Martensitic Transformation in $\text{Ti}_{36.5}\text{Ni}_{48.5}\text{Hf}_{15}$ High Temperature Shape Memory Alloy

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The lattice invariant shear of the martensitic transformations in the $\text{Ti}_{36.5}\text{Ni}_{48.5}\text{Hf}_{15}$ alloy was determined as a (001) B19' compound twin by *in-situ* TEM technique. The morphological features of the (001)B19' twin lamellas were revealed in detail. The shapes of the martensite variants were either the form of triangular, quadrilateral or lath plates. The mosaic-like morphology of the martensite variants corresponds to the cross section of the triangular, quadrilateral prisms, or the lath plates. The vertical section of the lath plates appears with a spear-like feature. The self-accommodation of the triangle, lateral prisms and the lath plates is usually composed of four martensite variants. There are 18 four-variants combinations of the mosaic-like martensite variants.

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I. Introduction

Shape memory effect (SME), psuedoelasticity (PE) and two-way memory effect (TWME) were observed in many alloy systems. SME is generally associated with thermoelastic martensitic transformation, and self-accommodation of martensite variants. The junction planes between martensite variants and the variants' combination play a very important role in the interface movement, as well as the variants coalescence, when the specimen is deformed. The SME in most of Cu-based alloys is associated with the thermoelastic transformation from B2 (or DO₃) to 9R (18R), 3R or 2H close-packed stacking order structure. The (110) planes in the parent phase correspond to the close-packed basal plane, i.e. the stacking plane, in the martensite⁽¹⁾⁻⁽⁴⁾. In fact, the self-accommodation mechanism for 3R, 9R (18R) and 2H martensites is all the same. The 24-habit plane variants come from six martensite variant groups. Each group is composed of martensite variants that are close to and symmetrically clustered around one of the six $\langle 110 \rangle$ poles of the parent phase. The four variants form a typical two-dimensional diamond shape morphology⁽¹⁾⁽²⁾. The crystallography of Cu-based shape memory alloys (SMAs) was relatively well understood.

Although the parent phase of TiNi binary alloy possesses the B2 superlattice, the martensite structure and variants combination are different from Cu-based SMAs.

The martensite in the TiNi binary alloy is a three dimensional close-packed structure⁽⁵⁾⁽⁶⁾. The self-accommodation of the martensite variants in the TiNi alloy is also different. The martensitic transformation of TiNi binary alloys takes place by forming a typical triangular morphology consisting of three variants. Under this condition, the [011]B19' Type II twin serves as the lattice invariant shear⁽⁷⁾⁽⁸⁾. There are altogether 16 groups of self-accommodating variants about each of the {100}B2 poles, resulting in 48 possible combinations⁽⁹⁾. Apart from the dominant [011]-Type II twin, complicated substructures were also found in TiNi binary alloys. It have been reported that there are (011) Type I⁽¹⁰⁾, (1 1 -1) Type I⁽¹⁰⁾⁽¹¹⁾, (111) Type I⁽⁶⁾⁽⁸⁾, (001)⁽¹⁰⁾ and (100)⁽¹²⁾ compound twins in the martensites of TiNi alloys. (011) Type I twins and (1 1 -1) Type I are also the phase transformation twin⁽¹³⁾.

High-temperature shape memory alloys (HTSMAs) have been an interesting and important research subject for nearly two decades. Owing to the serious problems in thermal stability and phase transformation kinetics of Cu-based and NiAl HTSMAs, respectively, the prospects of these SMAs are quite obscure. Recently, the better formability⁽¹⁴⁾⁽¹⁵⁾ and the interesting phase transformation behaviour⁽¹⁶⁾ of TiNiHf(Zr) HTSMAs have attracted the attention of many researchers⁽¹⁷⁾⁻⁽²⁰⁾. Unlike the Ti-Ni-Cu(Au) and Ti-Ni-Pt(Pd) SMAs, the monoclinicity of the martensite in the Ti-Ni-Hf(Zr) alloys remains. With the increasing Hf(Zr) content⁽¹⁶⁾⁽¹⁹⁾⁽²¹⁾, however, the monoclinic angle increases.

In our previous papers⁽¹⁶⁾⁽²²⁾, the crystallographic pa-

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rameters and substructure of the martensite were investigated mainly by conventional transmission electron microscopy (TEM). The purpose of the present study is three folds: The first is to clarify the phase transformation mechanisms by *in-situ* TEM technique, the second is to study the morphological features of the (001) twins, and the third is to study self-accommodation phenomenon of the martensite variants in the $\text{Ti}_{36.5}\text{Ni}_{48.5}\text{Hf}_{15}$ alloy.

II. Experimental Procedure

The mixture of electrolytic nickel, sponge titanium and hafnium was arc-melted four times to obtain the homogenous ingots. The composition of the ingots was $\text{Ti}_{36.5}\text{Ni}_{48.5}\text{Hf}_{15}$ (at%). The ingots were heat-treated at 1273 K in vacuum for 10 h. The hot working temperature of the ingot was 1273 K. After hot working, the specimens were heat-treated at 1273 K for 1 h in vacuum. Then they were spark-cut into TEM samples. The TEM foil were mechanically polished to 80 μm , and then electrochemically polished using a twin jet electropolisher in a solution of 80% H_2SO_4 in methanol. The microscopic observations and structural analysis were carried out in a Philips CM-12 TEM equipped with a Gatan double tilt heating stage holder.

III. Results and Discussions

1. The lattice invariant shear of the martensitic transformations

The martensitic structure of the $\text{Ti}_{36.5}\text{Ni}_{48.5}\text{Hf}_{15}$ HTSMA is basically the same as the TiNi binary alloys except for the monoclinic angle and the lattice parameters. Figure 1 shows a set of selected area electron diffraction patterns (EDPs) of the martensite. The results show that the martensite in $\text{Ti}_{36.5}\text{Ni}_{48.5}\text{Hf}_{15}$ alloy is of B19' monoclinic structure. The monoclinic angle is larger than that in TiNi binary alloys. The zone axes are indicated at the left-bottom of each EDP, and the main reflections of each EDP are also indexed. The lattice parameters were determined as $a=0.293$ nm, $b=0.411$ nm, $c=0.473$ nm and $\beta=100.4^\circ$.

Both the (001)B19' and (100)B19' compound twins were observed in TiNi binary alloys⁽¹¹⁾⁽¹²⁾. However, they should be the deformation twins due to the thin foil effect⁽¹¹⁾⁽¹³⁾ rather than the phase transformation twins because there were no phenomenological solutions in theory. In our previous work⁽¹⁶⁾⁽²²⁾, we observed that the substructure in a martensite variant was (001)B19' twins. This type of twins appeared in every martensite variant. Therefore, we believed that the (001)B19' twin is the phase transformation twin.

In order to clarify whether the (001)B19' compound twin is responsible for the lattice invariant shear, we have studied the structure transformation from the B19' to the B2 parent phase in detail. With the ± 60 degrees double tilt heating stage, we can select a proper reciprocal plane of the martensite to conveniently observe the reverse

Fig. 1 A set of EDPs showing the monoclinic structure of the martensite. The zone axis is indicated at the bottom of each EDP.

transformation during heating. The (010)*B19' reciprocal plane of the present TiNiHf HTSMA can reflect the (001)B19' twin, as well as the monoclinic structure. This enabled us to determine the monoclinic angle directly (The monoclinic angle $\beta=180^\circ-\beta^*$, where β^* is the reciprocal monoclinic angle between the [100]B19' and [001]B19' reciprocal vectors). Therefore, the (010)*B19' reciprocal plane was chosen for the *in-situ* TEM observations.

Figure 2 shows a set of EDPs taken from the same area at different temperatures. The foil orientation is kept invariant during heating. Figure 2(a) is a superimposed EDP consist of two sets of (010)*B19' reciprocal planes with respect to the (001)B19' twin plane. This is identical to Fig. 1(d). Figure 2(f) consists mainly of the [011]B2 zone EDP of the parent phase as indexed in the pattern, while other spots come from the precipitates⁽²³⁾, or the oxygen and hydrogen interstitial ordering⁽²⁴⁾. Figure 2(f) indicates that the martensite almost completely transforms to the B2 parent phase. In Figs. 2(b) and (c) the $\pm(0-1)B2$ spots indicated by arrows near the positions of $\pm(002)B19'$ spots have a slightly larger distance from the central spot. This is consistent with the fact that the related magnitudes of the reciprocal vectors

Fig. 2 *In-situ* electron diffraction patterns of $\text{Ti}_{36.5}\text{Ni}_{48.5}\text{Hf}_{15}$ alloy obtained at different temperatures during heating showing a transformation from (001)B19' twinning martensite to the B2 parent phase. (a) at 273 K, (b) at 423 K, (c) at 498 K (d) at 548 K, (e) at 773 K and (f) held at 773 K for 5 h.

are $g(0\ -1\ 1)\text{B2}=4.577\ \text{nm}^{-1}$, and $g(002)\text{B19}'=4.292\ \text{nm}^{-1}$.

The characteristic of the $(010)^*\text{B19}'$ reciprocal plane disappears completely in Fig. 2(e). The bright spots in Fig. 2(e) can be indexed as the $(011)^*\text{B2}$ reciprocal plane. The $\pm(200)\text{B2}$, $\pm(2\ -1\ 1)\text{B2}$ and $\pm(2\ 1\ -1)\text{B2}$ spots are broadened along the tangent direction. The result indicates that the shear features of the martensitic transformation and the consecutive transformation characteristics of the monoclinic angle. In Fig. 2(e), the $(0\ -2\ 2)\text{B2}$ spot is very weak while the $(0\ 2\ -2)$ spot is very strong. This implies that Fig. 2(e) is not at an axial $[011]\text{B2}$ zone axis. Since Fig. 2(e) was derived from the $(010)^*\text{B19}'$ reciprocal plane, it can be deduced that the $[010]\text{B19}'$ zone axis is not parallel to the $[011]\text{B2}$ zone axis. In fact, this observation only shows the following lattice correspondence: $[010]\text{B19}'-[011]\text{B2}$, $[100]\text{B19}'-[100]\text{B2}$ and $[001]\text{B19}'-[0\ 1\ -1]\text{B2}$.

One point should be mentioned here is that the lattice correspondence is not equivalent to the orientation relationship. In our previous work⁽¹⁶⁾, we observed the following orientation relationship between B2 parent phase and B19' martensite: $[100]\text{B19}'\parallel[100]\text{B2}$, and $(011)\text{B19}'\parallel(001)\text{B2}$. According to the orientation relationship, $[010]\text{B19}'$ and $(001)\text{B19}'$ deviate from $[011]\text{B2}$ and $(0\ -1\ 1)\text{B2}$ respectively by 3° , which is consistent with the observations from Fig. 2. Since the B19' martensite is monoclinic, the B2 to B19' transformation needs to shear along the $\pm[001]\text{B19}'$ direction in the $(100)\text{B19}'$ plane. This shear changes the angle between $[100]\text{B19}'$ and $[001]\text{B19}'$ from 90° to the monoclinic angle (100.4°). Thus, two lattice correspondence variants formed, which are in a mirror relation with respect to $(001)\text{B19}'$ twinning plane as shown in Fig. 2(a). During heating these

two twin-related variants transform to a single B2 parent grain as shown in Fig. 2(f).

Considering the symmetry of the B2 parent phase, 12 lattice correspondence variants can be identified. They are shown in Table 1. The variants with and without prime symbol (*e.g.* 1 and 1') represent the correspondence variants with an opposite monoclinic shear along the $\pm[001]\text{B19}'$ direction in the $(100)\text{B19}'$ plane. These 12 lattice correspondence variants are the same as those found in TiNi binary alloys⁽⁹⁾. However, the $(001)\text{B19}'$ twin related variants 1 and 1' is the variants accommodation twin between habit plane variants. In the present work, the $(001)\text{B19}'$ twin is the phase transformation twin exist in the inner martensite habit plane variants. Due to the absence of the crystallographic parameters of habit planes, the variants described in the present study are the junction plane variants. These junction plane vari-

Table 1 The lattice correspondence variants between the B2 parent phase and the B19' martensite.

Variants	$[100]\text{B19}'$	$[010]\text{B2}$	$[001]\text{B2}$
1	$[100]\text{B2}$	$[011]\text{B2}$	$[0\ -1\ 1]\text{B2}$
1'	$[-1\ 0\ 0]\text{B2}$	$[0\ -1\ -1]\text{B2}$	$[0\ -1\ 1]\text{B2}$
2	$[100]\text{B2}$	$[0\ -1\ 1]\text{B2}$	$[0\ -1\ -1]\text{B2}$
2'	$[-1\ 0\ 0]\text{B2}$	$[0\ 1\ -1]\text{B2}$	$[0\ -1\ -1]\text{B2}$
3	$[010]\text{B2}$	$[101]\text{B2}$	$[1\ 0\ -1]\text{B2}$
3'	$[0\ -1\ 0]\text{B2}$	$[-1\ 0\ -1]\text{B2}$	$[1\ 0\ -1]\text{B2}$
4	$[011]\text{B2}$	$[1\ 01\ -1]\text{B2}$	$[-1\ 0\ -1]\text{B2}$
4'	$[0\ -1\ 0]\text{B2}$	$[-1\ 0\ 1]\text{B2}$	$[-1\ 0\ -1]\text{B2}$
5	$[001]\text{B2}$	$[110]\text{B2}$	$[-1\ 1\ 0]\text{B2}$
5'	$[0\ 0\ -1]\text{B2}$	$[-1\ -1\ 0]\text{B2}$	$[-1\ -1\ 0]\text{B2}$
6	$[001]\text{B2}$	$[-1\ 1\ 0]\text{B2}$	$[-1\ -1\ 0]\text{B2}$
6'	$[0\ 0\ -1]\text{B2}$	$[1\ -1\ 0]\text{B2}$	$[-1\ -1\ 0]\text{B2}$

ants will be discussed in detail later. In fact, every junction plane variant corresponds to two crystallographic equivalent habit plane variants. There are 24 habit plane variants in the B19' martensite.

2. The characteristics of (001)B19' compound twins

In references⁽¹⁶⁾⁽²²⁾, the (001) twins were observed closely along the $[010]\text{B19}'$ zone axis. Under this condition, the (001)B19' twin plane was parallel to the incident beam, and one can measure the ratio of the matrix and the twin section directly. In Section III.1, when the (001)B19' compound twin was determined as responsible for the phase transformation by *in-situ* TEM technique, the incident beam was along the $[010]\text{B19}'$ zone axis. However, the structural details of the (001)B19' compound twins were not revealed along $[010]\text{B19}'$. The aim of the present section focuses on the morphological details of (001)B19' compound twins. The (001) twin plates were observed along the inclined direction from the (001)B19' plane normal.

Figure 3 shows the morphologies of the (001)B19' twins when the incident beam is nearly parallel to the $[0\ 1\ -1]\text{B19}'$ direction. Figure 3(a) is the bright field image, while (b) is the corresponding dark field image of (a) and (c) is the corresponding EDP. The (111) spot of (c) was selected for taking the image of (b). The lamella structures are very obvious. The normal of the (001)B19'

plane is about 48° inclined to the incident beam. By trace analysis, the trace of the (011)B19' plane of the (001) twin lamella was determined. The projections of the $[100]$ and $[110]\text{B19}'$ directions were also determined by trace analysis as indicated in Fig. 3(a). In references⁽¹⁶⁾⁽²²⁾, the incident beam revealing the (001) compound twin was parallel to the $[010]$ zone axis, both the twin and matrix section of (001) twins were under the Bragg condition. However, only the (011)*B19' reciprocal plane of the (001)B19' twin matrix intersected with the Ewald sphere in Fig. 3. (The twin section was not at the Bragg condition.) In such condition, only the matrix can be clearly revealed. (i.e., the dark contrast area in (a) and the bright contrast one in (b)).

The morphology of Fig. 3(a) composes of variants A, B and C. All of them consist of parallel lamella, and almost all the lamellas of variant A cannot go through the variant. They are interrupted by dislocations, stacking faults or microtwins. These kinds of characteristics are similar to the ones in Fe-based alloys⁽²⁵⁾⁽²⁶⁾. However, these features are not the criterion for lattice invariant shear. The (001) twin lamellas are too thin for thickness measurement. Figure 4 is an enlarged view of the area highlighted by rectangles in Fig. 3(b). The superimposed twin lamellas are very obvious. The discontinuity of the

Fig. 3 The morphology of (001)B19' twin lamella when the incident beam is parallel to the $[0\ -1\ 1]\text{B19}'$ zone axis. The (111)B19' spot in the $(0\ -1\ 1)^*\text{B19}'$ was selected to take the dark field image. (a) bright field image, (b) dark-field image, (c) $(0\ -1\ 1)^*\text{B19}'$ reciprocal plane.

Fig. 4 A closer view at one area in Fig. 3. (a) dark field image, (b) bright field image arrows indicated represent the microtwins, dislocations or faults.

Fig. 5 A schematic illustration of the twin lamella. (a) the schematic illustration of the lamella structure of variant A. (b) the parallelepiped lamella with $(001)\text{B}19'$, $(011)\text{B}19'$ and $(1 -1 0.64)\text{B}19'$ planes.

$(001)\text{B}19'$ twin lamella indicated by arrows is also clearly seen, they may be the microtwins, faults or dislocations.

Given the morphologies of the $(001)\text{B}19'$ twin lamellas, the thickness of the twin lamella still cannot be revealed. Moreover, we can evaluate the three dimensional feature of the $(001)\text{B}19'$ twin plate. Since the junction planes of the martensite variants are $(0 1 1)\text{B}19'$ and $(1 -1 0.64)\text{B}19'^{(16)}$, the twin lamellas are supposed to be the hexahedron plates. A schematic illustration of the twin lamella structure is shown in Fig. 5. Figure 5(a) shows the lamellas in variant A and some crystallographic parameters are indicated. Figures 5(b) and (c) show the parallelepiped and the hexagonal plate lamellas respectively. The plane normals of the twin lamella are $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 1 -1 0.64 \rangle \text{B}19'$ (or $\langle -1 1 -0.64 \rangle \text{B}19'$) planes. The twin lamella tapers neither on the $(001)\text{B}19'$ plane nor on the $(1 -1 0.64)\text{B}19'$ plane. The width and length of the lamellas can be estimated from Figs. 3 and 4. The width of the twin lamella is about 0.05 to 0.08 μm and the length of the lamella is about 0.1 to 0.6 μm . The thickness of the twin lamella estimated from reference⁽¹⁶⁾ is approximately 0.01 to 0.03 μm .

3. Crystallography of the martensitic variants self-accommodation

Based on the orientation relationship between the parent phase and the martensite⁽¹⁶⁾, as well as the *in-situ* observation of the reverse transformation from $(010)^*\text{B}19'$

to $(011)^*\text{B}2$ reciprocal plane, we conclude that the (001) twin plane of the $\text{B}19'$ martensite originate from one of the $\{110\}\text{B}2$ planes of the $\text{B}2$ parent phase and the inhomogeneous shear during phase transformation takes place in this plane. There are six $\{110\}\text{B}2$ planes in the $\text{B}2$ parent phase. The 12 possible combinations of shear planes and shear directions lead to two possible crystallographic equivalent unrotated and undistorted habit planes. Thus 24 habit plane variants may result from a single grain of the parent phase. However, due to the absence of the habit plane parameters, the variants described in the present study are limited to be the junction plane variants. Detailed EDP investigation revealed that all of the martensite variants consist of $(001)\text{B}19'$ compound twins. As already mentioned in section III.1, every junction plane variant should correspond to two crystallographic equivalent habit plane variants.

(1) Twelve mosaic-like junction plane variants

In reference⁽¹⁶⁾, we have reported two kinds of martensite variant morphologies. One is the mosaic-like variant while the other is the spear-like one. In this section, we will re-examine the mosaic-like martensitic variants.

Figure 6(a) shows a group of mosaic-like martensite variants. Figure 6(b) is an EDP taken from area 1 of (a). Figure 6(c) is taken from area 2 of (a). Figure 6(b) can be indexed as two sets of $[0 -1 1]\text{B}19'$ EDP with respect to the $(011)\text{B}19'$ twin plane which is also the boundary

Fig. 6 A group of mosaic-like martensite variants. (a) bright field image; (b) EDP taken from area 1 of (a) showing the (011) twin relation, (c) EDP taken from area 2 of (b) showing the $(1 \ -1 \ 0.64)$ twin relation.

plane between the two martensite variants. Figure 6(c) can be indexed to consist of four twin related $[110]B19'$ EDPs, of which two EDPs derived from variant A are highlighted by solid lines, they are related by (001) compound twin. The other two from variant C are highlighted by dashed lines, they are also related to (001) compound twin. Variants A and C are related by an irrational plane $(1 \ -1 \ 0.64)$. Variants A, B and C form a triple junction. The foil was tilted 53° from (b) to (c), which is consistent with the calculated value of 52.17° from the $[0 \ -1 \ 1]B19'$ to the $[110]B19'$ zone axis. In the present study, we tend to describe the accommodation morphologies of the mosaic-like martensite variants by four coalescence.

Figure 7(a) shows a typical morphology of the mosaic-like martensite variants. Figure 7(b) is the schematic illustration of Fig. 7(a). The encircled area is a typical four variants coalescence unit. The incident beam is parallel to the $\langle 100 \rangle B2$ direction. The martensite variants can be triangular, quadrilateral or polygonal in shape. Although the shapes of the mosaic-like variants are complicated, the crystallographic relationship between these variants is simple. All the interfaces (or boundaries) between these mosaic-like martensite variants belong to either the $(011)B19'$ or $(1 \ -1 \ 0.64)B19'$ type. There are six types of interfaces or boundaries between these martensite variants. The variants classes of I_1 , II_1 , III_1 and IV_1 (the subscript 1 is used to represent the mosaic-like variants) in Table 2 are introduced to explain the variants combinations in Fig. 7. The (001) twin plane of variants

Fig. 7 A typical morphology of the mosaic-like martensite variants. (a) the bright field image when the incident beam is nearly parallel to $[-1 \ 3 \ -3]B19'$ i.e., the $[100]B2$ direction, (b) the schematic illustration of (a), see text for details.

Table 2 Four mosaic-like martensitic junction plane variants from $[-1 \ 3 \ -3]B19' // [100]B2$ direction (the symbol $//$ represent nearly parallel to in the present study).

Variants	(001)B19' derived from	(001)B19' being parallel to
I_1	(011)B2	(001)B2
II_1	$(0 \ 1 \ -1)B2$	(001)B2
III_1	(101)B2	(010)B2
IV_1	$(1 \ 0 \ -1)B2$	(010)B2

I_1 , II_1 , III_1 and IV_1 are derived from $(011)B2$, $(0 \ 1 \ -1)B2$, $(101)B2$ and $(1 \ 0 \ -1)B2$ respectively. I_1/II_1 and III_1/IV_1 are $(011)B19'$ twin related ($I_1/II_1 // (001)B2$, and $III_1/IV_1 // (010)B2$), while I_1/III_1 , II_1/IV_1 are $(1 \ -1 \ 0.64)B19' // (1 \ -1 \ 0)B2$ twin related, and the I_1/IV_1 , II_1/III_1 are $(1 \ -1 \ 0.64)B19' // (110)B2$ twin related. Every polygon, triangle, or quadrilateral possesses one kind of the $(011)B19'$ twin plane which is parallel to the $(010)B2$ or $(100)B2$. Another kind of the $(1 \ -1 \ 0.64)B19'$ twin plane is parallel to the $(110)B2$ or $(1 \ -1 \ 0)B2$ planes. The appearance ratio of $(1 \ -1 \ 0.64)B19'$ twin plane to

Fig. 8 The (001)B2 stereographic projection showing the combination of four mosaic-like martensite variants. The indices with round and square bracket indicate the plane normals and zone axis of the B19' martensite, respectively. Those without bracket represent the B2 parent phase.

(011)B19' is 2:1. These four-variants combinations can be illustrated in a (001)B2 stereographic projection as shown in Fig. 8. Since the orientation relationship between the B2 parent phase and the B19' martensite is $\langle 100 \rangle B2 \parallel [100] B19'$ or $\{001\} B2 \parallel (011) B19'^{(16)}$, the (011) B19' great circle is superimposed on one of the $\{010\} B2$ great circles. One of the $[100] B2$ zone axes is superimposed on the $[100] B19'$ one, i.e., the (011)B19' poles of variants III₁ and IV₁ are superimposed on (100)B2, while the (011)B19' of variants I₁ and II₁ are superimposed on (010)B2 pole. In order to describe these variants relationships more conveniently, the $[-1 \ 3 \ -3] B19'$ zone axis is introduced. The $[-1 \ 3 \ -3] B19'$ zone axis is in a 88.5° from the $[100] B19'$ zone axis. When the B2 parent phase is in a $[001] B2$ zone axis, all four kinds of mosaic-like variants of I₁, II₁, III₁ and IV₁ are almost in the $[-1 \ 3 \ -3] B19'$ zone axis (deviate by 1.5°). Since when the B2 parent phase is in the $[001] B2$ zone axis the martensite will not be in an axial condition, we use the symbol $\parallel$ to represent the approximate parallel relationship between $\langle 001 \rangle B2$ and $[-1 \ 3 \ -3] B19'$. The $[-1 \ 3 \ -3] B19'$ zone axes of variants I₁, II₁, III₁ and IV₁ are indicated in Fig. 8. All of them are close to the (001)B2 pole. The indices with round and square brackets indicate the plane normal and the zone axis of B19' martensite. Those without brackets represent the B2 parent phase. When the incident beam is parallel to $[001] B2 \parallel [-1 \ 3 \ -3] B19'$ zone axis, all the junction planes between the mosaic-like variants are edge on, and the martensite variants will have good contrast. It is worth to mention here that the (001)B19' compound twin traces are not revealed in Figs. 6 and 7 (similar case is in Fig. 12). This is because when the electron beam was nearly parallel to the $[001] B2$ (1.5° from $[-1 \ 3 \ -3] B19'$) both the twin and matrix

section of the (001)B19' twin possess the same Bragg reflection condition. They have the same contrast, therefore we cannot differentiate the twin traces in the bright field image. If the foil was tilted and the twin section was made at the Bragg's condition but the matrix section deviated from the Bragg's condition, or vice versa, the twin traces could be revealed, as shown in Figs. 3 and 4. So the criteria of a twin structure should be the electron diffraction analysis with the combination of bright field image (trace analysis). The bright field image under such condition cannot be treated as a criteria for twin structure identification.

(2) Eighteen combinations of the mosaic-like martensite variants

Referring to Fig. 7, three kinds of mosaic-like variants combinations can be obtained directly. They are shown in Figs. 9(a), (b) and (d), respectively. We find that (a) and (b) are of the same kind, i.e., the quadra-variants combination comes from four kinds of variants, I₁, II₁, III₁ and IV₁. (d) belongs to another kind, the quadra-variants combination consists of three kinds of variants II₁, III₁, and IV₁. According to the variants combination shown in (d), the other three combinations should appear, they are shown in Figs. 9(c), (e) and (f). This is similar to the case of (d) from the crystallographic view point. All the variants combinations satisfy the description in Section III.3. (1). Six combinations are presented for one of $\{100\} B2$ pole. According to the symmetry of the B2 structure, there exist 12 kinds of combinations. Therefore, 18 kinds of mosaic-like variants combinations can be found in a B2 single crystal.

(3) Twelve spear-like martensite junction plane variants

Figure 10(a) shows four groups of orthogonal spear-like martensite variants. The incident beam is parallel to the $[100] B19' \parallel [100] B2$ direction. Figure 10(b) is an EDP

Fig. 9 The schematic illustrations of the mosaic-like martensite variants self accommodations. (a)-(f) indicating six kinds of combinations of the mosaic-like variants in one of $\langle 100 \rangle B2$ directions.

Fig. 10 Four groups of spear-like martensite variants and related EDP. (a) bright field image; (b) EDP taken from the area in (a) including A, B, C, and D groups; (c) the schematic illustration of (b).

taken from the area including four groups of variants A, B, C and D of (a). One of the EDPs is marked by two rectangles, highlighted by dashed lines, which corresponds to the twin-related martensite groups A and B. The other set is marked by solid rectangles which corresponds to groups C and D. Each set of EDPs consists of two $[100]_{B19'}$ EDPs related by a $(011)_{B19'}$ twin plane. Figure 10(c) shows the schematic illustration of Fig. 10(b). Groups A and B are equivalent and groups C and D are also equivalent. Groups A and B consist of variants I_2 and II_2 (the subscript 2 is used to represent the spear-like variants). Similarly, groups C and D consist of variants III_2 and IV_2 . I_2 and II_2 are $(001)_{B2} \parallel (011)_{B19'}$ twin related. While III_2 and IV_2 are $(010)_{B2} \parallel (011)_{B19'}$ twin related. The $(001)_{B19'}$ twin planes of variants I_2 and III_2 are both derived from $(0 - 1 1)_{B2}$. This kind of relationship is shown in a $(001)_{B2}$ stereographic projection in Fig. 11. The symbols in Fig. 11 are the same as those in Fig. 8. Although the $(001)_{B19'}$ planes of I_2 and III_2 are both derived from the $(001)_{B2}$ plane, the shear (or rotation required by the Invariant Plane Strain) direction is different. The angle between the $(001)_{B19'}$ planes of variants I_2 and III_2 is 7.48° at the $[100]_{B19'}$ great circle. Similarly, the angle between the $(001)_{B19'}$ planes of variants II_2 and IV_2 is also 7.48° . The angle between $(001)_{B19'}$ planes of variants I_2 and II_2 (III_2 and IV_2) is in 97.48° (or $180 - 97.48 = 82.52^\circ$), which is in good agreement with the experimental result of 98° (Figs. 10(b) and (c)). There are four kinds of dependent martensitic junction plane variants derived from a $[100]_{B2}$ pole. Similarly, according to the symmetry of the $B2$ structure, there are another 8 kinds of junction plane variants derived from a $B2$ single crystal. The crystallographic parameters of variants I_2 , II_2 , III_2 and IV_2 are shown in Table 3. Although all the variants consist of $(001)_{B19'}$ compound twins, both the twin and matrix sections of the $(001)_{B19'}$ twins of these

Fig. 11 A $(001)_{B2}$ stereographic projection showing the relationships between the spear-like martensite variants. The symbols in this figure are the same as those in Fig. 8.

Table 3 Four mosaic-like martensite junction plane variants from $[100]B19'$ being parallel to $[100]B2$ direction.

Variants	$(001)B19'$ derived from	$(011)B19'$ being parallel to	$[-1\ 3\ -3]B19'$ being nearly parallel to
I_2	$(0\ 1\ -1)B2$	$(001)B2$	$[010]B2$
II_2	$(011)B2$	$(001)B2$	$[010]B2$
III_2	$(0\ 1\ -1)B2$	$(010)B2$	$[001]B2$
IV_2	$(011)B2$	$(010)B2$	$[001]B2$

variants are in the axial $[100]B19'$ zone axis. Both of them show dark contrast and we cannot specify the $(001)B19'$ twin traces under this condition.

4. Discussion of the mosaic-like and spear-like martensite variants

In our previous work⁽¹⁶⁾, we proposed that the martensite variants in the $Ti_{36.5}Ni_{48.5}Hf_{15}$ alloy are in lath plate shape with $(001)B2$ and $(011)B2$ as junction planes. The long axis of the lath plate was almost parallel to the $[-1\ 3\ -3]B19'$ direction in the $(011)B19'$ plane. The mosaic-like martensite variants are the cross sections of the lath plates, while the spear-like ones are the vertical section of the martensite variants. However, from Fig. 7, the number of $(011)B2$, i.e., the $(1\ -1\ 0.64)B19'$ junction plane between the mosaic-like variants, is two times that of the $(001)B2$ boundaries. This suggests that in the vertical section of the lath plate, i.e., the spear-like martensite variants, the appearing ratio of the $(1\ -1\ 0.64)B19'$ junction plane should double that of the $(011)B19'$ junction plane. But this is incorrect because the dominant junction plane between spear-like martensite variants is the $(011)B19'$ boundary, i.e., the $(001)B2$ plane, as shown in Fig. 10. In addition, the size of the mosaic-like martensite variants is much larger and wider than that of the spear-like ones. Then what is the relationships between these spear-like and the mosaic-like variants? The doubt can be clarified as follows:

Figure 12 is a typical martensite variants group when the incident beam is nearly parallel to the $[-1\ 3\ -3]$

$B19'$ direction. Detailed investigation revealed that the relationships between three martensite variants satisfy the above relationship in Fig. 7. Figures 7 and 12 only focus on the polygonal blocks and the strips respectively. Many steps indicated by arrows appear at some joint point when four variants meet with each other in Fig. 12. These small steps are parallel to the $(1\ -1\ 0.64)B19'$ plane, i.e., parallel to either the $(011)B2$ plane or the $(0\ 1\ -1)B2$ plane. These steps are introduced to satisfy the triple interface junctions for reducing the transformation strain.

The strips shown in Fig. 12 can explain the vertical section of the lath plate variants, i.e., the spear-like martensite variants very well. Although the appearing ratio of the $(1\ -1\ 0.64)B19'$ (the $\{011\}B2$ boundaries) is still two times that of the $(011)B19'$ (the $\{001\}B2$ plane), the length of the $\{001\}B2$ junction planes is much longer than that of the $\{011\}B2$ planes. This result indicates that the vertical section of these mosaic-like martensite variants would be dominated by the $\{001\}B2$ junction planes, i.e., the $(011)B19'$ junction planes, no matter how these strips were cut.

The above results show that the martensite variants in the $Ti_{36.5}Ni_{48.5}Hf_{15}$ alloy should be in the form of polygonal prisms (triangular or quadrilateral) or the lath plates. No matter they are, the cross section of the martensite variants would appear as regular mosaic-like structure as shown in Figs. 6, 7 and 12. In this condition, the variant to variant coalescence unit can be described as a four variants group. When three variants meet with at one point, two $\{011\}B2$ and one $\{001\}B2$ planes must be introduced. The spear-like martensite variants are the cross section of the lath plates.

Although there were no solutions for the phenomenological theory of the $(001)B19'$ compound twins in the present $TiNiHf$ alloy, the variants combinations can be explained very well by this (001) twin substructure. The $(001)B19'$ twin is sure to be responsible for the phase transformation from the experimental results. The phenomenological theory should be improved for the present $TiNiHf$ alloy in order to obtain a better agreement between the experiments and the theoretical calculations.

IV. Concluding Remarks

As inferred from the experimental results, the (001) compound twin is responsible for the phase transformation. The $(001)B19'$ twin lamellas are described as the hexahedron plates with three characteristic planes being $(001)B19'$, $(011)B19'$ and $(1\ -1\ 0.64)B19'$. The shape of the martensite variants can be clarified into two kinds: the triangular prisms (the quadrilateral, or polygonal) and the lath plates. The spear-like ones are the vertical section of the lath plates. The mosaic-like martensite variants are the cross section of either the prisms or the lath plates. Every prism, or lath plate, possesses one $(011)B19'$ boundary and two $(1\ -1\ 0.64)B19'$ interfaces. The variant to variant self-accommodation of the prisms

Fig. 12 Another kind of typical mosaic-like variants, see text for details.

and the lath plates should be of four variants combination. 18 kinds of combinations can be formed in a B2 single crystal. For the variant to variant combination of the lath plates, some $(1 - 1 \ 0.64)\text{B}19'$ type steps must be introduced to ensure the crystallographic feasibility and to reduce the phase transformation strain. The group to group combination of the prisms or the lath plates is in an orthogonal relationship.

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