Antiphase Boundary-Like Structure of B19 Martensite in Ti-Ni-Pd Shape Memory Alloy

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The antiphase boundary (APB)-like structure of B19 martensite in the Ti-Ni-Pd alloy was investigated by means of conventional transmission electron microscopy and high-angle annular dark-field scanning transmission electron microscopy. Some APB-like structures with wide and curved contrast exhibited shifts along the (010)B19 and (001)B19 planes; that is, it exhibited facets composed of those planes at the atomic level. This atomic displacement reflects the atomic movement stemming from not only martensitic but also a kind of R-phase transformations.

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1. Introduction

Near equiatomic Ti-Ni and Ti-Pd alloys undergo thermoelastic martensitic transformation from the B2 to B19’ (monoclinic) and B19 (orthorhombic) structures upon cooling, respectively. The former alloy is a technologically important material with superior shape memory effect and superelasticity.1) The latter alloy is a candidate for high-temperature shape memory material because its transformation temperature is about 800 K.2) We have so far analyzed an antiphase boundary (APB)-like contrast of the martensite in Ti-Ni and Ti-Pd shape memory alloys.3,4) We characterized those APB-like structures as a kind of stacking fault with an APB-like morphology induced by the martensitic transformation. It has been reported that the atomic displacement of APB-like structure is influenced by not only martensitic but also pre-martensitic transformations. Concerning the pre-martensitic transformations, it is well known that the athermal ω-phase forms during quenching of β-Ti alloys, and that R-phase transformation in Ti-Ni-based alloys occurs. For example, Inamura et al.5) discovered an APB-like structure in a’-martensite in a Ti-Nb-Al alloy. The displacement vector was determined as a transformation-induced APB, with an additional small displacement stemming from a specific variant of the pre-existing athermal ω-phase. We also investigated an APB-like structure of the B19’ martensite via an R-phase transformation in a Ti-Ni-Fe alloy.5) It is concluded that the atomic displacement of an APB-like structure in a Ti-Ni-Fe alloy reflects the atomic movement stemming from the R-phase transformation itself, in addition to the displacement due to the atomic shuffling during the transformation directly from the B2 parent phase to B19’ martensite.

It is pointed out that the transition from B2 to B2(ω) structure before a martensitic transformation, meaning a pre-martensite, is caused by a substitution of Ni for Pd in the binary Ti-Pd alloy.6,7) Based on the increase of electrical resistivity during cooling process in the Ti-35.5 at% Ni-15.5 at% Pd alloy,8) the transition from B2 to B2(ω) is generally regarded as a kind of R-phase transformation. We therefore expect that the characteristics of APB-like structure of B19 martensite in the Ti-Ni-Pd alloy via a kind of R-phase transformation is different from those in Ti-Pd binary alloy without the pre-martensitic transformation. It is aim of the present paper is to clarify the crystallography and morphology of the APB-like structure of the B19 martensite in the Ti-Ni-Pd alloy by conventional transmission electron microscopy (CTEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The obtained results are discussed on the basis of the local heterogeneity of atomic movements during not only martensitic but also pre-martensitic transformations.

2. Experimental Procedure

A Ti-25.0 at% Ni-25.0 at% Pd alloy was prepared from 99.7% Ti, 99.9% Ni, and 99.8% Pd (mass%) by arc melting in an argon atmosphere. The ingots were homogenized in vacuum at 1273 K for 3.6 ks. Subsequently, the samples were solution-treated in vacuum at 1273 K for 3.6 ks, and then quenched into ice water. Differential scanning calorimetry (DSC) measurements were performed using a calorimeter (NETZSCH DSC-3500 Sirius) at a cooling and heating rate of 0.083 K/s. The TEM specimens were electropolished using a twin jet method in an electrolyte solution consisting of 20% H2SO4 and 80% CH3OH by volume at around 253 K. CTEM observation was carried out with a JEM-2000FX microscope (JEOL, Ltd., Tokyo) at an accelerating voltage of 200 kV. HAADF-STEM observations were performed using a JEM-ARM200F microscope (Cs-corrected 200 kV STEM; JEOL). The electron probe measured 0.1 nm and the current was approximately 20 pA. To obtain the HAADF-STEM images, the annular detector was set to collect electrons scattered at angles between 90 and 170 mrad. The HAADF-STEM allowed us to identify columns of relatively heavy atoms by their bright contrast in the image resulting from the atomic number (Z) contrast.9,10) The information that we obtained directly represented the structural image.

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corresponding to the actual atomic columns. HAADF-STEM is, therefore, a very powerful and useful technique for providing direct information on local structures at the atomic level. The crystal structure of the B19 martensite is of the AuCd-type with an orthorhombic cell. The lattice correspondence between the B2 parent phase and the B19 martensite is illustrated in Fig. 1.1) The dashed and solid lines indicated B2 and B19 structures, respectively. The following lattice parameters were used for the analysis: $a_{B19} = 0.278$ nm, $b_{B19} = 0.445$ nm, and $c_{B19} = 0.471$ nm.11)

3. Results and Discussion

Figure 2 shows DSC curves for the solution-treated Ti-25.0 at% Ni-25.0 at% Pd alloy. There is an exothermic peak corresponding to the B2 to B19 martensitic transformation during cooling. The martensitic transformation start ($M_s$) and martensitic transformation finish ($M_f$) temperatures are determined to be 425.4 K and 409.1 K, respectively. During heating an endothermic peak is observed. The reverse transformation start ($A_s$) and reverse transformation finish ($A_f$) temperatures are determined to be 332.8 K and 442.4 K, respectively. These transformation temperatures are almost agreement with previous results.12) The present alloy seems to undergo only martensitic transformation on the basis of each exothermic and endothermic peak.

Figures 3(a) and (b) show the typical bright field image and the electron diffraction pattern taken from the area marked B in (a), respectively, in the Ti-25.0 at% Ni-25.0 at% Pd alloy. This alloy is composed of B19 martensite as well as the near-equiaxial Ti-Pd alloy. The martensitic plates in this alloy are wider and larger than those of binary Ti-Ni and Ti-Pd alloys. The electron diffraction pattern shown in Fig. 3(b) consists of two sets of reflections, that are in mirror symmetry with respect to the (111)$_{B19}$ plane, from the [121]$_{B19}$ direction of a B19 structure. The trace of boundaries in region B is parallel to the (111)$_{B19}$ plane. This fact indicates that the two sets of reflections show a (111)$_{B19}$ twin pattern, and the platelet is a (111)$_{B19}$ type I twin, which is a lattice invariant shear of the martensitic transformation from the B2 to the B19 structures in the Ti-Ni-Pd alloy. These observations are consistent with the results provided in the previous reports.13,14) Note that many lined and curved contrasts are observed within the martensitic platelets, as indicated by the arrows in Fig. 3(a). In order to analyze these contrasts, CTEM observations are carried out from the [100]$_{B19}$ direction. HAADF-STEM observations were also performed along this direction, described below, because the atomic columns of Ti and Ni and/or Pd in the B19 structure can easily be distinguished.

Figures 4(a) and (b) show the bright-field image and corresponding electron diffraction pattern of [100]$_{B19}$ direction of a B19 structure, respectively. Some APB-like structures with wide and curved contrasts along both the (001)$_{B19}$ basal plane and (010)$_{B19}$ planes are observed in martensite plates of the Ti-25.0 at% Ni-25.0 at% Pd alloy, as indicated by the one and double arrows in Fig. 4(a), respectively, whereas APB-like structures with thin linear contrasts along the basal plane are observed in the B19 martensite plates of the equiaxial Ti-Pd alloy, as discussed in our previous reports.4) Figure 4(c), (d) and (e) shows dark-field images taken using 001$_{B19}$, 002$_{B19}$, and 003$_{B19}$ reflections, in which APB-like contrasts are observed. It has
been widely recognized that \( \pi \) contrast of APB induced by order-disorder transformations can be observed using superlattice reflections for the ordered structure, whereas no contrast is observed using fundamental reflections. The present APB-like contrast is observed when both the \( 001_{B19} \) and \( 003_{B19} \) superlattice and \( 002_{B19} \) fundamental reflections for the \( B19 \) structure are used. These facts mean that the APB-like contrast does not correspond to \( \pi \) contrast: they do, however, correspond to stacking faults with an APB-like morphology induced by the martensitic transformation, as expected from Ti-Ni and Ti-Pd alloys.\(^3\) The \( 020_{B19} \) reflection is used because the \( 010_{B19} \) reflection is forbidden according to the extinction rule of the \( B19 \) structure.\(^1\) No contrast is observed when the \( 020_{B19} \) reflection is used, as shown in Fig. 4(f).

The HAADF-STEM technique using \( Z \) contrast was performed to determine the positions of the atomic columns at the interface in APB-like contrasts. Figure 5(a) shows an HAADF-STEM image of the APB-like structure taken along the \( [100]_{B19} \) direction of a \( B19 \) structure. Figure 5(b) shows the image intensity profile taken along the white line X-Y in Fig. 5(a). It has been reported that Pd atoms can be located by electron channeling enhanced microanalysis at the Ni atom sites preferentially in the Ti-Ni-Pd alloy.\(^1\) Similarly, in the present case of Ti-25.0 at\% Ni-25.0 at\% Pd alloy Pd atoms are considered to be located at the Ni atom sites preferentially. Therefore, due to the nature of \( Z \)-contrast, the higher intensity profile shows Ni (\( Z = 28 \)) and/or Pd (\( Z = 46 \)) columns, whereas the lower intensity profile shows Ti (\( Z = 22 \)) columns. The bright and dim spots in Fig. 5(a), therefore, correspond to the Ni(Pd) and Ti atomic columns, respectively. The Fourier filter-processed image of Fig. 5(a) is presented in Fig. 5(c), and the atomic arrangements in Fig. 5(c) are schematically illustrated in Fig. 5(d). The open and solid circles indicate Ni(Pd) and Ti atom columns, respectively. We can see the atomic shifts along both the \( (010)_{B19} \) and \( (001)_{B19} \) planes by the arrows of Fig. 5(d). That is to say, the APB-like structure consists of facets composed of both \( (010)_{B19} \) and \( (001)_{B19} \) planes at an atomic level, as indicated by the line between the arrows of Fig. 5(d).

Based on the results of CTEM of Fig. 4 and HAADF-STEM of Fig. 5, we discuss the atomic displacement of the
APB-like structure in the present Ti-25.0 at% Ni-25.0 at% Pd alloy. We previously reported that the displacement vector of the APB-like structure on the B19 martensite in equiatomic Ti-Pd alloy can be expressed as $R = (0 1/2 1/3)_{B19}$, where the lattice correspondence of B19 martensite for B2 parent phase in equiatomic Ti-Pd alloy is in accordance with that in the present Ti-25.0 at% Ni-25.0 at% Pd alloy. The value of $R$ in equiatomic Ti-Pd alloy is equal to the displacement caused by atomic shuffling alone during the martensitic transformation to maintain the B19 structure between domains. Therefore, if the atomic displacement of the APB-like structure in the B19 martensite of Ti-25.0 at% Ni-25.0 at% Pd alloy is equal to the displacement caused by atomic shuffling alone during the martensitic transformation as well as the equiatomic Ti-Pd alloy, the value of $R$ in the present Ti-25.0 at% Ni-25.0 at% Pd alloy should be expressed as $R = (0 1/2 1/3)_{B19}$, meaning that no APB-like contrast was observed using each $g = 02n0$, and $003n$, where $n$ is an integer, by the relationship between the phase angle and $R$. As seen in Fig. 4(f), no APB-like contrast is observed using $g = 020_{B19}$. HAADF-STEM observation of Fig. 5(c) also supports that the atomic displacement along $b$-axis of APB-like contrast in the present Ti-Ni-Pd alloy is 1/2 by the positions of the atomic columns at the interface in APB-like contrasts. However, APB-like contrast is observed using $g = 003_{B19}$ shown in Fig. 4(e), meaning that the atomic displacement along $c$-axis in the APB-like contrast is not 1/3, which is not consistent with the $R$ of equiatomic Ti-Pd alloy.

Furthermore, to confirm the atomic displacement along the $a$-axis in APB-like structure, CTEM observations were carried out along the [001]$_{B19}$ direction; these revealed the displacement along the $a$-axis on the $a$-$b$ plane. Figures 6(a) and (b) shows a bright-field image and corresponding electron diffraction patterns of [001]$_{B19}$ direction of a B19 structure, respectively. Some APB-like structures with curved contrasts are observed in martensitic plates as well as those along [100]$_{B19}$ direction of a B19 structure in Fig. 4. Figures 6(c) and (d) shows dark-field images taken using 100$_{B19}$ and 020$_{B19}$ reflections, respectively. The APB-like contrast is observed when the 100$_{B19}$ reflections, indicating that the APB-like contrast shows a displacement in its $a$-axis component. No contrast is observed when using the 020$_{B19}$ reflection, as shown in Fig. 6(d). Figure 7(a) shows an HAADF-STEM image of the APB-like structure along the
[001]_{B19} direction of a B19 structure. The Fourier filter-processed image of white framed area indicating APB-like contrast in Fig. 7(a) is presented in Fig. 7(b). The bright and dim spots in Fig. 7(b) correspond to the Ni(Pd) and Ti atomic columns, respectively, because of the nature of Z contrast, as was found in Fig. 4(a). As indicated by the area between the arrows in Fig. 7(b) the contrasts of atomic columns on the (100)_{B19} planes becomes obscure. To enhance the visibility of the atomic column, a Fourier filtered images using only \{100\}_{B19} and \{200\}_{B19} reflections marked in the diffractogram Fig. 7(d) is presented in Fig. 7(c), indicating that the distortion of atomic columns on the (100)_{B19} planes is observed around APB-like structure. On the other hand, no atomic displacement on the (010)_{B19} planes is observed in Fig. 7(e), which is a Fourier filtered images using only \{020\}_{B19} reflections marked in the diffractogram Fig. 7(f). This proves that APB-like contrast in the present Ti-25.0 at\% Ni-25.0 at\% Pd alloy has a displacement along a-axis component in contrast to that in equiatomic Ti-Pd alloy. That is to say, the \( R \) of APB-like structure in both alloys is different although the crystal structure of both alloys is the same as B19 martensite at room temperature. These mean that the atomic displacement of the APB-like structure in the present Ti-25.0 at\% Ni-25.0 at\% Pd alloy is not only due to the atomic shuffling during the martensitic transformation directly from the B2 phase to B19 structure, which is different from the APB-like structure in equiatomic Ti-Pd binary alloy.

We further discuss about the \( R \) of APB-like structure on the B19 martensite in the present Ti-25.0 at\% Ni-25.0 at\% Pd alloy. As described above, it has been so far reported that the atomic displacement of APB-like structure is influenced by not only martensitic but also pre-martensitic transformations.\(^5\)\(^6\) In the case of the present Ti-Ni-Pd alloy, there seems to be no clearly additional peak indicating the R-phase transformation except for martensitic transformation shown in DSC curves of Fig. 2. However, the existence of a kind of R-phase transformation as a pre-martensite is pointed out on the basis of the increase of electrical resistivity during cooling process in ternary Ti-Ni-Pd alloy containing much Pd.\(^7\)\(^8\) The R-phase lattice can be described by stretching the B2 parent lattice along the \{111\}_{B2} diagonal directions. Since there are four \{111\}_{B2} orientations in the B2 parent lattice, four lattice correspondences are possible between the B2 parent lattice and the R-phase lattice.\(^18\)\(^-\)\(^20\) These suggest that the displacement along \{111\}_{B2} direction of the B2 parent phase stemming from the R-phase transformation corresponds to either the \{101\}_{B19} direction on the \{010\}_{B19} or the \{110\}_{B19} direction on the \{001\}_{B19} plane for the B19 martensitic lattice, as shown in Fig. 1. That is to say, these displacements can be expressed as \( R_{xz} = (\delta, 0, \delta)_{B19} \) and \( R_{xy} = (\delta, \delta, 0)_{B19} \), respectively. Therefore, the displacement adding the \( R_{xz} \) to the displacement vector caused by atomic shuffling during the martensitic transformation; that is, \( R = (0 -1/2 1/3)_{B19} + (\delta, 0, \delta)_{B19} = (\delta, -1/2 1/3 + \delta)_{B19} \), can explain the APB-like contrasts using each \( g = 020_{B19} \) and \( 003_{B19} \). The \( R_{xy} \) associated with the APB-like contrasts using \( g = 020_{B19} \) is now under study. From the relationship of \( g R \) in the present APB-like contrasts described above, it is concluded that atomic displacement of the APB-like structure of the martensite via a kind of R-phase in the Ti-Ni-Pd alloy reflects the atomic movement stemming from a kind of R-phase transformation, meaning that the APB-like structure is affected by the atomic movements during not only marten-
sitic but also a kind of R-phase transformations. As a matter of concern, the crystallography and exact transformation temperature region of a kind of R-phase transformation itself in this alloy should be investigated by in-situ TEM observations before and after the transformation and measuring the electrical resistivity. The present obtained results provide that it is important to characterize the APB-like structure for the elucidation of the atomic movements during pre-martensitic and martensitic transformations, resulting in a further understanding of the shape memory behavior.

4. Conclusion

An APB-like structure of the B19 martensite in the Ti-Ni-Pd alloy was investigated by means of CTEM and HAADF-STEM. Some APB-like structures with wide and curved contrast exhibited shifts along the (010)_{B19} and (001)_{B19} planes; that is, it exhibited facets composed of those planes at the atomic level. The atomic displacement on the APB-like structure of the B19 martensite in Ti-Ni-Pd alloy reflects the atomic movement stemming from a kind of R-phase transformation, in addition to the displacement due to the atomic shuffling during the transformation directly from the B2 parent phase to B19 martensite.

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