Martensite structure in polycrystalline Fe–Pd

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Abstract

The martensite structure in polycrystalline Fe–Pd has been examined from a mechanics and a crystallographic point of view. The structure consists of dark and bright plates, parallel to {110}, which, under no stress, exist in an equal amount. A plate has a fine structure, in which a set of twin-related variants adjoining on {110} interfaces is stacked together. That is, the dark plate contains two twin-related variants as does the bright plate. One variant in the bright plate is the same as one in the dark. The others are twin-related. In total, a grain is covered by equal amounts of three variants when transformation is completed. Straining caused by uniaxial loading is evaluated. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Martensitic transformation, from fcc to fct, in Fe–Pd was extensively studied by an Osaka University group in the past [1–7]. There has been a revival in interest recently as, from a practical point of view, Fe–Pd has potential to be used as a magnetic field controlled actuator [8,9]. Actuation is produced by the formation of certain variants by martensitic transformation or a change in the fraction of variants in the martensite state. The deformation caused by these changes should be understood in terms of micrcostructure and changes in microstructure. Oshima et al. have examined the structure of martensite [1–4]. Martensite consists of alternating lamellar plates. Each plate further consists of two types of twin domains stacked on each other on {110}, twin interfaces in fct. The lamellar interface is also {110}. Apparently such an interface is not a habit plane of a twinned martensite plate (TWP). Despite temperature dependence of lattice parameters in the martensite phase [1–3], such a simple lamellar interface

is always observed regardless of temperature. This paper presents a reason for this observation. A polycrystal material is most likely to be used in application. Therefore, the present study examines the detailed martensite structure characteristic of a polycrystal. However, part of the study of course applies to a single crystal state. Further, a change in structure in a stressed polycrystal is discussed.

2. Analysis

2.1. Martensite plates

Three Bain correspondent variants (BCVs) exist for the fcc to fct transformation in Fe–Pd. Their transformation strains are written as

$$\varepsilon^{\mathrm{T}}(1) = \begin{bmatrix} \varepsilon_c & 0 & 0 \\ 0 & \varepsilon_a & 0 \\ 0 & 0 & \varepsilon_a \end{bmatrix} \quad \text{in BCV(1).}$$

$$\varepsilon^{\mathrm{T}}(2) = \begin{bmatrix} \varepsilon_a & 0 & 0 \\ 0 & \varepsilon_c & 0 \\ 0 & 0 & \varepsilon_a \end{bmatrix} \quad \text{in BCV(2),}$$

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$$\varepsilon^{T}(3) = \begin{bmatrix} \varepsilon_a & 0 & 0 \\ 0 & \varepsilon_a & 0 \\ 0 & 0 & \varepsilon_c \end{bmatrix} \quad \text{in BCV(3).} \tag{1}$$

Here, the coordinate system is taken as the austenite orthogonal system.

$\varepsilon_a = (a - a_0)/a_0$ and $\varepsilon_c = (c - a_0)/a_0$. a_0 is the lattice parameter of austenite and a is the lattice parameter of the two a-axes and c that of the c-axis in martensite. Throughout this paper, we will use an infinitesimal deformation approach to analyze the geometry and structure of martensite [10]. A single BCV cannot form

30μm

Top surface (0.390 0.558 0.732)

Fig. 1. Optical micrograph of martensite in an Fe–30.5% alloy cooled to 14 °C. Three austenite twin boundaries in the central grain can index the interfaces of bright and dark martensite plates with the matrix. It is seen that the two alternately stacked plates have equal fractions.

500nm

Fig. 2. Two adjoining martensite plates (TWPs) have smaller twins, each of which is a BCV, inside the plates (transmission electron micrograph).

a stress free martensite plate [10]. Thus, we must examine a combined variant that has an invariant plane interface with the matrix. Any combination of two BCVs can form a combined variant plate, in which two BCVs stack together on undistorted planes. For example, consider BCV(1) and BCV(2). The difference of the transformation strain between these BCVs is written as

$$\delta\varepsilon^{T} = \varepsilon^{T}(2) - \varepsilon^{T}(1) = \begin{bmatrix} \varepsilon_a - \varepsilon_c & 0 & 0 \\ 0 & \varepsilon_c - \varepsilon_a & 0 \\ 0 & 0 & 0 \end{bmatrix}. \tag{2}$$
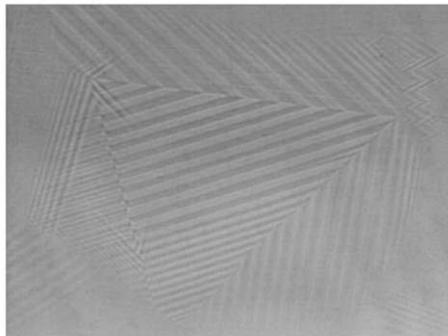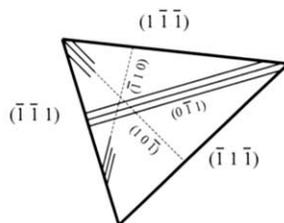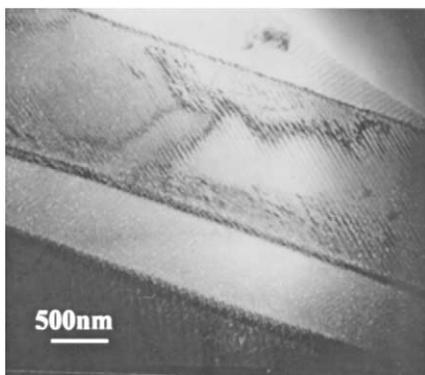
Eq. (2) satisfies the condition that two variants can meet on an undistorted plane [10]. Further, Eq. (2) means that the undistorted interface of these BCVs is (110) or ($\bar{1}$10) [10]. These two planes coincide with a twinning plane for these BCVs, as reported by Sugiyama, Oshima and Fujita [3,4]. The undistorted plane of the combination of BCV(2) and BCV(3) is (011) or (0$\bar{1}$1) and that of BCV(3) and BCV(1) is (101) or (10$\bar{1}$).

A combined variant can form a plate, which does not cause (long range) stress, as discussed before [10] and will be examined later in the present specific problem. As seen in Fig. 1, when a grain transforms into a fully martensitic state, a martensite colony which consists of two sets of parallel plates (e.g. dark and bright plates) stacked alternatively is formed. These plates have fine structures, as shown in the electron micrograph of Fig. 2. Two adjoining domains in a zone, which appears as a plate under optical microscopy, are twin-related with a twinning plane of {110}. This agrees with the above crystallographic examination and with the observation of Sugiyama, Ohshima and Fujita [3]. Apparently, the parallel plates seen in optical microscopy constitute an ensemble of compound twins. We will examine the geometry of such an ensemble in the following manner.

First, the average transformation strain of a TWP in a compound twin ensemble is examined. For example, consider again a combined martensite plate, TWP(1, 2), consisting of BCV(1) and BCV(2). Its average transformation strain is written as

$$\overline{\varepsilon}^{T}(1, 2) = \begin{bmatrix} \varepsilon_a - f_0(\varepsilon_a - \varepsilon_c) & 0 & 0 \\ 0 & \varepsilon_c + f_0(\varepsilon_a - \varepsilon_c) & 0 \\ 0 & 0 & \varepsilon_a \end{bmatrix}$$

in TWP(1, 2). \tag{3}

Here, f_0 is the fraction of BCV(1) in this plate of TWP(1, 2). Suppose that another TWP(2, 3) is formed by the combination of BCV(2) and BCV(3). The average transformation strain of TWP(2, 3) is written as
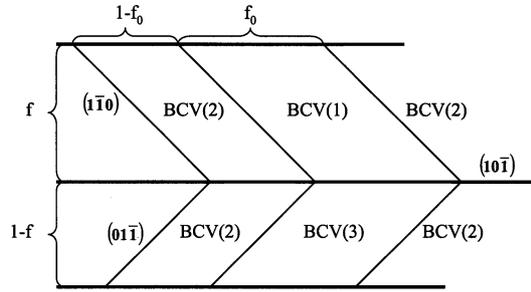
Fig. 3. Part of two adjoining plates in a martensite ensemble, consisting of two parallel TWPs and having BCVs in them, is schematically drawn. BCV(1) is twin-related to BCV(2) and BCV(3), and BCV(2) to BCV(3).

$$\overline{\varepsilon}^{\mathrm{T}}(2, 3) = \begin{bmatrix} \varepsilon_a & 0 & 0 \\ 0 & \varepsilon_a - f_0'(\varepsilon_a - \varepsilon_c) & 0 \\ 0 & 0 & \varepsilon_c + f_0'(\varepsilon_a - \varepsilon_c) \end{bmatrix}$$

in TWP(2, 3). (4)

Here, f_0' is the fraction of BCV(2) in this combined martensite plate. Using a previous result [10], it can be shown that TWP(1, 2) and TWP(2, 3) can have an undistorted interface of (101) or ($\overline{1}$01), if

$$f_0 + f_0' = 1. \tag{5}$$

That is, TWP(1, 2) and TWP(2, 3) can join together on (101) or ($\overline{1}$01) without causing elastic strain. This geometry is shown in Fig. 3. As seen here, BCV(1) in TWP(1, 2) and BCV(3) in TWP(2, 3) also join on their undistorted twin plane, (101). There is, in reality, no boundary between BCV(2) in TWP(1, 2) and BCV(2) in TWP(2, 3). By further stacking the identical set of two TWPs, a martensite ensemble consisting of the two TWPs is formed. In this ensemble, there are three BCVs. There are two other equivalent combinations of TWPs to form an ensemble of compound twins.

Briefly stated, the {110} interface of two TWPs, as reported by Sugiyama, Oshima and Fujita [3,4], can be understood in two ways. One is crystallography and the other mechanics and geometrical analysis facilitated by an infinitesimal deformation approach [10].

The present study has also confirmed {110} interfaces of TWPs in a martensite ensemble by using, for example, Fig. 1. The central grain, as schematically drawn below, has three different austenite twin boundaries, {111}. Thus, the orientation of the grain can be indexed and its normal is (0.390 0.558 0.732). Similarly, the traces of the three austenite twin planes are indexed. The grain also has three different martensite ensembles. All the traces of the TWP interfaces of these ensembles on the surface of the grain can be consistently accounted for, if the TWP interface is indexed as {110}. Also, by analyzing traces of TWP interfaces in some more grains having two different austenite boundaries, the {110} TWP interfaces have been further confirmed.

A set of TWPs which is produced, for example, by replacing TWP(2, 3) by TWP(2, 1) in Fig. 3 cannot form. In this configuration, BCV(2) replaces BCV(3) and BCV(1) BCV(2) in Fig. 3. If this were so, the twin interface in TWP(1, 2) would be (110), while that in TWP(2, 1) would be (110). The interface between TWP(1, 2) and TWP(2, 1) would then become (010) or (100). These are neither undistorted twin interfaces between BCV(1) and BCV(2) nor the observed interface of two TWPs in an ensemble. That is, a BCV in TWP(1, 2) cannot adjoin another BCV in TWP(2, 1), to which the former BCV is twin-related.

The remaining task is to determine the fraction of constituent TWPs in an ensemble and that of a certain BCV in a TWP, e.g. BCV(1) in TWP(1, 2). If an ensemble of compound twins covers a whole single crystal, these fractions can take any value, as far as geometry is concerned. This is clear from Fig. 3. However, if it is formed in a grain surrounded or constrained by other grains as in a polycrystal, a particular set of the fractions make elastic energy minimum. The analysis given assumes a spherical grain and isotropic elasticity.

2.2. Martensite in a polycrystal

Suppose that a grain is completely covered by an ensemble (the influence of other transformed grains will be discussed later). The average transformation strain for a grain in the above example is written as

$$\varepsilon^* = f\overline{\varepsilon}^{\mathrm{T}}(1, 2) + (1 - f)\overline{\varepsilon}^{\mathrm{T}}(2, 3). \tag{6}$$

Here, f is the fraction of TWP(1, 2) in the ensemble. For convenience, Eq. (6) is explicitly written as

$$\varepsilon^* = \frac{2\varepsilon_a + \varepsilon_c}{3} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + (\varepsilon_a - \varepsilon_c)$$

$$\times \begin{bmatrix} 1/3 - ff_0 & 0 & 0 \\ 0 & f_0 - 2/3 & 0 \\ 0 & 0 & 1/3 - f_0(1 - f) \end{bmatrix}. \tag{7}$$

Here, Eq. (5) is used. The first term causes hydrostatic stress in the grain and does not interact with the second term, the deviatoric part of the average transformation strain, in terms of energy. Further, the first term is independent of f and f_0 and only the second term depends on these f-parameters describing the structure of the ensemble. Thus, we seek the combination of f and f_0 which minimizes the elastic energy due to the second term of Eq. (7) to determine the structure of a martensite ensemble in a polycrystal.

Using Eshelby [11] and Mura [12], the stress in a spherical inclusion is calculated as

$$\sigma_{ij} = -2\mu \frac{(1+5v)}{15(1-v)} \varepsilon_{kk}^* \delta_{ij} - 2\mu \frac{(7-5v)}{15(1-v)} \varepsilon_{ij}^*. \tag{8}$$

Here, μ is the shear modulus, v the Poisson ratio and δ_{ij} the Kronecker delta. Thus, the stress due to the second term in Eq. (7) is written as

$$\sigma = -2\mu \frac{(7-5v)}{15(1-v)}(\varepsilon_a - \varepsilon_c)$$

$$\times \begin{bmatrix} 1/3 - ff_0 & 0 & 0 \\ 0 & f_0 - 2/3 & 0 \\ 0 & 0 & 1/3 - f_0(1-f) \end{bmatrix}. \tag{9}$$

The elastic energy due to this term is calculated by a standard formula of $-(V/2)\sigma_{ij}\varepsilon_{ij}^*$ [11,12] (V is the volume of the inclusion). Thus, the elastic energy due to the second term of Eq. (7) is given by

$$E = \frac{2\mu(7-5v)}{15(1-v)} V \left(f^2 f_0^2 - ff_0^2 + f_0^2 - f_0 + \frac{1}{3} \right). \tag{10}$$

It is clear that the elastic energy is minimized, when

$$f = \frac{1}{2} \quad \text{and} \quad f_0 = \frac{2}{3}. \tag{11}$$

are satisfied. That is, a single grain has a structure in which the fractions of two TWPs are equal and the fraction of a BCV, common to two TWPs forming an ensemble, is 1/3. This means that three BCVs exist in an equal amount in an ensemble. The above analysis, which led to 1/3 is different from that for a single crystal assuming that the transformation involves no volume change [13]. This point will further be discussed later. The equal fraction of two TWPs is always observed in our metallographic observations. An example is seen in Fig. 1.

The above solution of Eq. (11) makes the configurational ectropy maximum. Let the fractions of BCV(1), BCV(2) and BCV(3) be f_1, f_2 and f_3, respectively. The configurational entropy per unit volume is calculated as $-(k/\Omega)\ (f_1 \log f_1 + f_2 \log f_2 + f_3 \log f_3)$, using Boltzmann's standard expression. Here, k is the Boltzmann
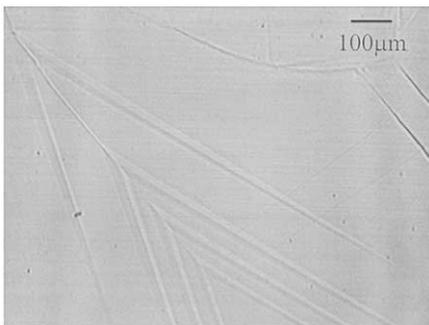
constant and Ω is the atomic volume. When $f_1 = f_2 = f_3 = 1/3$, the configurational entropy becomes maximum. This condition coincides with Eq. (11), as mentioned in the previous paragraph. In total, the Helmholtz free energy, the sum of elastic energy and the negative of entropy times temperature, becomes minimum when Eq. (11) is satisfied.

The effects of surrounding grains on the transformation of a grain is briefly discussed. When the f-parameters take the values given by Eq. (11), the deviatoric part in Eq. (7) vanishes. That is, the average transformation strain of the grain becomes uniform expansion or contraction. This applies to other grains. Thus, the relative misfit between a particular grain and its surrounding vanishes. This result occurs only when Eq. (11) is satisfied. This result is valid even though the orientations of martensite variants differ from grain-to-grain, depending partly on the orientations of original austenite grains.

We also note that the above conclusion is valid as long as a material has elastic constants with cubic symmetry. Firstly, this is because the second term in Eq. (7) vanishes in the energy minimum condition. Secondly, the first term causes hydrostatic stress in a grain having cubic symmetry, even when a single grain transforms, while other grains are in the austenite phase. The martensite of Fe–Pd is almost cubic in structure and for all practical purposes can be analyzed by the present method.

We have noticed that in the very beginning of transformation in Fe–Pd, long before a whole grain is covered by a martensite ensemble, an isolated wedge shaped martensite plate appears; an example is shown in Fig. 4. A complete experimental analysis could not be performed for this type of wedge shaped and isolated plate. This is because a wedge shaped martensite grows rapidly. Once it hits a grain boundary, other martensite plates are formed in contact with the first one (the interfaces of these plates are the same as that of a martensite ensemble). However, we believe that an isolated wedge shaped martensite is a combination of two TWPs. The central plane is the undistorted matching plane examined for the interface of two TWPs and the outer interfaces with the matrix is undistorted planes of TWPs to the matrix. An undistorted plane of one TWP can be analyzed using a previously reported method [10]. Consider a single TWP consisting of BCV(1) and BCV(2). Using the previous study [10], it can be shown that if f_0 in Eq. (3) is given by

$$f_0 = \frac{\varepsilon_a}{\varepsilon_a - \varepsilon_c}, \tag{12}$$

or

$$f_0 = -\frac{\varepsilon_c}{\varepsilon_a - \varepsilon_c}, \tag{13}$$

Fig. 4. A freshly formed martensite on cooling. This type of isolated martensite has a wedge shape.

100μm

this TWP (combined martensite variant) can contact the matrix on an undistorted plane (habit plane). The orientation of the undistorted plane is given by

$$\left(0 \quad \sqrt{\frac{(\varepsilon_a + \varepsilon_c)}{\varepsilon_c}} \pm \sqrt{\frac{-\varepsilon_a}{\varepsilon_c}}\right), \tag{14}$$

for Eq. (12) and

$$\left(\sqrt{\frac{(\varepsilon_a + \varepsilon_c)}{\varepsilon_c}} \quad 0 \pm \sqrt{\frac{-\varepsilon_a}{\varepsilon_c}}\right). \tag{15}$$

for Eq. (13). Of course, these planes are different from the undistorted plane of two TWPs in a compound twin ensemble. Using the lattice parameters reported by Oshima [2], the undistorted plane is calculated to be (0 0.557 ± 0.830) or (0.557 0 ± 0.830) just below the Ms temperature (~ 20 °C). We would also like to mention that the fraction of one BCV in a TWP is, in general, not a simple fraction. If $2\varepsilon_a + \varepsilon_c = 0$ holds, as assumed in a study of In–Tl [13], the fraction of a BCV in an isolated TWP becomes 1/3 or 2/3. The condition of $2\varepsilon_a + \varepsilon_c = 0$ is coincidental. Thus, the condition for the fraction of one BCV in a martensite plate to be 1/3 or 2/3 must not be taken for granted, as sometimes assumed [4,8,13]. On the contrary, equal fractions of three BCVs in a martensite ensemble in grains in a polycrystal hold, as long as transformation is from cubic to tetragonal. It is independent of such parameters as the axial ratio of martensite or the absolute values of the lattice parameters. Thus, even if the lattice parameters of martensite sensitively depend on temperature, as reported in Fe–Pd [1–3], $f = 1/2$ and $f_0 = 2/3$ must be observed. Similarly, the interfaces of two adjacent TWPs are also {110} under the same situation.

2.3. Straining by transformation or variant change

When martensite is stress induced or a transformed specimen is additionally stressed, the fraction of TWPs constituting a compound twin ensemble (e.g. dark and bright bands in Fig. 1) changes. Also, the fractions of two BCVs in a TWP changes. When stress becomes extremely large, a grain becomes mono-toned and shows no contrast under optical microscopy, as will be reported in a separate paper. We can estimate the maximum strain attained by changes in the fractions of constituting BCVs in grains of a polycrystal. These fractions satisfy

$$f_1 + f_2 + f_3 = 1. \tag{16}$$

The grain has the average uniaxial transformation strain given by

$$\varepsilon = \varepsilon_a - (\varepsilon_a - \varepsilon_c)(f_1 \ell_1^2 + f_2 \ell_2^2 + f_3 \ell_3^2) \tag{17}$$

Here, ℓ_1 is the direction cosine of [100] of the grain to the loading (tensile or compression) axis. Similar definitions are given to ℓ_2 and ℓ_3. Since Eq. (17) is a linear

function of f_1, f_2 and f_3 and these are bound by Eq. (16), the maximum ε_T or minimum ε_C of Eq. (17) can be easily found. That is, ε_T and ε_C are, respectively, equal to the smallest and largest of $f_i \ell_i^2$, $i = 1$ to 3 (in Fe–Pd, $\varepsilon_a - \varepsilon_c > 0$). This means that the maximum tensile strain or compressive strain is attained by grains having the tensile direction of $\langle 100 \rangle$, while such strains are the smallest in grains having the tensile direction of $\langle 111 \rangle$.

This conclusion holds for the strain in a grain of a polycrystal, whether it is strained before or after thermal transformation. The former applies to stress-induced transformation and the latter to straining due to a change in the variant fraction by loading of a transformed polycrystal. We are currently studying uniaxial stress–strain curves of a polycrystal in the above cases. In these cases we have to calculate elastic energy in a polycrystal, the elastic energy which is caused by differences in transformation strain between differently oriented grains. The calculation is straightforward and will be reported in separate papers. The maximum (for tension) and minimum (for compression) strains attained by a ploycrystal having randomly oriented grains can be calculated without the above procedure. For example, when straining occurs by the variant change in a fully martensite state, the maximum strain attained by a polycrystal is $(2/\pi)(1 - 1/\sqrt{3})(\varepsilon_a - \varepsilon_c)$ and the minimum strain $2/(\sqrt{3}\pi)(\varepsilon_a - \varepsilon_c)$.

3. Summary

The structure of fct martensite formed from fcc austenite of Fe–Pd is studied from a micromechanics point of view on the basis of an infinitesimal deformation approach. The structure is also examined in terms of crystallography. When fully developed, martensite takes the form of an ensemble, in which a TWP adjoins another TWP. In this ensemble, all three BCV are twin-related. The interface between two plates as well as that between two BCVs in a plate is {110}. The elastic energy caused by martensitic transformation in a polycrystal is formulated. It becomes minimum, when the fractions of adjoining martensite plates are equal and the ratio of one BCV to the other BCV in a plate is 2 to 1. That is, when the elastic energy is minimized, all three BCVs are equally present in a grain by forming a martensite ensemble. Straining by variant change under uniaxial loading is briefly discussed.

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