HREM STUDY ON THE INTERVARIANT STRUCTURE OF Ti-Ni-Hf B19' MARTENSITE

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Introduction

Ternary Ti-Ni-Hf alloys are newly-developed shape memory alloys and recognized as one of the potential candidate materials for high temperature applications. In a recent investigation on the Ti36.5Ni48.5Hf15 alloy, (001) compound twin was found to be the substructure of the martensite whereas (011) Type I and (1 1 0.64) Type II twinning relationship were reported to exist between two neighboring martensite variants [1]. According to Bilby and Crocker [2], the \( h_1 \) direction is the only rational direction contained in the irrational twinning plane \( K_1 \) for the Type II twin. Using this argument based partly on geometric consideration, the full twinning elements for the (1 1 0.64) Type II twin can be theoretically suggested: \( K_1 = (1 1 0.60232) \), \( h_1 = [110] \), \( K_2 = (110) \), \( h_2 = [1 1 0.43995] \), \( s = 0.75884 \). (Here the method of Jaswon and Dove [3] and the crystallographic parameters reported by Han et al. [1] were used.) The orientation relation between two (1 1 0.64) Type II twin related variants should satisfy the symmetry through the rotation of \( \pi \) about \( h_1 \) according to the definition of Type II twin, but the two sets of reflections owns a rotation symmetry about [110] zone orientation with the angle of rotation about 127°, as shown in Fig. 9(b) of Ref. [1]. This indicates the indexing as “Type II twin” is unreasonable. Further detailed experimental work on this kind of twinning mode is clearly desirable. The <011> Type II twin, as the common phase transformation twin of the martensite in TiNi alloy, has not been observed after the addition of Hf as yet. It is necessary to ascertain the existence or inexistence of this twinning relation.

The objective of the present work is to investigate deeply on the microstructure of martensite in the Ti-Ni-Hf alloy by using HREM technique, of particular interest is the twinning relationship between neighboring martensite variants and corresponding twinning boundary structure.

Experimental

A Ti36.5Ni48.5Hf15 alloy was prepared by consumable arc melting under an Ar atmosphere in a water-cooled copper crucible of 60 mm in diameter. The electrode was a compact of 99.92 wt.% sponge Ti, 99.95 wt.% electrolytic Ni plate and 99.90 wt.% Hf shot. Then the ingot was remelted twice to ensure composition homogeneity by a levitation method under an Ar atmosphere and the melt was poured into a graphite mold of 35 mm in diameter. After homogenizing at 1223K for 1.5 hours, the ingot was hot
rolled into plate of 2.1 mm thickness. Specimens were solution-treated at 1273K in vacuum for 1 hour and then quenched into water, thereafter they were mechanically polished to 50 μm and electrochemically polished by the twin jet method in an electrolyte of 20% H2SO4 and 80% methanol around 253K. HREM observations were performed by a JEOL-2000EX II electron microscope operated at 200 kV using a top-entry type double-tilt specimen stage with angular ranges of ± 10°.

The following lattice parameters of the monoclinic martensite were measured by X-ray diffraction for the present alloy; a = 0.2454 nm, b = 0.4087 nm, c = 0.4791 nm, β = 99.32°. The phase transformation temperatures of the alloy were determined by differential scanning calorimeter to be Mf = 425K, Ms = 457K, As = 491K, Af = 507K.

**Results and Discussion**

Spear-like and mosaic-like martensite variants, as the cross-section and vertical section morphologies of the lath plate groups reported by Han et al. [1], are generally observed in the present study. But they are found to be (011) Type I twin or <011> Type II twin related. The (1 1 0.64) Type II twinning relation reported by Han et al. [1] is not reconfirmed between variants exhibiting these two kinds of morphologies. Spear-like martensite variants are taken as an example to illustrate it, as shown in Fig. 1(a). The diffraction patterns corresponding to the three variants A-C in Fig. 1(a) is shown in Fig. 1(b) after the calibration of the image rotation. The spots indicated by an arrow in Fig. 1(b) represent the common (011) reflections of these three variants. Fig. 1(c) shows the HREM image of variants A/B twinning boundary taken along the [211]A,B zone orientation, as clearly indexed in Fig. 1(d). Variants A and B are found to be (011) Type I twin related, with a straight and coherent interface and having mirror symmetry with respect to the (011) plane. Fig. 1(e) illustrates the [011] Type II twinning boundary between variants B and C observed from the [211]B and [211]C orientations, as clearly indexed in Fig. 1(f). The angular difference between these two near parallel zone axes was theoretically calculated according to the work by Knowles and Smith [4] to be:

\[ [211]_B \land [211]_C = 4.2° \]

The error of the angular difference is relatively big comparing with that in binary TiNi alloy [4]. It might arise from the inaccuracy of the lattice parameters of martensite. The intervariant boundary between variants B and C shown in Fig. 1(e) can be characterized as a gradually and randomly curved one without ledge or step structures. This situation is close to that of the <011> Type II twin in TiNi alloy reported by Nishida et al. [5], though <011> Type II twin might act as a variant accommodation twin instead of a lattice invariant shear after the addition of Hf.

A new morphology is found to be the wedge-like martensite variants, which appear in two types of forms. The first one can be seen in Fig. 1(a) where the small variant E tapers and terminates within the big variant D. The second one appears in Fig. 2(a) where the small variant A penetrates through the big variant B and terminates at the intervariant boundary without intruding into the big variant adjoining to variant B. Fig. 2(b) shows the EDPs corresponding to variant A and B in Fig. 2(a) which is similar to Fig. 9(b) in Ref. [1]. Obviously, each variant consists of (001) compound twin related substructure. For each variant, the set of EDP with relatively strong intensity corresponding to the large region in the banded substructure is indexed as matrix and that with relatively weak intensity corresponding to the small region in the banded substructure is indexed as twin, represented by subscripts M and T of the indices respectively. Variants A and B is considered to be (111) Type I twin related since the variants A and B have an mirror symmetry with respect to (111) plane. The splitting of the (111) common spots in Fig. 2(b) stems from the deviation of the planes in martensite lattice from their “originating” planes upon martensitic transformation. Similar to the analysis on 18R Cu-Zn-Al martensites [6], crystallo-
graphic relations between any martensite variant pair can be derived by representing the lattice directions and plane normals in the B19' martensite with respect to the B2 parent phase basis. Yet the transformation matrices used for this purpose are fail to be calculated since no solution exist for the phenomenological crystallographic theory when (001) compound twin is considered to be the lattice
invariant shear for the present alloy. The wedge-like martensite variants are more likely to be the mixing of variants of different plate groups, as close to the situation reported by Adachi and Wayman [7].

Fig. 2(c) shows the high-resolution image of the framed area C in Fig. 2(a). It can be seen that the two parts of the variants A and B fit one into the other. They do not show a rigid atomic arrangement.
along the impingement junction planes. Lattice rotations happen in order to increase coherency, which gives rise to a complicated arrangement of atom columns in the twin region. The twin “plane” is no longer planar but wavy. This “interlacing” obviously minimizes the strain energy. Singular, apparently ending, rows of bright dots are present in the vicinity of the intervariant boundary. Their presence is required in order to accommodate the misfit between (001) compound microtwins of different widths on both sides of the intervariant “plane.” The above features are similar to that of the “macrotwin” with polysynthetic microtwin on \{111\} planes reported in tetragonal \(\theta\) martensite in near-equiaatomic Ni-Mn alloy [7–8].

Fig. 2(d) depicts schematically the relative atomic orientations across the junction plane between variant A and B in Fig. 2(a). Three types of atomic configuration can be abstracted from Fig. 2(b) and Fig. 2(c), they are as follows:

\[
\begin{align*}
(\overline{1}11)_M^A & \not\subset (\overline{1}11)_M^B 9.4^\circ \\
(\overline{1}11)_M^A & \not\subset (\overline{1}11)_M^B \text{ or an equivalent one } (\overline{1}11)_M^A \not\subset (\overline{1}11)_M^B 4.1^\circ \\
(\overline{1}11)_M^A & \not\subset (\overline{1}11)_M^B 17.7^\circ
\end{align*}
\]

Clearly, the reasonably good matching between planes of types (2) and (4) can be realized simply by lattice rotation. Small adjustments by means of misfit dislocations and lattice rotations are necessary for the combination of type (3), since the atomic distance is about 0.5580 nm along [11\#1] direction whereas it is about 0.4952 nm along [111] direction.

**Conclusion**

High resolution TEM has been used to study the intervariant structure in Ti-Ni-Hf monoclinic martensite. The (011) and (0.60928 1 1) planes are found to be the junction planes between neighboring spear-like and mosaic-like martensite variants. The (011) Type I twinning boundary is straight whereas the <011> Type II twinning boundary is gradually and randomly curved. The (111) Type I twinning relationship is found to exist only between wedge-like martensite variants with a wavy interfacial structure.

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**References**