***In situ* scanning electron microscopy study of the thermoelastic martensitic transformation in Ti-Ni shape memory alloy**

Y. Soejima¹, S. Motomura¹, M. Mitsuhashi², T. Inamura³, M. Nishida^{2*}

¹*Interdisciplinary Graduate School of Science and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*

²*Department of Engineering Science for Electronics and Materials, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*

³*Precision and Intelligence Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

*Corresponding author: *Department of Engineering Science for Electronics and Materials, Kyushu University* nishida.minoru.355@m.kyushu-u.ac.jp

6-1 Kasuga-Koen, Kasuga, Fukuoka 816-8580, Japan

Tel.: +81-92-583-7534

Fax: +81-92-583-7534

E-mail address

Y. Soejima: 3ES14008P@s.kyushu-u.ac.jp

S. Motomura: MOTOMURA.Shunichi@nims.go.jp

M. Mitsuhashi: mitsuhashi@asem.kyushu-u.ac.jp

T. Inamura: inamura.t.aa@m.titech.ac.jp

Abstract

The thermoelastic martensitic transformation from the B2 to B19' structures in the Ti-Ni shape memory alloy was observed by *in situ* scanning electron microscopy in order to investigate the self-accommodation microstructure. Nucleation of the V-shaped habit plane variant cluster (2HPVC) triggers the formation of the hexangular HPVC (6HPVC) that is formed by six habit plane variants in the grain interior. The triangular morphology (3HPVC) is a derivative of 2HPVC. The autocatalytic transformation spreads from the 6HPVCs to the grain boundary and the reverse transformation proceeds like a rewind of the forward transformation. 2HPVC and 6HPVC are the most favorable morphologies for nucleation and growth, respectively, as explained by the analysis of the kinematic compatibility at junction planes.

Keywords: Ti-Ni; Shape memory alloy; Thermoelastic martensitic transformation; *In situ* SEM, Nucleation site

1. Introduction

Near-equiatomic Ti-Ni alloys are widely used in engineering, aeronautics, dentistry, and medical fields because of their superior shape memory effect and superelasticity. These properties are associated with the thermoelastic martensitic transformation from the cubic (B2) to the monoclinic (B19') structure [1]. The self-accommodation microstructure is characteristic of thermoelastic martensite because it reduces the elastic strain energy during transformations through combining multiple habit plane variants (HPVs) [1-5]. We have investigated the self-accommodation morphologies of B19' martensite in Ti-Ni alloys as shown in the schematic illustration in Fig. 1 [6-8]. The HPV notation follows Miyazaki's notation [9]. We found that there are three pairs of minimum units consisting of two HPVs with V-shaped morphology connected to the $\{\bar{1}\bar{1}1\}_{B19'}$ type I twins that have the K_1 plane normal perpendicular to $[111]_{B2}$. The theoretical habit plane index $\{0.88888\ 0.40443\ 0.21523\}_{B2}$ [9, 10] was approximated to $\{942\}_{B2}$ to simplify the analysis. We defined this V-shaped habit plane variant cluster (HPVC) as '2HPVC' [6-8]. There are twelve pairs of minimum units in the whole crystal. Three kinds of self-accommodation morphologies based on 2HPVC develop around the $[111]_{B2}$ trace, which have triangular, rhombic, and hexangular shapes that consist of three HPVs (3HPVC), four HPVs (4HPVC), and six HPVs (6HPVC), respectively. There are six combinations of 3HPVC, three combinations of 4HPVC, and only one combination of 6HPVC; therefore, there are 24, 12, and 4 combinations in the whole crystal, respectively. 3HPVC is equivalent to the

morphology reported by Madangopal [11]. 6HPVC has been observed in *in-situ* and *ex-situ* nanoindentation tests on $\langle 111 \rangle$ orientated surfaces of a Ti-Ni alloy [12].

Although the pentagonal morphology (5HPVC) can be imagined geometrically (gray lines in Fig. 1), we have not observed it experimentally [6-8]. Because these results were obtained from static observations, such as reverse transformation relief, there is no dynamical information, such as the nucleation and growth of the martensitic phase. We have investigated the multistage martensitic transformation in aged Ni-rich Ti-Ni alloys by *in situ* scanning electron microscopy (SEM), which enables extensive observation at a high resolution [13-15]. This technique has the advantages of optical microscopy and transmission electron microscopy (TEM).

In this study, we directly observed the microstructural changes during the thermoelastic martensitic transformation from B2 to B19' structures by *in situ* SEM. We examined the nucleation and growth of the martensitic phase, the interaction between HPVCs, and the forward and reverse transformation sequences, focusing on the order of HPVC formation. We have proposed that 6HPVC is the most favorable morphology for relaxing the incompatibility at the junction planes of the HPVs, and that 3, 4, and 6HPVCs are derivatives of 2HPVC, based on the geometry of the transformation [6-8]. The *in situ* observation identified the HPVC with the lowest energy barrier for the formation and the microstructure properties.

2. Experimental Procedures

A commercially available Ti-50.8 at.% Ni alloy rod 3 mm in diameter was used. The rod was cut into disks 1 or 0.5 mm thick for the differential scanning calorimetry (DSC) measurements and SEM observations, respectively. The disks were solution treated at 1173 K for 3.6 ks and then quenched in ice water. The DSC measurements were performed on a calorimeter (DSC-60, Shimadzu) with a cooling and heating rate of 0.17 K/s. The martensite start temperature (M_s), martensite finish temperature (M_f), austenite start temperature (A_s) and austenite finish temperature (A_f) are 236, 221, 254, and 269 K, respectively. The disks for the SEM observations were electropolished in $\text{HNO}_3/\text{CH}_3\text{OH}$ (1:3 v/v) above M_s to prevent the formation of a reverse transformation relief [6]. A field-emission scanning electron microscope (FE-SEM; Ultra55, Carl Zeiss) equipped with an annular backscattered electron (BSE) detector and electron back scatter diffraction (EBSD) was used. The annular BSE detector visualizes the channeling contrast, depending on the crystal structure and orientation in crystalline materials [16]. The B2 grains with a surface normal almost parallel to $\langle 111 \rangle_{\text{B2}}$ were selected by EBSD measurements before the *in situ* SEM observations, to compare the surface relief directly with the HPV configuration in Fig. 1. A Peltier stage (Coolstage, Deben) with a working temperature of 220–320 K was used for the *in situ* SEM observations. The specimen was cooled or heated continuously with 0.025 K/s and the images were captured at 20 s intervals.

In the TiNi alloy, the HPVs often have wavy habit plane, as shown in Fig. 5 of Ref. [6].

In addition, the trace of the lattice invariant deformation (LID) twin inside each HPV

was not clearly visible in this experiment because the resolution was traded off against scanning speed for the video capture. The explicit notation of the HPV could not always be determined reliably by the single-trace analysis, especially for distinguishing $n'(+)$ and $n'(-)$. The V-shaped clusters and triangle clusters observed in this study were assigned as 2HPVC and 3HPVC, respectively, as defined in our previous study because the two clusters are the major kinds of HPVCs in the fully transformed specimens [6-8].

3. Results

3.1 Overview of forward and reverse transformations

Figure 2 shows a series of *in situ* SEM images of the quenched Ti-50.8 at.% Ni alloy after solution treatment at 1223 K ([Supplementary Movie M1](#)). The surface normal is $[17\ 13\ 14]_{B2}$ in grain B. There are no characteristic microstructures in the parent phase at 290 K, except for grain boundaries and nonmetallic inclusions, visible as the darkest contrast in Fig. 2a. The martensitic phase with V-shaped (2HPVC) and hexangular morphologies (6HPVC) initially appear at 232 K in grains A and B (Fig. 2b). A pair of bright and dark contrasts spreading from the obtuse vertices of 6HPVC is seen along $\{110\}_{B2} \langle 112 \rangle_{B2}$ in the parent phase, as indicated by white single arrows. These are a type of strain contrast induced by the formation of the martensitic phase, because the annular BSE detector can visualize the channeling contrast. The local change in the

crystallographic orientation in the parent phase is detected as the pair of bright and dark contrasts. 2HPVC changes to 6HPVC, and then the strain contrast expands (Fig. 2c). The unique HPV indices in 2HPVC and 6HPVC in Fig. 2c can be identified by the straight habit plane, although the trace of the $\langle 011 \rangle_{B19'}$ type-II twin as the LID is not visible. The bright triangular contrast from the acute vertices of 6HPVC is also visible (white double arrows, Fig. 2c). The former strain contrast from the obtuse vertices of 6HPVC is sharper than the latter one from the acute vertices of 6HPVC. Because the *in situ* cooling observations and the EBSD and SEM measurements cannot be performed simultaneously in the present study, quantitative analysis of the strain contrast has not yet been completed. Further investigations are required to clarify the origin of the strain contrast formation. However, the autocatalytic transformation occurs along the strain contrast, spreading from the 6HPVCs to the grain boundary. During continuous cooling, 2HPVCs and 3HPVCs appear along the strain contrasts and develop over the whole area (Figs. 2d and e). In addition to the martensitic phase, there are different surface reliefs with straight, shallow roughness (white triple arrow, Fig. 2d), which are identified as the stress-induced R-phase. Upon heating, the surface reliefs nearly disappear in the reverse order of appearance, such as the three 6HPVCs indicated by the black single arrows in Fig. 2f. Although the two 6HPVCs on the right hand side appear earlier than the 6HPVC on the left hand side in the grain B (Figs. 2b and c), the latter remains in Fig 2g. After reverse transformation, there are many small dots with bright contrast in the parent phase at 290 K (Fig. 2h), even though the HPVCs have

completely disappeared at 274 K. These dots are residual martensite, arising from a surface effect. The reverse transformation is probably prevented by surface layers, such as oxide films formed during electropolishing. The progress of the reverse transformation starts around the grain boundaries and converges at the center of the grain in the exact reverse of the forward transformation. The martensite that appeared first upon cooling disappeared last upon heating. The M_s and A_f temperatures were determined as 235 and 273 K, respectively by neglecting the dot-like contrast in the *in situ* observations and were in good agreement with those obtained by the DSC measurements. However, the M_f and A_s temperatures were not correctly recognized because of the limitation of the cooling temperature of the Peltier stage. This result is supported by the presence of untransformed regions at 222 K (white single arrows, Fig. 2e).

3.2 Stress-induced R-phase

Figure 3 is an enlarged view of the area indicated by the triple headed arrow in Fig. 2d at 226 K. Banded structures with alternated platelets are visible, which become clearer as the temperature decreases. We assume that the platelets are the R-phase, which is a martensitic transformation product in Ti-Ni alloys [1, 2, 17]. According to the traces of the possible twinning plane among R-phase variants 1, 2, 3, and 4, as defined by Fukuda et al. [17], group 1b matches the observed microstructure, although variant 2 is absent. The R-phase could not be detected by the DSC measurements, because there

are no Ti_3Ni_4 precipitates and high-density dislocations to induce the R-phase transformation. Therefore, the R-phase is a stress-induced product at the early stage of the martensitic transformation and can only be observed by *in situ* microscopy.

3.3 Nucleation and growth of HPVC

3.3.1 Nucleation

Figures 4a and b are enlarged micrographs of Figs. 2b and c, respectively, ([Supplementary Movie M2](#)). 2HPVC and 6HPVC are homogeneously nucleated at the grain interior rather than heterogeneously from the grain boundary or interface between the nonmetallic inclusions and parent phases. The 2HPVC (single arrow, Fig. 4a) changes to a 6HPVC (Fig. 4b). A scheme of this process is shown in Fig. 4c. The two martensite plates are asymmetrically nucleated from their junction plane that is deduced to be the K_1 plane of the $(\bar{1}11)_{\text{B19'}}$ type I twin, which is derived from $(0\bar{1}1)_{\text{B2}}$ [6-8, 11, 18-20]. These two plates eventually correspond to HPVs $6'(+)$ and $4'(-)$ that form a 2HPVC [6, 8]. The side edge in these two plates, indicated by dotted lines, is different from the theoretical habit plane of $\{942\}_{\text{B2}}$ indicated by the solid line in Fig. 4c. After the 2HPVs grow to the 6HPVC, the side edge in each HPV coincides with the theoretical habit plane (Fig. 4c). These observations indicate that the junction plane between the two HPVs is formed prior to the stable habit plane in each HPV during the initial stage of nucleation. These observations could also visualize the lattice deformation and subsequent LID to produce the invariant habit plane. Although the

reproducibility of this phenomenon was confirmed several times ([Supplementary Movie M3](#)), it should be investigated in shape memory alloys other than Ti-Ni.

3.3.2. Growth and formation of microstructure

Upon further cooling, many HPVs appeared around the 6HPVC. Figures 5a–f show the enlarged views of the formation of 2HPVC and 3HPVC upon continuous cooling from 230 to 224 K. The area in Fig. 5 is around the largest 6HPVC in Fig. 2c. The double headed arrow and the triple headed arrow in Fig. 5 indicate 2HPVC and 3HPVC, respectively. First, 2HPVC nucleates around the obtuse vertices of 6HPVC (Fig. 5a). This trend was also observed around other 6HPVCs. Another 2HPVC is nucleated around the obtuse vertices of 6HPVC (Fig. 5b). The strain contrast running perpendicular in Fig. 5a is disturbed and weakened by the nucleation of 2HPVC (Fig. 5b). This indicates that 2HPVC was preferentially nucleated to relax the internal stress. During the transformation, the strain contrasts initially present in Fig. 5a are weakened or changed. The change in the strain contrast clearly demonstrates that the stress-field of the former martensite mediates the autocatalytic transformation. The 2HPVC nucleated in Fig. 5b grows to 3HPVC in Fig. 5c. This is direct evidence that the 3HPVC derives from 2HPVC, confirming that the minimum unit of HPVC is 2HPVC, as suggested by our previous studies. All 3HPVCs may be formed in this way, although most of the growth of 3HPVCs could not be captured.

There are three formation sequences for 2HPVC. The first is the simultaneous

nucleation, as in Figs. 5d or 3. The second is the collision of two growing HPVs. For example, the HPVs indicated by a single arrow in Fig. 5d collide in Fig. 5e and immediately grow to 3HPVC. The third is branching from a pre-existing HPV (Fig. 5f). The crystallographic character of the junction plane appears to depend on the formation process, as observed in β -titanium shape memory alloy [21].

The growth behavior of 3HPVC is different from that of 6HPVC. 3HPVC exhibits inward growth, whereas 6HPVC exhibits outward growth. The 3HPVCs in Figs. 5c and e grow inward, as seen in Figs. 5d and f, respectively. The inward growth does not reach completion often and complicated structures were observed in the center of 3HPVC. These structures correspond to fine martensites consisting of $(001)_{B19'}$ compound twins, which have been observed previously by conventional TEM [18, 20]. The formation of 3HPVC is often interrupted by the formation of another HPVC (Figs. 5e and f). An HPV grows (single headed arrow) from the 2HPVC in Fig. 5e and appears to form a 3HPVC. However, the formation of another 2HPVC interrupts the formation of a 3HPVC (Fig. 5f).

As the transformation proceeds, the area of the untransformed region decreases, and the frequency of the interruption increases. As the result, the morphology of the martensite plates becomes fine and irregular in the final stage of the transformation; the higher driving force of the transformation is necessary to form such an incompatible microstructure. In the final stage of the transformation, the HPV description is no longer applicable. This is because decreasing the temperature

increases the driving force through supercooling.

3.4 Microstructural repeatability

There is a microstructure memory effect, where the selective nucleation of martensite variants occurs in the same region in some shape memory alloys during thermal cycles [22, 23]. We completed *in situ* thermal cycling observations in the same specimens used in Fig. 2. However, it became difficult to identify the martensite variants as the number of thermal cycles increased because of the increase in the number of residual martensite areas. We controlled the electropolishing conditions, and then performed the *in situ* thermal cycling observations immediately after electropolishing to eliminate the formation of a surface layer. Figures 6a, c, and e show the surface morphology observed during the initial stage of the transformation in the first, third, and fifth thermal cycles, respectively. The micrographs in Figs. 6b, d, and f were taken around the M_f temperature after the first, third, and fifth thermal cycles, respectively. There is no residual martensite in the parent phase in Figs. 6c and d. Some 6HPVCs are indicated by dotted circles. The positions of those circles varied with each thermal cycle. These results suggest that there is no microstructure memory effect in Ti-Ni shape memory alloys under these experimental conditions. The absence of the reversibility in the microstructure implies that the preferential nucleation site is different in each thermal cycle; the formation of the martensite microstructure changes the sub-structure of the alloy. We are currently examining the effect of further thermal

cycles on the microstructure memory effect.

The strain contrast in Figs. 1b and c is clearer than in Figs. 6a, c, and e. This result suggests that the surface condition may affect the quality of SEM imaging with channeling contrast. Although this is interesting, it is beyond the scope of the present study.

4. Discussion

The Gibbs energy of the martensite phase is equal to that of the parent phase at the equilibrium temperature, T_0 . In general, the martensitic transformation does not start at T_0 because the driving force required to overcome the energy barrier is the sum of elastic strain energy and dissipation energy [24]. Supercooling (or superheating in the reverse transformation) is necessary to supply the driving force. In Ti-Ni, the driving force is stored by supercooling or superheating at a slope of 50~70 kJ/(kg K) [25]. As the temperature decreases, the driving force increases and the transformation starts at the temperature, M_s , at which sufficient energy is stored to nucleate the first martensite plate. Therefore, the martensite plate that forms at M_s has the lowest energy barrier to complete the nucleation and the growth. In other words, the HPVC that appears at M_s has the lowest energy barrier of the possible morphologies of the HPVCs. Figure 3a shows that the nucleated martensites initially form 2HPVC and do not grow as they are; three 2HPVCs immediately nucleate and grow into 6HPVC. 3HPVC also forms

from a pre-existing 2HPVC (Fig. 5c). 2HPVC is the most favorable morphology for the nucleation and is not the most suitable morphology for further growth. In general, the smaller the size of the product phase, the higher the ratio of the interfacial energy to the total energy of the product phase [26]. The 2HPVC junction plane, defined as “interface I” in our previous study [8], has the smallest interfacial energy of the possible characteristic interfaces. This shows that the kinematic compatibility (KC) condition [27] is not the only factor determining the dominant morphology of the real microstructure. The rotation to satisfy the KC condition (a measure of the incompatibility [28-30]) at interface I is 2.2° , and that of interface IV is 0.23° , whereas the HPVC nucleation is observed only at interface I. As shown in our previous study, the KC condition and the exact $\{111\}_{B19'}$ type I twin orientation are simultaneously satisfied only at interface I [8]. The present results demonstrate the importance of the interfacial energy determined by the arrangement of atoms at the interface and the KC condition, especially in the nucleation stage of the transformation, as suggested in the β -titanium shape memory alloy [31].

In 2HPVC, only one end of the HPV is connected to an end of another HPV, and the transformation strain is not relaxed locally. The formation of another HPV is necessary to close the HPVC and to lower the total energy of the fully grown HPVC. This is one reason why 2HPVC is not suitable for further growth, even though it is favored during nucleation.

Figure 7 shows the observed number of HPVCs in grain B in Fig. 1. Each of data

points is the number of the observed HPVCs at each temperature and then there is an indeterminacy of 1K for the formation temperature of the newly formed HPVCs.

Some HPVCs were omitted in the final stage of the transformation because they were too small to identify their morphology. The 2HPVCs counted in Fig. 7 are the stable 2HPVCs, unlike the 2HPVCs that transformed into 6HPVC in Fig. 3. The total number of 2HPVCs decreases at 231, 228, and 224 K because some 2HPVCs grew into 3HPVCs (Figs. 5b and c). The further growth of the 14 2HPVCs remaining at 222 K to 3HPVCs was probably interrupted by other HPVCs. However, the number of 3HPVCs and 6HPVCs increased monotonically as the temperature decreased. In the early stage of the transformation, 6HPVC was the dominant morphology. 6HPVC has the lowest energy barrier for growth, which is in good agreement with the analysis of HPVC geometry [8]; all junction planes are almost compatible only in 6HPVC. Further cooling provides a sufficient driving force allowing the formation of other HPVCs with a higher energy barrier. The formation and growth of 2HPVC and 3HPVC were activated below 229 K. As the transformation proceeded, the stress field in the untransformed parent phase was disturbed by the pre-existing martensites; a variety of morphologies relaxed the local stress. The pre-existing martensites were also expected to disrupt the formation of new 6HPVCs. Therefore, the formation of 2HPVCs and 3HPVCs increased as the transformation proceeded owing to the driving force provided by supercooling.

5. Conclusion

The following microstructural aspects were obtained by *in situ* SEM observations of thermoelastic martensitic transformation from the B2 to B19' structures in the Ti-Ni shape memory alloy.

1. The hexangular morphology consisting of 6 HPVs (6HPVC) homogeneously appeared in the interior of grain during the initial stage of transformation. Nucleation of 2HPVC triggered the formation of 6HPVC.
2. Other morphologies, such as V-shaped (2HPVC) and triangular (3HPVC) morphologies, appeared along the strain gradient produced by the formation of 6HPVC.
3. The stress-induced R-phase transformation was observed during the early stage of martensitic transformation.
4. Each of HPVCs had similar thermal hysteresis. The first martensite that appeared upon cooling disappeared last upon heating, in the exact reverse order.
5. There was no microstructure memory effect in Ti-Ni shape memory alloys under the experimental conditions.
6. 3HPVCs are also a derivative of 2HPVCs; an additional HPV is nucleated at the tip of a 2HPVC and grows inward.
7. 2HPVC and 6HPVC are the most favorable morphologies for nucleation and growth, respectively, as explained by the analysis of the KC at junction planes.

8. Our results demonstrate that FE-SEM with the annular BSE detectors and EBSD is a promising tool for dynamic visualization of thermoelastic martensitic transformation with *in situ* stages.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (A: No. 26249090, B: No. 15H04143) from the Japanese Society for the Promotion of Science and a Grant-in-Aid for Scientific Research on Innovative Areas, “Bulk Nanostructured Metals”, No. 25102707, from MEXT, Japan. This work was also partially supported by the Advanced Low Carbon Technology Research and Development Program (JY220218) from the Japan Science and Technology Agency.

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Figures Caption

Figure 1 Schematic illustrations of the self-accommodation morphologies of B19' martensite and characteristic interfaces between HPVs around the $[111]_{B2}$ trace [6-8].

Figure 2 Series of *in situ* SEM images of the quenched Ti-50.8 at.% Ni alloy after solution treatment at 1223 K at (a) 290, (b) 232, (c) 231, (d) 228, and (e) 222 K upon cooling, and (f) 265, (g) 267, and (h) 290 K upon heating.

Figure 3 Enlarged view of the area indicated by the triple headed arrow in Fig. 2d captured at 226 K, showing the stress-induced R-phase.

Figure 4 Enlarged micrographs of Figs. 2b and c, showing the nucleation of 2HPVC and 6HPVC in the grain interior. The 2HPVC indicated by single arrow in (a) transforms into a 6HPVC in (b). (c) Scheme of the nucleation of 2HPVC and its transformation to 6HPVC.

Figure 5 Series of enlarged views of the formation of 2HPVC and 3HPVC at (a) 230, (b) 228, (c) 227, (d) 226, (e) 225, and (f) 224 K upon cooling.

Figure 6 Series of *in situ* SEM images showing the effect of thermal cycle on self-accommodation morphologies in specimens after the (a), (b) first, (c), (d) third,

and (e), (f) fifth cycles.

Figure 7 Number of 2HPVCs, 3HPVCs, and 6 HPVCs in grain B in Fig. 1 upon cooling.

Supplementary Movie M1: Movies of *in situ* SEM observations of the quenched Ti-50.8 at.% Ni alloy after solution treatment at 1223 K upon (a) cooling and (b) subsequent heating.

Supplementary Movie M2: Movies of *in situ* SEM observation of the quenched Ti-50.8 at.% Ni alloy, showing nucleation of 2HPVC and its growth to 6HPVC.

Supplementary Movie M3: Another example of 2HPVC nucleation and its growth to 6HPVC.

Figure 1

Characteristic interfaces of CVs and HPVs

.....	$\langle 011 \rangle_{B19}$, type-II twin
————	I $\{ \bar{1}\bar{1}\bar{1} \}_{B19}$, type-I twin
-----	II
- - - - -	III
- . - . -	IV

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7