Reverse Transformation in Fe–Ni Bicrystals

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The effect of grain boundary character on the reverse phase transformation was investigated using Fe–Ni bicrystals containing a 90° (211) symmetric tilt or a 90° (211) twist boundary, focusing on the transformation temperature during heating, the morphology of reversed austenite and the variant selection. Martensitic transformation behaviour in bicrystals depends strongly on the type of grain boundary. The tilt bicrystals showed a characteristic self-accommodation of martensites across the boundary called cooperative nucleation (C–N) and higher martensite-start temperature (Ms). On the other hand, the reverse transformation-start temperature (Ar) of bicrystals with the tilt boundary was higher than that of single crystals or bicrystals with the twist boundary. By in-situ observation, a retardation of reverse transformation of cooperatively nucleated martensites was confirmed in the vicinity of the tilt boundary on heating. The C–N reduces a local stress field around martensites which helps the reverse transformation. Therefore, the bicrystals with the tilt boundary containing the C–N show higher Ms than the others. Many martensites near the tilt and the twist grain boundary returned to the austenite phase inheriting the initial orientation. However, numerous sub-boundaries were retained near the tilt boundary. The C–N seems responsible for the lack of information about initial orientation of austenite. Thus, the reverse transformation behaviour in bicrystals was also found to depend strongly on the grain boundary character.

KEY WORDS: grain boundary character; martensitic transformation; martensite; reverse transformation; Fe–Ni alloys.

1. Introduction

Martensitic transformation has an important role in mechanical or functional properties such as the shape memory effect, the pseudoelasticity effect and the transformation induced plasticity (TRIP) phenomenon. A nucleation of martensite is known to occur heterogeneously depending on lattice defects such as dislocations and grain boundaries. Many researchers have investigated the effect of grain boundary on martensitic transformation behaviour,1–3) and much useful information has been reported. In previous papers, the exact effects of grain boundary character on martensitic transformation were examined using several Fe–Ni bicrystals containing a grain boundary with controlled character.4–6) Limited grain boundaries with a specific character could activate martensitic transformation effectively; symmetric tilt boundary acted as a favourable nucleation site for martensites, while twist boundary did not. In the vicinity of grain boundary, a limited set of variants with the habit plane almost parallel to the boundary was preferentially selected among 24 habit plane variants in Fe–Ni bicrystals. Furthermore, the equivalent variants in the neighbouring grains were symmetrically adjoined at the tilt boundary to maintain the compatibility of the transformation strains across the boundary, resulting in an increase in the martensite-start temperature (Ms). Thus, grain boundary and its character strongly influence the martensitic transformation behaviour; controlling factors for a favourable nucleation of martensites at the grain boundary were determined by bicrystal study.

From a practical viewpoint, however, reverse transformation of martensite is no less important than the forward transformation in several properties such as shape memory effect or pseudoelasticity effect. Up to now, reverse transformation behaviour has been studied in several materials from the viewpoint of the crystallography, the kinetics and so on.7–14) The refinement of grains in ferrous alloys is accomplished by martensitic transformation and its reverse as an example. In particular, the variant selection at favourable nucleation sites during a series of phase transformations is responsible for obtaining ultra fine-grain materials.15) Since martensitic transformation is strongly affected by grain boundary, its reverse transformation is naturally expected to have a grain boundary character dependence of several behaviours: transformation temperature, variant selection, and so on. Therefore, exact knowledge of the effect of grain boundary character on forward and reverse transformation near the boundary must contribute to the development of more favourable thermo-mechanical processing such as ausforming or to improvement of the shape memory effect in polycrystalline materials.

The purpose of this work was to investigate the effect of grain boundary character on the reverse transformation behaviour using Fe–Ni bicrystals containing a 90° (211) tilt or a 90° (211) twist boundary focusing on the transformation temperatures, the morphology of reversed γ phase and the
variant selection.

2. Experimental Procedure

A master ingot of Fe–32at%Ni alloy was prepared by melting high-purity Fe and Ni in a plasma arc furnace. Single crystal was grown from the ingot by the floating zone method at a rate of 5 mm h⁻¹ under high purity Ar gas flow. The crystal was homogenised at 1473 K for 48 h. Two plates with controlled crystal orientations were cut from the crystal by spark machining. After mechanical and electrolytic polishing, these plates were diffusion bonded at 1273 K for 100 h. Two-type bicrystals containing a 90° (211) tilt or a 90° {211} twist boundary were obtained as shown in Figs. 1(a) and 1(b), respectively. It is also noticed that the bicrystal system (x, y, z) is set up, where y is perpendicular to the grain boundary. The specimens for electrical resistivity measurement were cut from the bicrystals by spark machining, homogenised at 1273 K for 1 h and subsequently quenched in ice water. After martensitic transformation induced by cooling, the specimens were heated at a constant rate of 2 K min⁻¹. Electrical resistivity measurement to determine the reverse transformation start ($A_r$) and finish ($A_f$) temperature was carried out by a four points method using a constant current of 100 mA. After the surface relief due to the martensitic transformation had been removed by mechanical and electrolytic polishing, an in situ observation of the reverse transformation during heating was performed using an optical microscope equipped with a hot stage. The specimens for crystallographic analysis were again polished to remove the surface relief of reversed γ phase. Crystallography of the reversed austenite was analysed by the scanning electron microscope-electron back scatter diffraction pattern (SEM-EBSP) method in 5 μm steps.

3. Martensitic Transformation Behaviour in Fe–Ni Bicrystals

Before discussion of the reverse transformation behaviour in Fe–Ni bicrystals, significant results of martensitic transformation behaviour near grain boundaries are briefly summarised. In order to investigate the dependence of grain boundary character on martensitic transformation behaviour, two types of Fe–Ni bicrystals containing the 90° (211) tilt or the 90° {211} twist boundary and single crystals were prepared. The specimens were slowly cooled at a constant rate of 1 K min⁻¹ to induce martensitic transformation. In the process, the electrical resistivity gradually decreased and then suddenly dropped at each martensite start temperature ($M_s$) due to the burst transformation to martensite. The $M_s$ for bicrystals with the tilt boundary, bicrystals with the twist boundary and single crystals were 210, 169 and 142 K, respectively. There was no big difference in the between single crystals and bicrystals with the twist boundary. In contrast, bicrystals with the tilt boundary showed significantly higher $M_s$ than single crystals by more than 60 K.

Optical micrographs of thermally transformed martensites just below the $M_s$ are shown in Fig. 2. Although the lenticular martensites are observed in all tested specimens, the size and distribution depend on the type of crystal. In single crystal and bicrystal with the twist boundary, tiny martensites are homogeneously formed and a small quantity of γ phase is retained, as shown in Figs. 2(a) and 2(c). In contrast, coarse lenticular martensites are symmetrically formed in neighbouring grains as shown in Fig. 2(b). Moreover, there exists a great deal of retained γ phase apart from the boundary. This result suggests that the tilt boundary acts as a favourable nucleation site of martensites although the twist boundary does not. Furthermore, the crystallographic analysis of martensites was carried out using the SEM-EBSP method. All observed martensites with bcc structure satisfied the Nishiyama–Wassermann (N–W) relationships with the γ parent phase with fcc structure: $\{111\}/(110)_M$ and $\{112\}/(110)_M$. There exist 24 habit plane variants, all N–W variants are randomly nucleated in single crystals. On the other hand, some variants with the habit plane almost parallel to the boundary are preferentially selected among the 24 habit plane variants in the vicinity of the grain boundary. Moreover, equivalent variants are symmetrically adjoined at the tilt boundary. This characteristic arrangement of variants can be regarded as a self-accommodation across the boundary; we call this type of nucleation “cooperative nucleation” (C–N). The C–N must enhance the heterogeneous nucleation in the vicinity of the grain boundary, resulting in an increase in the $M_s$ of bicrystals with the tilt boundary. Thus, grain boundary and its character play an important role in the martensitic transformation behaviour.
4. Results

4.1. Reverse Transformation Temperatures in Fe–Ni Bicrystals

The reverse transformation start \((A_s)\) and finish \((A_f)\) temperature were determined by the change in electrical resistivity on heating with the Fe–Ni single crystals and bicrystals containing martensites which were thermally induced just below each \(M_s\). Figure 3 shows the changes in the electrical resistivity of such bicrystals and single crystals as a function of temperature. In all crystals, the electrical resistivity increases with increasing temperature and the resistivity curve has two inflections corresponding to the onset and the completion of the reverse transformation of martensite to austenite, respectively. The \(A_s\) and \(A_f\) are determined by a tangent method from the resistivity curves. Figure 4 shows the transformation temperatures in Fe–Ni single crystal and bicrystals. The \(A_s\) increases in this order: single crystal, bicrystal with the twist boundary and bicrystal with the tilt boundary. This sequence is equivalent to that of the \(M_s\). The \(A_f\) is not as sensitive to the type of crystals, however, though the \(A_f\) of bicrystals seems to be slightly higher than that of single crystal.

The bicrystal with the tilt boundary shows not only much higher \(M_s\) than single crystals but also the heterogeneous nucleation of martensites at the boundary, as mentioned above. If this bicrystal with the tilt boundary is cooled below the martensite finish temperature \((M_f)\), martensites are formed inside the grains in addition to the cooperatively nucleated martensites at the boundary. The resistivity was measured for such fully transformed bicrystals with the tilt boundary, and an interesting resistivity curve was obtained as shown in Fig. 5. The curve has three inflection points. The inflection of C shows the completion of reverse transformation, and two of those indicated by A and B seem to correspond to the onset of reverse transformation of martensite in grains and at the grain boundary, respectively.
4.2. Morphology and Variant Selection of Reversed Austenite in Fe–Ni Bicrystals

The reverse transformation is known to occur martensitically in Fe–Ni alloys.\textsuperscript{18,19} If the surface relief due to martensitic transformation is removed, the reverse transformation of martensites can be detected by surface relief on heating. By this topographic analysis, the formation process of reversed austenite was observed in bicrystal with the tilt boundary, which was cooled below the $M_f$ and fully transformed to martensites. \textbf{Figure 6} shows a sequence of morphology changes in the same area near the tilt boundary on heating at a constant rate of 1 K min$^{-1}$. Formation of the reversed austenite can be recognised as a change in the contrast due to surface relief. No remarkable changes in the surface are seen below 513 K as shown in Figs. 6(a)–6(c). At 533 K, fine martensite plates nucleated randomly inside grains transform to austenite (Fig. 6(d)). This tendency can be recognised clearly at 553 K (Fig. 6(e)). However, cooperatively nucleated martensites at the boundary or coarse martensites within grain remained stable even at 573 K, as shown in Fig. 6(f). Thus the reverse transformation occurs heterogeneously depending on the self-accommodation or the size of martensite.

Crystallography of reversed austenite was analysed using the SEM-EBSP method. Since highly dense dislocations are introduced in the reversed austenite,\textsuperscript{19,20} the specimens were annealed at 873 K for 3 h to obtain clear Kikuchi patterns in EBSP analysis. \textbf{Figures 7(a)} and \textbf{7(b)} show the orientation image of reversed austenite in bicrystal containing the tilt and the twist boundary, respectively. In this study many martensites near the tilt and the twist boundary return to austenite with the initial orientation. However, many low angle boundaries are observed in the vicinity of the tilt boundary, while there are none near the twist boundary. The sub-boundary seems to inherit the interface of martensite plates. Thus, the morphology and the variant selection of reversed austenite are strongly influenced by the type of grain boundary.

5. Discussion

5.1. Variation in the Transformation Temperature Depending on the Type of Crystal

As reported previously,\textsuperscript{4–6} the martensitic transformation behaviour in Fe–Ni bicrystals depends strongly on the grain boundary character. The reverse transformation behaviour also turned out to be also influenced by the grain boundary: The $A_s$ of bicrystals with the tilt boundary was higher than that of single crystals and bicrystals with the twist boundary. Furthermore, the retardation of the reverse transformation of coarse or self-accommodated martensites was recognised compared with the fine ones randomly nucleated inside grains, as shown in Fig. 6. The characteristic resistivity curve in the tilt bicrystal (Fig. 5) and the \textit{in-situ} observation must be closely related, and the $A_s$ seems to depend strongly on the initial morphology of martensites.

Generally, the reverse transformation occurs when the driving force reaches a required energy by heating or external factors as shown in \textbf{Fig. 8}. In martensitic transformation, the influence of external factors on the heating or external factors as shown in \textbf{Fig. 8}. In martensitic transformation, the influence of external factors on the $M_f$ has been explained using the equation of Clausius–Clapeyron, its

![Fig. 5](image-url)  
**Fig. 5.** Change in electrical resistivity of bicrystal with the 90° (211) tilt boundary as a function of temperature on heating. The specimens which were fully transformed to martensite by cooling below martensite-finish temperature were used.

![Fig. 6](image-url)  
**Fig. 6.** Change in surface due to the reverse transformation of martensites on heating in fully transformed Fe–Ni bicrystal with the 90° (211) tilt boundary; (a) R.T., (b) 493 K, (c) 513 K, (d) 533 K, (e) 553 K and (f) 573 K.
The formation of martensites induces a stress field around the martensite plates, and the local stress helps the reverse transformation of martensites during heating. The effect of the local stress is reflected in the term of \( W \) in Eq. (1), and the \( A_s \) term \( \Delta G^{ch}(T) \) is also determined by \( \Delta G^m \). Since the term \( \Delta G^{ch} \) is constant in Fe–32 at\%Ni alloys.

The cooperatively nucleated martensites are dominant in bicrystal with the tilt boundary though fine martensites are randomly distributed in single crystals. The C–N is one of self-accommodation across the boundary; it decreases the local stress around martensites. That is to say, such martensites give small \( W \) in Eq. (1). As a result, the delay of the reverse transformation in cooperatively nucleated martensites seems to be detected on heating, and bicrystal with the tilt boundary show higher \( A_s \) than single crystal.

When the bicrystal with the tilt boundary is cooled below the \( M_f \), it contains two types of martensites: the cooperatively nucleated ones at the boundary and randomly nucleated fine ones apart from the boundary. The fine martensites with large local stress first transform to austenite and then cooperatively nucleated martensites successively go on during heating. As a result, fully transformed bicrystals with the tilt boundary shows the characteristic resistivity curve as shown in Fig. 5. That is, the inflections indicated by A and B in the figure are corresponding to the reverse transformation of randomly nucleated martensites inside grains and cooperatively nucleated martensites at the boundary, respectively. Thus, the \( A_s \) changes depending on the initial morphology of martensites, which is attributable to the effect of the grain boundary character on the martensitic transformation.

5.2. Sub-boundary of Reversed Austenite in Bicrystals with the Tilt Boundary

The bicrystals with the tilt boundary show higher \( A_s \) than the others; this can be explained from the viewpoint of the self-accommodation at the boundary as mentioned above. Therefore, the C–N must play an important role in the formation of sub-boundaries near the tilt boundary.

Figure 9 shows the phase image (a) and (100) pole figure (b) for the reversed \( \gamma \) phase in components A and B of tilt bicrystal by the EBSP analysis. There are three (100) poles for each component crystal, two of which are deviated from the poles for the initial \( \gamma \) phase marked by open circles and rotated around a specific pole of \( P_1 \) or \( P_2 \) which exists almost on the grain boundary plane. The characteristic reorientation of austenite occurs near the tilt boundary during \( \gamma \rightarrow M \rightarrow \gamma \) transformation. The formation process of such reversed austenite is then expected to be as follows. At first, cubic axes \((\bar{v}_1, \bar{v}_2, \bar{v}_3)\) are set up in initial austenite as shown in Fig. 10(a), which correspond to \((100)\) of initial \( \gamma \) phase. The superscript denotes the component crystal of A or B. In the bicrystal with the tilt boundary, the axis of \( v_1 \) corresponds to the pole lying almost on the boundary plane indicated by \( P_1 \) or \( P_2 \) as shown in Fig. 9.

When the \( \gamma \) phase transforms to martensite, the axes \((\bar{v}_1, \bar{v}_2, \bar{v}_3)\) of initial austenite are distorted to the axes of \((\bar{v}_1, \bar{v}_2, \bar{v}_3)\) with the transformation strain along the axes as shown in Fig. 10(b). The compatibility of shape strains is always maintained by the C–N at the tilt boundary. In particular, the displacements of transformation strain along the axes of \( v_1 \) more strongly influence each other beyond the boundary than those along the other axes since the axes of \( v_1 \) lie on the boundary plane. In other words, the shared ratio of displacement along the axis of \( v_1 \) is the highest among \((100)\) axes.

As mentioned above, the reverse transformation of some
martensites proceeds with the help of the back stress around martensite plates. In addition, the back stress around martensites promotes the reverse transformation to austenite with initial orientation, just like a shape memory effect. However, characteristic self-accommodation called C–N reduces the back stress around the martensites, leading to a lack of information about the initial orientation of austenite. Such accommodated martensites must return to austenite under the relaxed back stress; therefore, martensites cannot necessarily return to \( \gamma \) phase with initial orientation. The axes of \( \bar{v}_1 \) in component crystals are adjoining and the equivalent back stresses symmetrically stay on the boundary. The overlap of back stress seems to facilitate the back motion of martensite to austenite. The reverse motion along the axis of \( \bar{v}_1 \) occurs accurately through the opposite path of the transformation whereas the back motion along the other two axes does not. As a result, the reversed austenite seems to rotate around a specific (100) pole of \( P_1 \) or \( P_2 \) which exists on the boundary, as shown in Fig. 10(c).

Furthermore, two types of rotation indicated by \( (A_1, A_2) \) and \( (B_1, B_2) \) are confirmed as shown in Fig. 9. This indicates that two kinds of C–N by different variants exist near the tilt boundary. Thus, the self accommodation reduces the back stress around martensites, resulting in induction of the rotation of \( \gamma \) phase and the formation of sub-boundaries in the reversed austenite.

6. Conclusions

The effect of grain boundary on the reverse transformation behaviour was examined using Fe–Ni bicrystals. The results were summarised and the following conclusions were reached.

(1) The reverse transformation temperature, the morphology and the orientation of reversed austenite in Fe–Ni single crystals and Fe–Ni bicrystals containing the tilt or the twist boundary depend strongly on the type of crystal.

(2) The \( A_s \) is strongly influenced by the morphology and the self-accommodation of martensites. The bicrystal with the tilt boundary shows higher \( A_s \) than the others, whereas the \( A_s \) is not sensitive to the type of crystals. The C–N is one of self-accommodation across the boundary, it reduces the local stress field around martensites. As a result, the retardation of the reverse transformation can be observed in the bicrystal with the tilt boundary on heating.

(3) Many martensites near the 90° (211) symmetric tilt and the 90° (211) twist boundary return to austenite inheriting the initial orientation. However, many sub-boundaries are observed in the vicinity of the tilt boundary, although they are not near the twist boundary. Since the self-accommodation leads to reduction of the back stress around the martensites, the cooperatively nucleated martensites can not necessarily return to austenite with the initial orientation.

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