Characteristics of the A/D type twin boundary in 18R martensite in a Cu–Zn–Al alloy

J.X. Zhang a,*, Y.F. Zheng a,b, B.M. Huang a, W. Cai a, L.C. Zhao a

a School of Materials Science and Engineering, Harbin Institute of Technology, Harbin, 150001, China
b Laboratory of Atomic Imaging of Solids, Institute of Metals Research, Chinese Academy of Sciences, Shenyang, 110015, China

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Abstract

The A/D type twin boundary between 18R martensite plates in a Cu–Zn–Al alloy has been studied by both transmission electron microscopy (TEM) and high resolution electron microscopy (HREM). It is curved in TEM and has irregularly serrated steps in HREM. The randomly distributed faults have no obvious influence on the boundary orientation. The boundary segments consist of respective basal planes of the two variants. Crystallographic analysis shows that the macroscopic curve results from the non-self-accommodation of transformation strain of the two variants. The calculated boundary energies based upon the model of a small-angle tilt grain boundary indicate that the deviation from the exact twin orientation and the irregularly serrated steps result from energy minimization. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Twin orientation relationships are an essential feature of martensites in shape memory alloys [1–3]. The process of deformation twinning enables numerous interfaces to exhibit high mobility under applied stress, leading to the shape memory behavior [1], indicating the importance of the structure of the intervariant interfaces and their mobility in understanding the mechanical behavior of these alloys.

Three types of twin are seen in Cu–Zn–Al martensite variants, viz., the habit plane type, (128) and (1010) twins, termed A/B, A/C, and A/D types [4], respectively. Many investigations have been carried out on these three kinds of twin boundaries by TEM and HREM [4–7]. It has been shown that the A/B type pair [4] and A/C type pair [5,6] all have coherent, straight intervariant boundary planes, but the A/D pair has a curved one [6]. Adachi et al. explained the zigzagged shape of the A/D boundary by a matching between 18R martensite and 2H type stacking faults [6]. However, the spacing of the random faults required to ensure that the habit plane is invariant is calculated to be 47.28 Å [1], that is to say, along the boundary, the connected parts are mostly 18R/18R. Therefore, the curvature of 18R/18R boundary is still in question.

In this work, a high resolution electron microscopy observation has been carried out to elucidate the exact characteristics and nature of the A/D type boundary in 18R martensite in a Cu–Zn–Al alloy.

2. Experimental details

A Cu–20.4Zn–5.6Al (wt.%) alloy was prepared by melting the elements (≥99.99% in purity) in an induction furnace. After homogenization at 850°C for 12 h, the ingot was rolled into sheet 1 mm in thickness. The specimens were held at 850°C for 10 min, quenched in boiling water, aged at 100°C for 30 min, and then air cooled to room temperature. The transformation temperatures were determined by calorimetry to be Ms = 78°C, Mf = 40°C, As = 50°C, Af = 86°C. The specimens were then mechanically thinned to 50 μm. Discs 3 mm in diameter were then cut and electropolished using a conventional electrolyte of HNO₃:CH₃OH = 1:2 at 14 V and about −35°C. Ob-
servations were made at room temperature in a H-800 and JEM 2000EX II electron microscopy operated at 175 Å and 200 kV, respectively.

3. Results

Fig. 1 is a low-magnification photograph of A/D type boundary and its corresponding selected area diffraction pattern. It is obvious that the boundary is not as straight as an A/C type boundary, and the curvature is different for different A/D pairs (note the lower two A/D pairs—this kind of curve is referred to as macroscopic curve). As pointed by Adachi et al. [4,6], the A/B and A/C type variant plate combinations have straight twin boundaries because of their self accommodation of the martensite shear deformation, while non-self-accommodating A/D pairs are thought to appear in order to adjust the local stress field or to accommodate changes in growth direction. Because the non-self-accommodation of A/D variants, they can not grow together like A/C variants, but a D variant would impinge a previously formed A variant (or vice versa) [1]. This process frequently occurs and results in a ‘wavy’ (1010)_{18 R} junction plane. Thus it can be concluded that this kind of macroscopic curve is ascribed to non-self-accommodation of A/D type variant couplings.

Though A/D type boundaries have different curvatures depending on their site and location, they have similar characteristics as seen in high-magnification. Fig. 2 is a high resolution image showing the (1010)_{18 R} A/D type twin boundary taken along the [010]_{18 R} zone axis. The upper variant appears misoriented which may be due to the fact that the [010] directions of the two variants are not exactly parallel (based on a calculation using the phenomenological theory [8], the angle between [010]_{A} and [010]_{D} is 2.9°). The same phenomenon was observed by Wang et al. [7] for the same boundary and Lovey et al. [5] for A/C type twin boundary. Microscopically (on an atomic scale), the A/D type boundary consists of irregularly-serrated steps, with the
facet parallel to the basal plane of one or the other variant. Along the facet there is a distorted area where the facet deviates from its corresponding basal plane (shown by arrows B,C). A basal plane stacking fault can be identified in martensite variant D of the Fig. 2. The fault is a cubic fault (α type) (according to the definition given by Nishiyama et al. [9]). Unfortunately, the other stacking faults can not be distinguished from the stacking sequence due to the misorientation. It can be seen that there is no significant difference in the boundary orientation, no matter whether the stacking sequence in the martensite variant is perfect or a single fault is present. In other words, a single fault has no obvious influence on the boundary structure.

4. Discussion

The (1010) plane in martensite is derived from the (100) plane in the original b.c.c. lattice [2], but the two variants A and D do not possess a straight (1010) boundary. This is mainly ascribed to the crystallography of A and D variants. Fig. 3 is the calculated orientation relationship between major planes of martensite variants A and D plotted on an (001)β1 stereographic projection. As a twin plane, the poles of (1010) planes in variants A and D do not coincide, but are 3.87° apart. Schroeder et al.’s work showed that the energy of the A/D boundary is fairly high, because in two bonds out of three across the boundary two atoms belonging to the two variants respectively are brought very close together [1]. The non-coincidence of the (1010) twin plane of the considered variants maybe lead to a boundary similar to a tilt grain boundary, which will make the boundary energy higher. On the other hand, the WLR theory [8] predicts that the (0018) basal plane of one variant is only 2.13° away from the (101)
plane of the other. It is reasonable that the boundary
segments (0018)\(\alpha\)/(101)\(\beta\) or (0018)\(\alpha\)/(101)\(\beta\) might have
a lower energy than the boundary (1010)\(\alpha\)/(1010)\(\beta\)
(\(\approx 3.87^\circ\)) (not close packed planes).

4.1. Probability of the junction of (101) and (0018)
planes

It is well known that the planes (0018) and (101) in
martensite are all derived from \{110\} close packed
planes in the original b.c.c. lattice [2]. Though the
indices are different, some of these planes have, in fact,
a very similar atomic arrangement, as shown in Fig. 4.
In this figure, the (0018) section and the (101) section of
the two lattices are compared, and the similarity of
their atomic arrangements implies that the two lattices
in this orientation relation could combine relatively
easily, with some misfit dislocations to adjust the small
difference in atomic correspondence in the interfacial
junction plane. In addition small shufflings are needed
to bring both variants into coincidence.

4.2. Calculation of the boundary energy

A twin boundary is one kind of special large-angle
grain boundary, which is obtained by a 85.8° rotation
along the [100] axis in the martensite lattice to produce
the present A/D type twin. One may classify twin
boundaries as either coherent or partially coherent.
Complete coherency in the boundary is obtained with-
out any straining of the lattices because a perfect
register of the lattices is naturally obtained at this
special boundary. If the matching planes in the twinned
parts are not coincident, one obtains a partially coher-
ent twin boundary. For the coherent twin boundary,
the boundary energy is relatively low (the measured
value in Cu for coherent twin boundary is 21 mJ.m\(^{-2}\),
498 mJ.m\(^{-2}\) for a non-coherent boundary, and 623
mJ.m\(^{-2}\) for a large-angle grain boundary [15]). When
the twin boundary plane is misoriented, the boundary
energy increases almost exponentially, which greatly
exceeds the increase in misorientation for a small-angle
boundary.

According to the calculations based on the WLR
theory, the (1010) plane of one variant makes an angle
of 3.87° with the (1010) plane of the other variant, so
we can first preliminarily estimate the boundary energy
arising from the misorientation according to a small-
angle grain boundary model. Then on the basis of the
fact that the A/D type twin boundary is a special
large-angle grain boundary, we reconsider the
boundary energy again.

The mean separation between dislocations in the
boundary is

\[
D = \frac{b}{2 \sin(\theta/2)}
\]

(1)

where \(b\) is the magnitude of Burgers vector, \(\theta\) the angle
between two planes.

According to the description by Hirth et al. [7], the
boundary energy per unit area is

\[
\gamma \approx \frac{\mu b^2}{4\pi(1 - \nu)D} \ln \frac{exD}{2\pi b}
\]

(2)

where \(\mu\) is the shear modules of the material, \(\nu\) the
Poisson’s ratio, \(D\) the separation between the edge
dislocations, and \(x\) a factor (\(x \approx 1\) [7])

Eq. (2) can also be expressed as follows

\[
\gamma \approx M \left(\frac{b^2}{D} \ln N + \frac{b^2}{D} \ln \frac{D}{b}\right)
\]

(3)

where

\[
M = \frac{\mu}{4\pi(1 - \nu)} \quad N = \frac{ex}{2\pi}
\]

For the (1010)\(\alpha\)/(1010)\(\beta\) boundary with a tilt angle
of 3.87°, the boundary is composed of only one set of
dislocations, with Burgers vector \(b = 3.024\ \text{Å}\) (the
spacing between two neighboring (1010) planes). The
boundary energy is estimated according to Eq. (3) to be

\[
\gamma_{(1010)} = M(0.2042 \ln N + 0.5504)
\]

(4)

Now we consider the atomic matching between the
(101) plane and the (0018) plane in variants A and D.
Along the [100] direction in the (0018) plane, the spacing
between the neighboring atoms is 4.553 Å, while

4.3. Atomic arrangement diagrams for (101)\(\alpha\) and (0018)\(\beta\)
sections, showing the similarity of the two lattice planes. Circle,
triangle and square symbols refer to atoms in, above and below
the plane of the figure. Open and solid symbols refer to the two respective
atomic species in the ordered structure.
along the [101] direction in the (101) plane, atoms are located with an average spacing of 13.081/3 = 4.360 Å. In Fig. 4, however, when we examine the Burgers circuit of the misfit dislocation viewing along the [010] direction, the atoms in 1/2 site should be taken into consideration, thus the spacing between the neighboring atoms should be $a_s/(4.553/2) = 2.277$ Å and $a_\beta = (4.630/2) = 2.180$ Å, respectively. Thus a disregistry factor in [100] direction in (0018) plane is calculated to be $\delta = 0.0424$ and the average spacing of misfit dislocations is $D_1 = 51.42$ Å, where

$$\delta = \frac{a_s - a_\beta}{a_s} \quad D_1 = \frac{a_\beta}{\delta}$$

and the value of the Burgers vector is $b_1 \approx a_s + a_\beta/2 = 2.228$ Å.

Similarly, for [010] common orientations, $\delta = 0.0000$ and $D = \infty$ are obtained. However the simple calculations above seem sufficient to show the capability of the (101) and (0018) planes to combine across a semi-coherent interface with misfit dislocations. Here we take the model for a tilt boundary to treat the disregistry in a given direction, so the boundary energy per unit area resulting from these dislocations is given by Eq. (3)

$$\gamma_1 = M(0.0965 \ln N + 0.3030) \quad (5)$$

The deviation of 2.13° between the (101) plane and (0018) plane in the two variants consists of another small-angle tilt boundary. For the dislocations associated with this misorientation, $b_2 \approx d_{(202)} + d_{(0018)/2} = 2.217$ Å, $D_2 = 59.64$ Å and

$$\gamma_2 = M(0.0824 \ln N + 0.2713) \quad (6)$$

For simplicity, the boundary energy is assumed to be the sum of both separately-calculated results: $\gamma_1$ and $\gamma_2$, i.e.

$$\gamma_{(101)/(0018)} = \gamma_1 + \gamma_2 = M(0.1789 \ln N + 0.5743) \quad (7)$$

Comparing Eqs. (4) and (7), it is possible that $\gamma_{(101)/(0018)} = M(0.0253 \ln N - 0.0239) > 0$ exists, because $\ln N > 1$ can be guaranteed due to $x \gg 1$. On the other hand, the calculation of $\gamma_{(101)/(0018)}$ is a simple sum of two parts of the boundary energies ($\gamma_1$ and $\gamma_2$). Actually, the $\gamma_{(101)/(0018)}$ should be less than ($\gamma_1 + \gamma_2$) because of mutual counteraction of the dislocation strain field resulting from misorientation or disregistry. Therefore, as far as the discussion is concerned, $\gamma_{(101)/(0018)} < \gamma_{(101)}$ exists. Because of the lower energy of the junction of (101) and (0018) planes between the two variants than (1010) planes, the stepped structure forms.

## 4.3. Influence of stacking faults on the boundary structure

An appreciable quantity of randomly distributed basal plane stacking faults are often observed within the martensite plate. These stacking faults have been assumed to constitute the lattice invariant deformation mode of the 9R(18R) martensites in noble metal base alloys. It has been reported that in general, there are two types of faults ($x$ and $\beta$) [13,14], and a cubic type fault ($x$) can be differentiated in Fig. 2. The knowledge of the fault types and their influence on the boundary structure is important in understanding the mobility of the boundaries in shape memory alloys. Stoiber et al. [10] have discussed the effects of the two kinds of faults on the A/D type boundary structure. In their discussion, they assumed the (1010) boundary, the theoretical twinning plane, on the variant A and variant D, but our HREM observations show that the A/D type boundary is zigzagged. The actual boundary is not a (1010) interface plane, but is composed of segments of (0018)$_A$/((101)$_D$ or (0018)$_D$/((101)$_A$.

In order to understand this discrepancy, let us consider the atomic arrangement across an A/D type boundary, as shown in Fig. 5. Due to the similarity of (101) and (0018) planes, a row of atoms in the (0018)$_D$ plane is drawn to simplify the drawing. The energy of the A/D boundary is fairly high because two out of three atoms in the (101) plane are not in the plane. In the perfect 18R structure, where no random stacking faults appear, the atomic matching between the two kinds of planes is very good with small shuffling, as shown in Fig. 5(a). However, if random stacking faults, which are necessarily present in the 18R structure, are introduced, the atomic arrangement across the A/D boundary becomes energetically less favorable. Fig. 5(b) and (c) show the case where a cubic type stacking fault ($x$) or a hexagonal type fault ($\beta$) of the variant A encounters the boundary (the basal plane of variant D), respectively. It is obvious that each fault results in more serious atom deflection from the (101) plane where the fault exists or at its other neighboring locations (sites I and II in Fig. 5(b) or site I in Fig. 5(c)). The resulting boundary energy of the A/D twin is visibly higher because more atom shifts are needed to combine the plane (0018) with the plane (101), i.e. atom relaxations are needed where faults terminate. This situation will give rise to a local distortion, as seen by the fact that some (0018) plane segments are obviously curved near the boundary (shown by arrows B, C in Fig. 2). However, a single fault cannot change the boundary orientation. When many stacking faults combine together and form a region with h.c.p. or f.c.c. structure, the faults may have some influence on the boundary structure or the boundary orientation, just as analyzed by Adachi et al. [6].
4.4. Stepped boundary structure and dislocations

For the deviation from exact twin orientation, a dislocation network accommodating the deviation is expected, but irregular steps are observed along the boundary. It can be said that the dislocations are associated with well-defined steps which adopt a preferential shape with the facet parallel to the basal plane of either variant. However, it appears difficult to define the Burgers vectors of such dislocations from only the information given by Fig. 2. On the other hand, these calculated data are expected to have a little change in a fully martensitic state, because the calculated angle above is obtained by the parent-to-martensite transformation crystallography (habit plane must be an invariant plane, i.e. undistorted and unrotated [8]). But the martensite variant, when combined with each other, need not retain this condition, and a lattice rotation exists in order to attain a maximum-extent boundary coherency. The lattice rotation mechanism by means of basal plane faulting was proposed by Adachi et al. [3]. Adjustment of stacking faults on the basal is carried out by the movement of partial dislocations, which has often been reported [10–12]. Changes in the basal plane stacking sequence can effectively shear a lattice, so as to bring some of the \{110\}β₁- or \{100\}β₁-derived planes into parallelism. With the change of angular separations between major near-parallel planes, the number of dislocations to compensate the misorientation will decrease.

5. Conclusions

1. A/D type twin boundaries in a Cu–20.4Zn–5.6Al (wt%) alloy are randomly curved, as seen by TEM, and the macroscopic curve results from the non-self-accommodation of transformation strain.
2. On an atomic scale the A/D type twin boundary is not the theoretical (1010) boundary plane, but consists of the irregularly-serrated steps, which are composed of segments of (101)\textsubscript{A}/(0018)\textsubscript{D} or (0018)\textsubscript{A}/(101)\textsubscript{D}. The deviation from exact twin orientation and a preferential orientation for a lower boundary energy result in the irregularly-serrated steps.
3. The randomly-distributed stacking faults resulting from invariant plane strain condition for the martensitic transformation have no obvious influence on the boundary orientation in the present alloy.

Acknowledgements

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