this system. From the X-ray diffraction study on single crystals of Ti$_{50}$Ni$_{50}$Fe$_{1.2}$, Shapiro et al. [8] reported the incommensurate phase whose incommensurability depends on the Brillouin zone. They noted that the incommensurate structure was approximately interpreted as the low-temperature trigonal structure. In addition to specific heat, resistivity and susceptibility measurements, Salamon et al. [9] carried out an X-ray and neutron diffraction study on a polycrystal of Ti$_{49.8}$Ni$_{37.2}$Fe$_{3}$ and single crystals of Ti$_{50}$Ni$_{46}$Fe$_{2}$, they reported that there were two stages in the development of satellite reflections relevant to the precursor effect. On cooling, one appears at 232 K with superlattice reflections at...
incommensurate positions, while the other appears at 224 K with a rhombohedral distortion that locks the superlattice peaks to commensurate positions. In order to explain the experimental data they proposed a model, which involves discommensurations in the lattice strain analogous to discommensurations in the charge-density wave phase. Although transmission electron microscopy is a useful method for clarifying the microstructure change in phase transformation, in general, weak diffuse scattering is sometimes rather hard to analyze. This is because there is a strong background in the electron diffraction patterns caused mainly by plasmon excitation. Actually, in the electron diffraction pattern of the parent phase of Ti50Ni48Al2, diffuse scattering could be observed, but its intensity was too weak to image the microstructure by dark-field electron microscopy [13]. Also, in order to remove the inherent effect of surfaces and thin films, the electron microscopy study on phase transformation should be carried out with relatively thick crystals. Eventually, the background in the electron microscope images and electron diffraction patterns is enhanced significantly. In addition, dynamical diffraction effect should be taken into account in such a thick crystal even for weak scattering [15].

In our previous report [5,6,16], it is pointed out that the energy-filtered electron diffraction is quite effective to clarify the existence of weak diffuse scattering in the premartensitic state of Ti50Ni48Fe2. Furthermore, from the detailed energy-filtered electron diffraction study, the existence of transverse atomic displacement in the premartensitic state was confirmed through the analysis on the extinction rule of the diffuse scattering. It was also clarified that the incommensurate structure with atomic displacement in the premartensitic state forms microdomains less than 5 nm [5,6].

Following our previous electron microscopy study [6], in this paper we intend to investigate details of the microstructure in the premartensitic state of Ti50Ni48Fe2 by utilizing energy-filtered electron microscopy. Besides, in situ dark-field electron microscopy is carried out to observe the dynamic growth process of the microdomains in the premartensitic state.

2. Experimental

A Ti50Ni48Fe2 alloy was prepared by an induction melting method. The ingot was hot-forged and then hot-rolled into a thin plate. After spark cutting into small disks of 3 mm diameter, the specimens were lightly, mechanically polished. These specimens were solution treated at 1173 K for 3.6 ks in Ar atmosphere, followed by quenching in ice-water. They were finally jet-electropolished with a mixture of HClO4 and CH3COOH. The R-phase transformation start temperature (Rs), which was defined as the temperature at which the sharp and intense superlattice reflections appeared [6], was estimated to be at about 278 K. Appearance of these superlattice reflections was confirmed to be parallel to the morphological change due to the phase transformation as presented below.

The structure change of Ti50Ni48Fe2 with the decrease in temperature was investigated with a JEM-2010 electron microscope installed with an omega-type energy filter [17] utilizing a cooling stage. As shown in Fig. 1, the omega-type filter consists of four sector-type magnets. Due to the symmetrical configuration of the magnets, it is known that energy-filtered electron microscopy and diffraction show very small distortion in images and diffraction patterns, respectively. Electron microscope images, diffraction patterns and electron energy-loss spectra were recorded...
Fig. 3. Comparison of: (a) unfiltered, and (b) filtered electron diffraction patterns of Ti₅₀Ni₄₈Fe₂ observed at 280 K. Intensity profiles are shown below.

Fig. 4. Comparison of energy-filtered dark-field electron microscope images of: (a) the parent phase, and (b) the R-phase observed with fundamental reflection and/or diffuse scattering as indicated in the inset.
with the imaging plates (FDL-UR-V), which have a wide
dynamic range and good linearity for electron intensity [18].
For in situ study, dark-field electron microscope images
were recorded with a TV system (Gatan-622SC).

One of the energy-loss spectra of Ti50Ni48Fe2 observed
with this microscope and the imaging plate is shown in
Fig. 2. The width of the energy slit is set to be 20 eV for
removing the plasmon scattering as indicated below the
spectrum. It is noted that through the energy-loss spectra,
crystal thickness can be estimated easily [3]. Fig. 3 shows
the effectiveness of energy filtering in electron diffraction,
comparing the intensity profiles of a conventional (unfil-
tered) electron diffraction pattern and an energy- filtered
one of Ti50Ni48Fe2. The incident electron beam is parallel
to the \( [\bar{1}11] \) direction. Due to the energy filtering, the back-
ground resulting from the plasmon scattering was drasti-
cally reduced and weak diffuse scattering in the parent
phase is clearly seen.

3. Results and discussion

Here, we firstly compare the microstructures of the parent
phase and the R-phase. Fig. 4(a) and (b) show dark-field
electron microscope images of the parent phase and the R-
phase observed at 296 and 248K, respectively. In dark-field
electron microscopy, a fundamental reflection and/or diffuse
scattering were selected as indicated in the insets. The elec-
tron diffraction patterns in the insets were observed with the
\([1\bar{1}1]\) incidence. Although the R-phase is basically trigonal
[19], the reflections are indexed in terms of the B2 structure
of the parent phase for easiness of comparison. Since the
microstructure of the parent phase is so tiny, not only the
diffuse scattering but also the fundamental reflection were
included. This observation mode is higher in both resolution
and image intensity than the conventional dark-field electron
microscopy for selecting one reflection for imaging.

Actually, this observation mode of dark-field electron
microscopy has successfully been applied to the analysis
of the modulated structure of alloy semiconductors [2]. In
Fig. 4(a), many tiny white dots smaller than 5 nm are seen in
the parent phase, indicating that the structure consists of
small domains, hereafter we call these microdomains. On
the other hand, the anti-phase boundary-like contrast is
observed in the R-phase. Since the R-phase is considered
to be a commensurate superstructure as shown by X-ray
diffraction [19] and electron diffraction [16] studies, the
contrast is interpreted to be something like anti-phase
boundaries in a single domain. It should be noted that the
anti-phase boundary-like contrast in the R-phase was sometimes mistaken for the microstructure of the premartensitic state in the parent phase in the previous conventional electron microscopy; the diffuse scattering in the parent phase is too weak to detect due to the strong background.

Fig. 5 shows the comparison of electron diffraction patterns of the parent phase (a, b) and the R-phase (c, d) observed at 280 K and 240 K, respectively. While (a) and (c) are observed with the \( ^{1}1^{1} \) incidence, (b) and (d) are observed with the systematic condition for suppressing the double diffraction effect. It is noted that the diffuse scattering around the 0 1/3 1/3 position is missing or forbidden in the diffraction pattern of Fig. 5(b). This is consistent with the X-ray [8] and neutron diffraction [9] studies. This feature is sharply different from the electron diffraction pattern of the R-phase in Fig. 5(d), whose structure was analyzed in detail by X-ray diffraction [19]. The missing of the 0\( hh \) type diffuse scattering directly indicates that the diffuse scattering in the parent phase results from a transverse type of atomic displacement whose propagation and displacement directions are such as [011] and [0\( \bar{1}1 \)], respectively. This may correspond to a softening of the [011] TA2-phonon mode around \( q_{01/31/3} \) as observed by the neutron inelastic scattering experiment [11]. The appearance of the diffuse scattering along the 0\( hh \) reciprocal lattice vectors across the origin in Fig. 5(a) is considered to result from the double diffraction effect. Note that the dark-field images in Figs. 4(a), 7 and 8 were observed carefully with the diffuse scattering, which is not produced by the double diffraction.

In Fig. 6(a), the intensity profiles of the diffuse scattering of the parent phase is shown as a function of the temperature. It is noted that the intensity of the diffuse scattering increases monotonously with the decrease in temperature. In Fig. 6(b), the position of the diffuse scattering of the parent phase and the superlattice reflection of the R-phase are shown as a function of the temperature. The peak position was evaluated with the distance from the fundamental reflection along the \( ^{1}1^{1} \) direction. Above 310 K, the peak position shows an incommensurate period of around 0.32 being constant, while the position of the diffuse scattering moves and comes close to the one-third position (0.333) below 310 K. Since the electron diffraction patterns were observed with the axial illumination condition, such as the \( ^{1}1^{1} \) incidence, some dynamical diffraction effect affects the intensity distribution of the diffuse scattering, as noted in Fig. 5(a). In particular, the interaction between the diffuse scattering, which is connected with the scattering vectors, corresponding to the fundamental reflections is relatively strong. Nevertheless, the trend of temperature dependence of the peak position of the diffuse scattering, i.e. not only the approach to the one-third commensurate position with
cooling but also the invariable incommensurability at higher temperature, is rather consistent with those observed in the previous neutron diffraction experiment [9]; although the compositions of the specimens are slightly different and the temperature range of the invariable incommensurability is much wider in our case. In Fig. 6(c), the full-width at half-maximum (FWHM) of the diffuse scattering is shown. It is interesting to point out that the FWHM is narrower in the [110] direction than in the [112] direction. This means that the microdomains tend to extend along the [110] direction preferably. It is also noted that the asymmetry becomes smaller at lower temperatures.

Fig. 7 shows a series of energy-filtered dark-field electron microscope images obtained with a fundamental reflection and the diffuse scattering indicated in the inset. Fig. 7(a) shows tiny microdomains as indicated by arrowheads oriented to the left. The sizes of the microdomains being less than 5 nm are similar to those observed in Fig. 4(a). In an energy-filtered dark-field electron microscope image of Fig. 7(b), which was observed with different diffuse scattering, distinct distribution of the microdomains was observed as indicated by arrowheads oriented to the right. This is consistent with the result of our previous paper [6]. After observing the image of Fig. 7(b), an energy-filtered dark-field electron microscope image under the same imaging condition as Fig. 7(a) was observed again (see Fig. 7(c)). Now, almost the same distribution of microdomains as that in Fig. 7(a) was observed. This correspondence indicates that the image contrast of the microdomains is not affected so strongly by the experimental condition of energy-filtered dark-field electron microscopy. On the other hand, in Fig. 7(d), an energy-filtered dark-field electron microscope image was observed with the larger objective aperture including diffuse scattering, which was used for imaging Fig. 7(a) and (b). As indicated by the two kinds of arrowheads, the positions of the small white dots correspond well to the microdomains in Fig. 7(a) and (b). Thus, this systematic study of the dark-field electron microscopy clearly demonstrates that each microdomain contributes to the diffuse scattering along one of the \langle110\rangle directions. In other words, each microdomain has a single transverse type of atomic displacement whose propagation and displacement directions are such as the [011] and [01\bar{1}] directions, respectively. Here, we should note that the microstructure with these microdomains is sharply different from that of the R-phase, which is created as a result of a combination of three \langle011\rangle\langle0\bar{1}1\rangle-type transverse displacement waves [19].

Finally, we carried out the in situ dark-field electron microscope observation with a TV system as shown in Fig. 8. With the decrease of temperature, the image contrast changed from (a) to (c) through (b). The diffraction condition and the objective aperture are shown in Fig. 8(d). Here, in order to get higher image intensity and to suppress the strong dynamical diffraction effect, only one fundamental reflection with an adjacent diffuse scattering is excited, and they are used for dark-field imaging as indicated by a white circle. In Fig. 8(a), microdomains in clear contrast are indicated by arrows. While the temperature decreases by about 1 K, small tiny domains appear and grow as indicated by arrowheads. It is interesting to notice that while these tiny domains grow, pre-existing microdomains indicated by the arrows do not grow appreciably, keeping their sizes less than 5 nm. These findings, based on dynamic observation, brought out the important features of the premartensitic state of this material, which satisfy the results obtained from the electron diffraction experiments, as noted below.

Firstly, it is noted that the number of microdomains increases with the decrease in temperature. This finding is consistent with the monotonous increase in the diffuse intensity with the decrease in temperature, as shown in Fig. 6(a).
and also as presented in the previous paper [6]. Secondly, the size of the microdomains does not exceed 5 nm. This finding explains the gentle slope of the FWHM of the diffuse scattering as a function of temperature in Fig. 6(c).

Also, the finding of the size limitation of the microdomains indicates that there exists some resistive force to the growing microdomains. If the microdomains consist purely of a single transverse type of atomic displacement with translational symmetry, they tend to grow large without a definite size limitation. The experimental result noted above clearly contradicts this tendency. One of the causes of the resistive force is the localized lattice strain between the matrix parent phase and the microdomains, and such lattice strain accompanying the single transverse type of atomic displacement in the microdomains may not have translational symmetry. Now, this lattice strain without the translational symmetry is considered to result in the characteristic movement of the peak positions of the diffuse scattering from one Brillouin zone to another as detected by the X-ray diffraction[8]. It is also noted that such a diffraction effect can be actually explained with the modulated lattice relaxation (MLR) model proposed on the basis of the embryos induced as defects, which were characterized by two types of displacements of atoms, i.e. one is [110]-shear and the other is [110]-elongation and [110]-contraction [20,21].

On decreasing the temperature, the lattice strain around the microdomains will be pronounced, it will induce the formation of new microdomains around it. As a result of the grouping of some microdomains, each of which has different propagation vectors of the displacement, the total energy will be reduced. When the temperature decreases further and comes down to $R_n$, it is reasonably considered that the lattice modulations of the microdomains, which consist of a single transverse type of atomic displacement and the lattice strain around it, are united to form a new structure in trigonal, i.e. the R-phase structure.

4. Conclusions

The present results obtained using energy-filtered electron microscopy and in situ electron microscopy on the premartensitic state of Ti$_{50}$Ni$_{48}$Fe$_2$ are summarized as follows.

1. Microstructure consisting of microdomains less than 5 nm in the premartensitic state is clearly contrasted with that showing the anti-phase boundary-like contrast in the R-phase through dark-field electron microscopy.

2. Through the analysis of the intensity distribution of energy-filtered electron diffraction patterns, the microdomains are found to extend along the (110) direction rather than the (112) direction with the incommensurate period that comes to the commensurate period of 3 with the decrease in temperature.

3. Each microdomain, basically, has a single transverse type of atomic displacement whose propagation and displacement directions are such as the [011] and [011] directions, respectively.

4. The growth process of the microdomains was clarified for the first time through in situ dark-field electron microscopy. Presence of the size limitation of growing microdomains, i.e. 5 nm as the maximum, is considered to result from the lattice strain without the translational symmetry accompanying the transverse type atomic displacement in the microdomains.

Acknowledgements

The authors wish to thank Professor K. Otsuka, University of Tsukuba for his interest and encouragement throughout the work. This study was partly supported by Grant-in-Aid for Scientific Research on the Priority Area ‘Investigation of Microscopic Mechanisms of Phase Transformations for the Structure Control of Materials’ from the Ministry of Education, Science, Sports and Culture of Japan, and for Encouragement of Young Scientists from the Ministry of Education, Science, Sports and Culture of Japan.

References

[1] D. Shindo, K. Hiraga, High-Resolution Electron Microscopy for Materials Science, Springer, Tokyo, 1998.
[2] D. Shindo, A. Gomyo, J.M. Zuo, J.C.H. Spence, J. Electron. Microsc. 45 (1996) 99.
[3] Y. Ikematsu, D. Shindo, T. Oikawa, Mater. Trans. JIM 41 (2000) 238.
[4] K. Otsuka, C.M. Wayman (Eds.), Shape Memory Materials Cambridge University Press, Cambridge, UK, 1998.
[5] D. Shindo, Y. Murakami, Y. Ikematsu, in: M. Koiwa, K. Otsuka, T. Miyazaki (Eds.), Proceedings of the International Conference on Solid–Solid Phase Transformations ’99 (JIMIC-3), The Japan Institute of Metals, 1999, p. 955.
[6] Y. Murakami, D. Shindo, Mater. Trans. JIM 40 (1999) 1092.
[7] M. Misumoto, T. Honma, Proceedings of the 1st International Symposium on Martensite, JIM, Kobe, 1976, p. 199.
[8] S.M. Shapiro, Y. Noda, Y. Fujii, Y. Yamada, Phys. Rev. B 30 (1984) 4314.
[9] M.B. Salamon, M.E. Meichle, C.M. Wayman, Phys. Rev. B 31 (1985) 7306.
[10] G.D. Sandrock, A.J. Perkins, R.F. Hehemann, Metall. Trans. 2 (1971) 2769.
[11] S.K. Satija, S.M. Shapiro, M.B. Salamon, C.M. Wayman, Phys. Rev. B 29 (1984) 6031.
[12] C.M. Hwang, M. Meichle, M.B. Salamon, C.M. Wayman, Philos. Mag. A 47 (1983) 9 (see also p. 31).
[13] T. Saburi, Proceedings of the International Conference on Martensitic Transformations, Monterey Institute for Advanced Studies, 1992, p. 857.
[14] M. Nishida, C.M. Wayman, Metallography 21 (1988) 255.
[15] D. Shindo, M. Hirabayashi, Acta. Crystallogr. Sect. A 44 (1988) 954.
[16] T. Tamiya, D. Shindo, Y. Murakami, Y. Bando, K. Otsuka, Mater. Trans. JIM 39 (1998) 714.
[17] G. Zanchi, J.Ph. Perez, J. Sévely, Microscopie Electronique à Haute Tension, Proceedings of the 4th International Conference for HVEM, Toulouse, 1975, p. 55.
[18] A. Taniyama, D. Shindo, T. Oikawa, J. Electron. Microsc. 46 (1997) 303.
[19] T. Hara, T. Ohba, E. Okunishi, K. Otsuka, Mater. Trans. JIM 38 (1997) 11.
[20] Y. Yamada, Proceedings of the International Conference on Marten- sitic Transformations, The Japan Institute of Metals, 1986, p. 89.
[21] Y. Yamada, Metall. Trans. 19A (1988) 777.