Formation process of the incompatible martensite microstructure in a beta-titanium shape memory alloy

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Abstract

The formation modes of habit plane variant (HV) clusters (HVCs) in a Ti-23Nb-3Al (mol%) shape memory alloy were investigated by *in situ* optical microscopy with high-speed digital video camera. In addition to the kinematic compatibility condition, the nucleation mode and the interfacial energy between martensites were clearly shown to have critical roles. The V_I cluster, which is formed by two HVs connected by a $\{111\}$ type I twin, predominated in the early stage of the martensitic transformation, and had a lower energy barrier to nucleation and growth than did the V_{II} cluster, which is formed by two HVs connected by a $\langle 211 \rangle$ type II twin. Eighty percent of the V_I clusters were observed to form by paired nucleation or branching, in which the junction plane corresponds to the nucleation site of the relevant HV(s). In contrast, V_{II} clusters formed as a result of collisions of HVs. Neither paired nucleation nor branching was observed for V_{II} . V_I nuclei rather than V_{II} nuclei had a strong tendency to form, and this difference was not fully explained by the kinematic compatibility (KC) conditions. The junction planes formed by the collision of growing HVs should have larger deviation from the KC condition. The compatibility of the junction plane between HVs depends on the formation modes.

Keywords: *in situ*, self-accommodation, kinematic compatibility, crystallography

1. Introduction

The martensite plate in most shape memory alloys (SMAs) has a habit plane that is an invariant plane as described by the phenomenological theory of martensite crystallography [1-3]. Such a martensite plate is conventionally called a “habit plane variant (HV)”. The martensite microstructure consists of clustering HVs that reduce the net strain of the martensitic transformation in general [4]. A cluster of HVs is termed an “HV cluster (HVC)” in this study. The concept of self-accommodation or that of the plate group well explain the nature of the martensite microstructure [4]. However, understanding the connection between HVs is necessary for completely understanding the martensite microstructure and the thermomechanical properties of SMAs. Recent studies have shown that understanding the kinematic compatibility (KC) [5] between HVs is a key to understanding the martensite microstructure [6-17] and to controlling the properties of SMAs [18-21].

The continuity of a deformation at the interface between domain Ω_A and Ω_B with constant deformation gradients $\mathbf{A}$ and $\mathbf{B}$, respectively, can be maintained if Eq. 1 has a solution for $\mathbf{Q}$, $\mathbf{n}$, and $\mathbf{a}$ [22].

$$\mathbf{QA} - \mathbf{B} = \mathbf{a} \otimes \mathbf{n} \quad (1)$$

In Eq. 1, $\mathbf{Q}$ is a rigid body rotation, and $\mathbf{a}$ and $\mathbf{n}$ are vectors, with the vector $\mathbf{n}$ being that normal to the plane of the interface between Ω_A and Ω_B . Eq. 1 corresponds to the KC condition for the HVC if Ω_A and Ω_B are HVs. The invariant plane condition at the habit plane is expressed by Eq. 1 assuming that $\mathbf{QA}$ is the deformation gradient of an HV and $\mathbf{B} = \mathbf{I}$, where $\mathbf{I}$ is the identity matrix representing the parent phase. For an HVC, A and B are the deformation gradients of the HVs and the rotation $\mathbf{Q}$ is the index of incompatibility of the connection between HVs. In general, SMAs, $\mathbf{Q} \neq \mathbf{I}$ and the junction plane between HVs maintains the KC condition when an HV is rotated by $\mathbf{Q}$; the rotation $\mathbf{Q}$ breaks the KC condition at the habit plane of the HV. Therefore, the incompatibility remains somewhere in the HVC for the case of $\mathbf{Q} \neq \mathbf{I}$ in general. Though the existence of the incompatibility is obvious, its location is not clear from geometrical considerations alone. Determining the location of the incompatibility is essential for understanding the nature of the martensite microstructure and the generation of lattice defects during cyclic actuation of SMAs.

In our previous work [9], the relationship between the frequency of formation of HVC and $\mathbf{Q}$ was investigated for a Ti-23Nb-3Al (mol%) SMA using transmission

electron microscopy (TEM). Figure 1 shows the typical morphologies and KC conditions of the HVCs of this alloy, which undergoes a β (bcc) – α'' (orthorhombic) martensitic transformation [23]. There is no lattice invariant deformation in the alloy because the middle eigenvalue of the lattice deformation is unity as reported in $\text{Ti}_{50}\text{Ni}_{39}\text{Pd}_{11}$ alloy [21]. There are 10 types of HVCs in combination logic and only two HVCs that have very small $\mathbf{Q}$ are dominant in the alloy. The first type is termed a “ V_I cluster” and is formed by two HVs with the junction plane corresponding to the K_I plane of the $\{111\}_\text{o}$ type I twin. The subscript “o” denotes α'' -martensite. The second type is termed a “ V_II cluster” with the junction plane corresponding to the K_I plane of the $\langle 211 \rangle_\text{o}$ type II twin. A theoretical analysis based on Eq. 1 showed the KC condition at the habit plane and junction plane to be conflicting each other in this alloy because $\mathbf{Q} \neq \mathbf{I}$; the rotation angle of $\mathbf{Q}$ was calculated to be 0.69° and 0.57° for V_I and V_II clusters, respectively. The KC condition at the junction plane is satisfied when $\mathbf{Q}$ is applied to one HV and then the exact $\{111\}_\text{o}$ type I twin orientation relationship (OR) and $\langle 211 \rangle_\text{o}$ type II twin OR appears across the junction plane for V_I and V_II , respectively. Interestingly the location of the incompatibility was found to depend on the type of HVC in our previous study using precise Kikuchi line analysis [9]. For the V_I cluster, 80% of the junction planes had a $\{111\}_\text{o}$ type I twin OR with angular deviation less than

0.1° (less than the error of the orientation analysis by Kikuchi line). Here, the rotation $\mathbf{Q}$ acts and the KC at the junction plane is maintained at the expense of the KC at the habit plane. However, for the V_{II} cluster, 70% of the junction planes showed angular deviations greater than 0.4° from the exact $\langle 211 \rangle_o$ type II twin OR. Here, most of the junction planes were incompatible with maintaining the KC condition at the habit plane. Note that a microscopic observation of the fully developed microstructure did not seem to be able to explain the relatively high degree of maintaining KC at the junction plane of the V_I cluster. Diversity of the microstructure in the vicinity of the junction plane has been considered to depend not only on the KC condition but also on the dynamic features of the formation of the microstructure [8]. Information obtained from a static observation of the fully transformed microstructure is, however, limited to the former factor.

Against this background, we focused on the dynamic process by which the martensite microstructure forms. The purpose of this study was to reveal this process and the origin of the location of incompatibility by *in situ* observation of the process of the martensitic transformation. According to these *in situ* observations, the V_I and V_{II} clusters showed distinct differences in formation modes, and these differences were related to the differences in their locations of incompatibility.

2. Experimental procedures

2.1. Alloy

Following our previous study [9], Ti-23mol%Nb-3mol%Al was selected for this study.

An ingot with a mass of about 10 g was fabricated from high-purity starting elements of Ti (99.99%), Nb (99.9%), and Al (99.99%) by Ar arc-melting with a non-consumable W-electrode in an Ar-1%H₂ reducing atmosphere. Each ingot was arc-melted and then flipped. This set of melting procedures was repeated five times to ensure homogeneity of the product. The change in weight caused by arc-melting was less than 0.16 wt % and was judged to be negligible, hence requiring no chemical analysis. The oxygen content of the ingots previously fabricated by this method was less than 400 ppm by weight; thus, we assumed that the oxygen content of the current ingot was similar. The ingot was wrapped in a Ti foil, encapsulated in a quartz tube filled with an Ar atmosphere, homogenized at 1273 K for 7.2 ks, and then quenched by breaking the quartz tube in iced water. The martensitic transformation temperatures of the ingot were determined by preliminary differential scanning calorimetry to be $M_s = 291$ K, $M_f = 249$ K, $A_s = 277$ K and $A_f = 319$ K. The hysteresis, $(A_f + A_s - M_f - M_s)/2$, was 28K and seemed to be high, comparing with that of Ti-Ni-Pd with middle eigenvalue of unity [19]. However,

according to that Ti-24mol%Nb-3mol%Al alloy has hysteresis of about 60K and the middle eigenvalue is 0.999 [24], the hysteresis seems to be lowered in the present alloy by the middle eigenvalue of 1.0003 as described in the following.

Owing to that $A_s < RT < A_f$, the lattice parameters of both phases were able to be determined directly at room temperature (RT, 298K) by a preliminary X-ray diffraction as $a_b = 328.0 \pm 0.5$ pm, $a_o = 317.5 \pm 0.7$ pm, $b_o = 479.0 \pm 0.1$ pm, and $c_o = 464.0 \pm 0.1$ pm, where the subscript b indicates the parent (bcc) phase. The eigenvalues of the lattice deformation with Au-Cd type lattice correspondence [25] were 0.9680, 1.0003 and 1.0326, with the middle eigenvalue being very close to unity at RT; no lattice-invariant deformation was observed by TEM [19, 23]. $\mathbf{Q}$ of V_I and V_{II} clusters are 0.64° and 0.54° for these lattice parameters, respectively. The thermal expansion coefficients of the parent and martensite phases were on the order of $10^{-5}/K$ [26], so the effect of the thermal expansion was neglected for the temperature range used in this study. Following the results of numerical analysis in the previous study[9], the crystallographic quantities are calculated using the following lattice parameters that are in good agreement with the present value within the experimental error: $a_b = 328.061$ pm, $a_o = 316.945$ pm, $b_o = 479.321$ pm, and $c_o = 463.948$ pm [9, 23]. The habit plane

was approximately $\{755\}_b$ and 12 HVs were present. The lattice correspondence and the

HV notation used here follows that of our previous study [9] and is summarized in Table 1; the habit plane normal ($\mathbf{p}$) and shape change direction ($\mathbf{d}$) are given in cubic coordinates.

2.2. Specimen preparation and observation

Figure 2 shows the procedure used to prepare the specimens. The specimens were cut by electrical discharge machining, polished by using emery paper and diamond paste (step 1) and finished by electropolishing in a solution of 6% perchloric acid, 35% butanol, and 59% methanol (step 2). The best temperature for electropolishing with this solution was 228 K for the Ti-23mol%Nb-3mol%Al alloy. According to the transformation temperatures, the specimen was in the martensite phase during the electropolishing and the surface was flattened in the martensite state (step 2). The surface relief due to the reverse transformation, therefore, appeared at RT after the electropolishing (step 3). The surface of the specimen was then finished by applying plasma etching (TENSEC, HORIBA) (step 4). The temperature of the specimen surface was higher than A_f during the plasma etching. The specimen surface could be flattened at the parent phase. A faint relief, however, remained even after the plasma etching. The crystallographic orientation of the specimen surface was identified by electron

backscatter diffraction (EBSD) analysis using a field-emission gun-type scanning electron microscope (S-4300SE, Hitachi) equipped with an EBSD detector (e-Flash¹⁰⁰⁰, Bruker).

In situ differential interference contrast microscopy was performed using a digital microscope (VHX-100F, Keyence) equipped with a high-speed digital video camera (VW-9000, Keyence), a data collection system (NR-600, Keyence) and a temperature-controlled chamber (LMT-600, Collet Kogyo). The specimen was attached to a specimen stage made of pure silver with heat-conducting grease. Two K-type thermocouples were used. The thermocouple on the specimen stage was used for controlling the temperature, and the other thermocouple on the side face of the specimen was used for measuring the actual temperature of the specimen. The specimen was first heated to 323 K and then cooled to 223 K at a cooling rate of 5 K/min in a near-vacuum condition of $< 3.0 \times 10^{-3}$ Pa. The HVs were identified by single-trace analysis of the surface reliefs that resulted from the martensitic transformation.

3. Results

The observed area was located at about the center of a coarse β -grain of several millimeters in diameter. The surface normal of the observed area was determined to be

$[88\ 40\ 100]_b$ by the preliminary EBSD analysis. Figure 3 shows a stereographic projection of $\boldsymbol{p}$ and $\boldsymbol{d}$ viewed from this surface normal and was used for the trace analysis of the micrographs.

3.1. Overview of the martensitic transformation

An overview of the martensitic transformation upon cooling is shown in Figs. 4(a) - (e). The temperature dependence of the formation frequency of HVCs is summarized in Fig. 4(f). Above 308 K (Fig. 4(a)), the specimen was fully in the parent phase but some traces that had not been removed completely in step 4 of Fig. 2 were seen. At about 303 K, martensite plates started to form in the interior of the grain. Each HV nucleated as a thin plate growing along the habit plane trace with a propagation velocity of 10^{-2} m/s on average and then thickened consecutively. Isolated martensite plates were uncommon; most of the HVs formed pairs. The formation of paired martensite HVs is effective for reducing net strain and is common in the martensitic transformation [4]. Some martensite plates that appeared to be isolated in the image were possibly paired with a specific HV inside the specimen.

Only V_I clusters appeared in the early stage of the transformation, as indicated by the arrow pointing to the HV notation in Fig. 4(b). A triangle (T) cluster was

observed, as indicated by the triple-headed arrow of Fig. 4(b), but is categorized as a V_I cluster here, because it was determined to be a derivative of V_I as demonstrated in the following section.

V_{II} clusters appeared upon further cooling, as indicated by the double-headed arrows in Figs. 4(c) and (d). The formation frequency of this type of cluster was, however, lower than that of the V_I cluster. The formation of the V_{II} cluster was significantly activated in the middle stage of the transformation, as seen in Fig. 4(f). The martensite microstructure became well developed with further cooling, and Fig. 4(e) shows the martensite microstructure at 223 K, which was the lowest temperature investigated in this experiment. As the transformation proceeded, the HVs became smaller because the untransformed parent phase became divided by larger HVs.

The numbers of HVCs below M_f that we identified are summarized in Fig. 5. Tiny HVs that were not confidently identified were not included in the statistics. The black cells and the gray cells in Fig. 5 indicate V_I and V_{II} clusters, respectively; the numbers of the observed HVCs are shown in the corresponding cells. The total number of the identified HVCs was 150.

The identified HV types were 1(+), 2(+), 3(+), 4(+), 5(+) and 6(-), whereas 1(-), 2(-), 3(-), 4(-), 5(-) and 6(+) were not detected even below M_f . Figure 3 explains why

some HVs were not observed. These undetected HVs would have habit planes nearly parallel to the surface normal or shape change directions almost perpendicular to the surface normal. The contrast of the interference image was weakened in these HVs because the slope of the surface relief on the specimen surface became flat. We therefore suggest that the undetected HVs formed in the area resembling the untransformed parent phase in Fig. 4(e). This is the reason why some parts of the specimen appeared at first glance as if they were untransformed even at 223 K and why the fractions of V_I and V_{II} determined in the present study were very different from the results in our previous study using TEM [9]. The shape change directions of the observed HVs were close to the surface normal and the transformation strains can be relaxed at the surface. This surface effect may have affected the fraction of the HVs in the present study [27]. Therefore, the fractions of HVs that formed V_I and V_{II} were not reliable here, and only the processes of HVC formation are considered in the following sections.

3.2. V_I cluster formation modes

The V_I cluster formation modes were analyzed in detail. There were three such modes of formation. The first one involved the simultaneous formation or “paired

nucleation” of HVs from their junction plane. Figure 6(a) shows snapshots of the paired nucleations for 2(+) and 6(-). This type of formation was detected only at the early stage of the transformation and 4% of the V_I clusters were formed by this process. The second mode involved the “branching” of an HV from a pre-existing HV and was the major process. This process is shown in Fig. 6(b), where the nucleation of a 6(-) HV from a pre-existing 2(+) HV was captured. This type of formation mode was observed for all temperatures tested and 75% of the V_I clusters formed by this process. The third mode involved the “collision” of two growing HVs as shown in Fig. 6(c) for 1(+) and 3(+) HVs. The fraction of V_I clusters formed by such collisions was about 20%. It should be noted that 80% of the V_I clusters formed by paired nucleation or branching, in which the junction plane corresponded to the nucleation site of the relevant HV(s).

The process used to form of a T cluster was also captured, as shown in Fig. 7. A V_I cluster first formed and then the third HV formed consecutively; this was the only formation process observed. The simultaneous formation of the three HVs was not observed. The T cluster shown in Fig. 7 was formed from 1(+), 3(+), and 5(+) HVs that were mutually related by the $\{111\}_o$ type I twin OR as determined by our previous study [9]. First, a V_I cluster was formed from 1(+) and 5(+) HVs and then a 3(+) HV was additionally formed by branching from the 1(+) HV. The 3(+) HV grew and collided

with a 5(+) HV, leading to the formation of a closed triangle. The T cluster was, therefore, regarded as a derivative of the V_I cluster. The increase in the HV thickness involved the growth being directed toward the interior of the triangle, as depicted in the insets in Fig. 7. The center of the T cluster, however, was not filled by the three HVs. This was due to the presence of a partial wedge disclination [9]. The detailed structure at the center of the T-cluster could not be identified in the present optical microscopy experiment.

3.3. V_{II} cluster formation modes

Two distinct modes of formation were observed for the V_{II} cluster. One was the “collision” of growing HVs as observed for V_I clusters and the other was the “reflection” of a growing HV at a point of collision with another HV. Figure 8(a) shows a formation of a V_{II} cluster resulting from the collision mode. Two HVs, namely, 2(+) and 5(+), were observed to grow in the directions indicated by the arrows. These two HVs eventually collided and then formed a V_{II} cluster. Fifty-three percent of the V_{II} clusters formed in this way. The formation of V_{II} by the “reflection” mode is shown in Fig. 8(b). A 2(+) HV was observed growing along the habit plane trace as indicated by the arrow, and collided with another HV. A new, 5(+) HV nucleated at the point of the collision and

started growing in the opposite direction, resembling a reflection (see the third frame of Fig. 8(b)). Forty-seven percent of the V_{II} clusters were formed by this process. It should be emphasized that paired nucleation and branching, which were commonly observed modes for forming V_I clusters, were never observed for formation of a V_{II} cluster.

3.4. Relationship between the magnitudes of the energy barriers to the formation of V_I and V_{II}

Figure 9 summarizes the temperature dependence of the frequency of each formation process for V_I and V_{II} clusters upon cooling. Only V_I formed in the early stage of the transformation (308 K to 303 K). The relationship between the magnitudes of the energy barriers to the formation of the HVC clusters was determined directly from the experimental results. In general, martensitic transformations require supercooling because the energy barrier that is the sum of the elastic energy and dissipation energy must be overcome by the accumulated Gibbs energy [28]. The lower the temperature, the higher is the accumulated Gibbs energy, and when the temperature is below the equilibrium temperature, T_o , the Gibbs energies of the parent and martensite are equal. In other words, the martensite plate or HVC that appears just below M_s has the lowest energy barrier to its nucleation and growth. Therefore, based on the results shown in Fig.

9, the V_I cluster was determined to be more energetically favored than the V_{II} cluster. Note that neither the nucleation nor growth of an HV from the junction plane was ever observed for V_{II} . The preferential formation of a specific HV cluster has also been observed *in situ* for the martensitic transformation in Ti-Ni [29]. The present experimental results taken together revealed the nucleation of the martensite from the V_I junction plane, that is, the K_I plane of $\{111\}_o$ type I twin, to be energetically favored, and the paired nucleation and branching modes of formation to then be significant for only the V_I cluster. The V_{II} cluster was clearly determined to be a product of the collisions of HVs growing as parts of V_I clusters, whereas the details of the reflection mode remain to be determined.

4. Discussion

4.1. Origin of the incompatible junction plane

As mentioned in the Introduction, Fig. 1 shows the fractions of the V_I and V_{II} clusters containing incompatible junction planes. Compatible junction planes were found in about 80% of the V_I clusters, whereas about 70% of V_{II} clusters had incompatible junction plane. A concurrence between the fractions of the clusters displaying incompatible junction planes (Fig. 1) and the fractions of the clusters formed by specific

modes was revealed by the present study. Figure 10 summarizes the fractions of V_I and V_{II} clusters formed by each mode. Approximately 80% of the V_I clusters were formed by paired nucleation (PN) or branching, in which the junction plane corresponded to the nucleation site of the relevant HV(s). This fraction matches the fraction of the V_I clusters containing compatible junction planes (Fig. 1). On the other hand, more than 50% of the V_{II} clusters were formed by collisions (Fig. 10), and this value approximately corresponds to the fraction of V_{II} clusters containing incompatible junction planes. By assuming that the exact $\{111\}_o$ type I twin OR yielded the lowest energy for the HVCs, this concurrence can be interpreted as follows without any contradiction to the present experimental results. Figure 11 shows the relationship between formation mode and location of the incompatibility. The formation of V_I clusters by paired nucleation or branching requires the $\{111\}_o$ type I twin relationship to be exactly held at the junction plane by breaking the compatibility of habit planes around the junction plane. As a result, the fraction of V_I clusters with compatible junction planes corresponded to the sum of the fractions of V_I clusters formed by paired nucleation and branching. On the other hand, the martensite plates maintain compatible habit planes during their growth; and the junction planes formed by collisions must be incompatible in this case because of the competition between the KCs at the habit plane

and junction plane. The fraction of the clusters with incompatible interfaces and the fraction of the clusters formed by collisions were, therefore, almost the same.

Delville et al. [21] pointed out that HVs collide each other and their junction planes form relevant twin boundary after the action of Q in $Ti_{50}Ni_{39}Pd_{11}$ alloy, which has middle eigenvalue of unity. In their work, however, the formation processes of the junction planes and the precise analysis of the incompatibility at twin boundary were not analyzed. In the case where the middle eigenvalue is not unity, diversity of the microstructure has been observed in the vicinity of the junction planes between internally twinned HVs in several alloys [7, 8, 11, 13, 17]. Tapering and bending of the internal twin of minor volume fraction and the rotation of lattice have been observed around the junction planes in $Ni_{65}Al_{35}$ [7, 8, 11, 17]. These microstructures are considered to relax the local incompatibility that is enforced by the coalescence or collision of growing HVs [7, 8, 11, 17]. In the present case, the local incompatibility at junction plane of V_{II} is expected to be accommodated by interfacial dislocations or local rotation of lattice in the vicinity of the junction plane because there is no internal twin to tune the total deformation of the HVs. According to the present results, it is emphasized that not only the coalescence but also the nucleation process of HV affects the character of the junction planes. An *in-situ* observation together with a precise

orientation analysis must be able to distinguish the compatible and incompatible junction planes and their origin that is related to the dynamical process of the transformation in other alloys.

4.2. Preferential nucleation of V_I

It is quite interesting that compared to the V_{II} cluster, the V_I cluster more easily nucleated despite its slightly larger rotation $\mathbf{Q}$ to maintain the KC condition at the junction plane as summarized in Fig. 1. This study clearly demonstrated that the KC condition does not fully describe the variant selection rule in the nucleation stage. A similar situation was shown for Ti-Ni [29]. The preferential V-shaped cluster can satisfy the KC condition and the $\{\bar{1}11\}$ type I twin orientation at the junction plane simultaneously and its $\mathbf{Q}$ is not the smallest one [14]. An explanation is the interfacial energy of the $\langle 211 \rangle_o$ type II twin boundary being much higher than that of the $\{111\}_o$ type I twin, and the paired nucleation of the V_{II} cluster being virtually impossible despite the rotation $\mathbf{Q}$ being smaller than that of V_I . This explanation is based on the general relationship between particle size and energy, namely, the smaller the particle, the higher the ratio of its interfacial energy to its total energy [30]. Our previous study[9] found the values of $\mathbf{Q}$ for the V_I (0.69°) and V_{II} (0.57°) clusters to be an order

of magnitude smaller than those for the other HVCs. Q is an indicator of the incompatibility that arises upon the formation of an HVC and is related to the elastic strain energy. The preferential formation of V_I and V_{II} clusters rather than the other HVCs is, therefore, well explained by Q without considering any other energy such as interfacial energy as demonstrated in our previous study [9]. However, interfacial energy may be comparable to the difference between elastic strain energy of V_I and V_{II} and may have affected the energy balance of the nuclei of V_I and V_{II} in this study.

An alternative explanation, one based on the dynamic motion of the atoms, may also be plausible. The directions of displacement, d , for the HVs forming the V_I cluster were found to be very similar, and to cluster around $\langle 111 \rangle_b$, as seen in Fig. 3; for example, see $d_{1(+)}$, $d_{3(+)}$, and $d_{5(+)}$. This finding suggested a cooperative motion of atoms at the V_I junction plane. On the other hand, the directions of displacement for the HVs forming the V_{II} cluster were found to differ by 120° ; see $d_{1(+)}$ and $d_{4(-)}$ in Fig. 3. That is, the projected displacements of atoms on the V_{II} junction plane varied considerably, suggesting the cooperative motion of atoms here to be impossible. Such a considerably greater cooperativity of the motions of the atoms at the V_I rather than V_{II} junction plane would thus also explain the preferred nucleation of the V_I cluster.

Though the nature of the preference for V_I nucleation is not clear, it is evident

that there is a strong tendency to form V_I rather than V_{II} in the nucleation stage and that this preference is not fully explained by a simple evaluation of Q . The location of incompatibility is governed by the formation sequence of the HVC, namely nucleation or collision, and this is another striking finding in this study.

5. Conclusions

The modes of formation of the HVCs in a Ti-23Nb-3Al (mol%) SMA was investigated by using *in situ* optical microscopy, and the following conclusions were obtained for this alloy.

1. The V_I cluster is the dominant type in the early stage of the martensite transformation of this alloy and has a lower energy barrier to nucleation and growth than does the V_{II} cluster, despite a larger incompatibility at junction planes.
2. A T cluster of this alloy can be formed by additional formation of a specific HV onto a pre-existing V_I cluster, and is hence a derivative of V_I .
3. A considerable majority of V_I clusters in this alloy form by paired nucleation or

branching, in which the junction plane corresponds to the nucleation site of the relevant HV(s). In contrast, V_{II} clusters primarily form as a result of collisions of HVs. (Neither paired nucleation nor branching was observed for V_{II} .) There is a stronger tendency to form V_I nuclei than V_{II} nuclei, and this difference is not fully a result of KC conditions. The effect of interfacial energy is a critical factor in the selection of the nucleation mode.

4. The junction planes formed by the collisions of growing HVs are thought to have larger deviation from the KC condition. The compatibility of the junction plane depends on the formation modes.

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Table caption

Table 1

Habit plane orientation and shape-change direction of HVs. Lattice correspondence and the notations of habit plane variants are following our previous study [9].

Figure captions

Figure 1: Typical morphologies and the KC conditions of the HVCs in Ti-23Nb-3Al. “V_I cluster” and “V_{II} cluster” are formed with the junction plane corresponding to the K_I plane of the $\{111\}_o$ type I twin and the $\langle 211 \rangle_o$ type II twin, respectively. The rotation angles for KC condition at junction plane ($\mathbf{Q}$) are 0.69° and 0.57° for V_I and V_{II} clusters, respectively. Our previous study showed that rotation $\mathbf{Q}$ acted only in V_I cluster and the junction plane of V_{II} is incompatible [9].

Figure 2: Specimen preparation procedure. The specimen surface was flattened in parent phase and the surface relief by the forward transformation upon cooling was observed.

Figure 3: Habit plane traces and shape change directions of the HVs. This stereographic projection of $\mathbf{p}$ and $\mathbf{d}$ shows the geometry of martensite on the specimen surface observed in this study.

Figure 4: Differential interference contrast image of the specimen surface at (a) 308 K, (b) 303 K, (c) 298 K, (d) 288 K and (e) 223 K, and (f) the number of identified HVCs at each temperature range. Most of the HVs formed pairs. Note that only V_I clusters appeared in the early stage of the transformation.

Figure 5: Number of identified HVCs below M_f . Undetected HVs would have habit planes nearly parallel to the surface normal or shape change directions almost perpendicular to the surface normal.

Figure 6: Formation of a V_I cluster by (a) paired nucleation, (b) branching and (c) collision. The 80% of the V_I cluster is formed by the paired nucleation or branching in which the junction plane corresponds to the nucleation site of the relevant HV(s).

Figure 7: Formation sequence of a T cluster. T cluster is formed from a V_I cluster and is a derivative of the V_I cluster.

Figure 8: Formation of V_{II} clusters by (a) collision and (b) reflection. Note that paired nucleation and branching, which were commonly observed modes for forming V_I clusters, were never observed for formation of a V_{II} cluster.

Figure 9: Number of V_I (upper) and V_{II} (lower) clusters formed by each mode of formation at each temperature range. Only V_I formed in the early stage of the transformation (308 K to 303 K). The martensite plate or HVC that appears just below M_s has the lowest energy barrier to its nucleation and growth in general. Therefore, V_I cluster was determined to be more energetically favored than the V_{II} cluster.

Figure 10: Fraction of the V_I (left) and V_{II} (right) clusters formed by each formation mode after the completion of the transformation. The fraction of V_I by paired nucleation and branching matches the fraction of the V_I clusters containing compatible junction planes. On the other hand, more than 50% of the V_{II} clusters were formed by collisions, and this value approximately corresponds to the fraction of V_{II} clusters containing incompatible junction planes.

Figure 11: Schematic diagrams of the relationship between the formation mode and the location of the incompatibility. The formation of V_I clusters by paired nucleation or branching requires the $\{111\}_o$ type I twin relationship to be exactly held. The junction plane formed by collision becomes incompatible.

HV	p	d	HV	p	d
1(+)	(-h, k, k)	[u, v, v]	4(+)	(k, h, -k)	[v, -u, -v]
1(-)	(h, k, k)	[-u, v, v]	4(-)	(-k, h, k)	[-v, -u, v]
2(+)	(h, k, -k)	[-u, v, -v]	5(+)	(k, k, -h)	[v, v, u]
2(-)	(h, -k, k)	[-u, -v, v]	5(-)	(k, k, h)	[v, v, -u]
3(+)	(k, -h, k)	[v, u, v]	6(+)	(k, -k, h)	[v, -v, -u]
3(-)	(k, h, k)	[v, -u, v]	6(-)	(-k, k, h)	[-v, v, -u]

h=0.705115, k=0.501405, u=0.0488206, v=0.0324642

Table 1

Figure 1

Figure 2

Figure 3

Figure 4

	1(+)	1(-)	2(+)	2(-)	3(+)	3(-)	4(+)	4(-)	5(+)	5(-)	6(+)	6(-)
1(+)	-				28				48			4
1(-)		-										
2(+)			-				3		6			35
2(-)				-								
3(+)	28				-				24			
3(-)						-						
4(+)			3				-		2			
4(-)								-				
5(+)	48		6		24		2		-			
5(-)										-		
6(+)											-	
6(-)	4		35									-

Figure 5

(a) Paired nucleation

(b) Branching

(c) Collision

Figure 6

Figure 7

(a) Collision

(b) Reflection

Figure 8

Figure 9

Figure 10

Figure 11

(a) Paired nucleation

(b) Branching

(c) Collision

The 80% of the V_I cluster is formed by the paired nucleation or branching in which the junction plane corresponds to the nucleation site of the relevant HV(s). In contrast, V_{II} cluster is originated to the collision of HVs. No paired nucleation and branching were observed for V_{II} . There is a strong tendency to form V_I rather than V_{II} in the nucleation and is not fully explained by the evaluation of KC conditions.