EBSD characterization of crystallographic orientations and twin interfaces of modulated martensite in epitaxial NiMnGa thin film

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Abstract. The crystal structure and the global texture of 7M modulated martensite in epitaxial Ni50Mn30Ga20 thin films were investigated by X-ray diffraction (XRD), and the local crystallographic orientations correlated with microstructural features were revealed by electron backscatter diffraction (EBSD). The microstructure of 7M martensite can be classified into two distinct constituents. One refers to long straight strips with relatively homogeneous contrast, running parallel to one edge direction of the substrate. The other refers to shorter and bent plates with relatively high relative contrast, being oriented with the plate length direction roughly in 45° with respect to the substrate edges. Each 7M martensite plate is designated as a single orientation variant, and four orientation variants that are twin-related one another constitute one variant group. With the local crystallographic orientations of martensite plates and the orientations of inter-plate interface traces, the Type I, Type II and compound twin interfaces in the low and high relative contrast zones were determined.

1. Introduction

The discovery of ferromagnetic Ni-Mn based Heusler alloys has quickly promoted a breakthrough in the development of magnetically-controlled functional materials. To date, giant magnetic-field-induced strain up to 12% can be achieved in bulk Ni-Mn-Ga single crystals [1]. It is established that the type and the character of twin boundaries are dominant factors affecting the magnetic-field-induced strains in ferromagnetic Ni-Mn-Ga alloys, as the so-called Type II twin boundaries of modulated martensite possess higher mobility [2-4]. So far, for bulk materials, these factors have been well clarified through direct orientation determination on individual martensitic variants.

As for thin films, the multi-scale microstructures formed through epitaxial growth are quite
different from those in polycrystalline bulk alloys [5-10]. Efforts have been constantly made to reveal the microstructural features and crystallographic organizations of martensitic variants in epitaxial Ni-Mn-Ga films [11-15]. However, the character of ultrafine microstructural constituents brings a major challenge to conventional crystallographic characterization in terms of feasible experimental techniques and correct result interpretations. For instance, only the so-called $a7M$-$c7M$ twin interfaces could be deduced by examining X-ray pole figures and local surface morphologies [14, 16]. In this connection, the spatially-resolved electron backscatter diffraction (EBSD) technique may be exploited to obtain precise local crystallographic information of martensitic variants in epitaxial thin films having ultrafine microstructures.

In this work, the crystal structure and the global texture of 7M modulated martensite in epitaxial Ni-Mn-Ga thin films were investigated by X-ray diffraction (XRD), and the local crystallographic orientations correlated with microstructural features were revealed by EBSD. Based on the local crystallographic orientations of martensitic variants, the type and the character of twin boundaries were analyzed.

2. Experimental

The Ni-Mn-Ga thin films with nominal composition (at.%) of $\text{Ni}_{50}\text{Mn}_{30}\text{Ga}_{20}$ and nominal thickness of 1.5 $\mu$m were epitaxially grown on MgO monocrystalline substrate. Prior to the microstructural observations and orientation measurements, the thin film samples were subject to thickness-controlled electrolytic polishing with a solution of 20%HNO$_3$ in CH$_3$OH at 12 volts at room temperature. The microstructures and crystallographic orientations of the thin films were analyzed using a field emission gun scanning electron microscope (SEM, Jeol JSM 6500 F) equipped with an EBSD system. The EBSD patterns from martensitic variants were manually acquired using Channel 5 Flamenco’s interactive option.

3. Results and discussion

3.1 Orientations and twin relationships of martensitic variants

Fig. 1 presents the SEM secondary electron images of 7M martensite plates after electrolytic polishing. According to the direction and the brightness of martensite plates (Fig. 1a), the self-accommodated groups of 7M martensite can be classified into low relative contrast zones (Group 1) or high relative contrast zones (Group 2). The low relative contrast zones contain long straight plates parallel to one of the substrate edges, whereas the high relative contrast zones contain shorter and bent plates oriented at specific angles (roughly 45°) with respect to the substrate edges. Detailed inspections show that the traces of the inter-plate interfaces have one orientation in the low relative contrast zones (marked by the white dotted line in Fig. 1a), but two distinct orientations in the high relative contrast zones (indicated by the yellow and blue dotted lines in Fig. 1b).
**Fig. 1.** (a) SEM secondary electron image of 7M martensite in thin films. (b) The magnified view of Group 2. The white dotted line in (a) and the blue and yellow dotted lines in (b) outline inter-plate interface traces in Group 1 and Group 2, respectively.

**Fig. 2.** Kikuchi line patterns acquired from one martensite plate in (a) low and (c) high relative contrast zones and (b and d) the corresponding indexed results.
Fig. 2 presents the Kikuchi line patterns acquired from one martensite plate in the low and high relative contrast zones. The measured patterns can be well indexed with the monoclinic superstructure of the 7M martensite. As compared to the case of two overlapping Kikuchi patterns for the NM martensite [17], there is only a single pattern with some satellite diffractions (marked with arrows in Figs. 2a and 2c). Thus, each 7M martensite plate is specified by a single crystallographic orientation, being designated as one orientation variant.

Further characterization demonstrates that there are in total four different orientation variants distributed in one plate group (Group 1 or Group 2). Here, the four orientation variants - representing one plate group with low or high relative contrast - are denoted by the symbols V₁, V₂, V₃, V₄ (Fig. 1a) and Vₐ, Vₐ, Vₐ, Vₕ (Fig. 1b), respectively. To specify the four orientation variants, the individually measured orientations of the 7M martensite plates in Group 1 and Group 2 are presented in the form of \{2\ 0\ 2\ 0\}\textsubscript{mono}, \{2\ 0\ -2\ 0\}\textsubscript{mono} and \{0\ 4\ 0\}\textsubscript{mono} pole figures, as shown in Fig. 3. In the low relative contrast zone (Group 1), the four variants V₁, V₂, V₃, V₄ are all with their (2\ 0\ 2\ 0)\textsubscript{mono} plane nearly parallel to the substrate surface (Fig. 3, left). These variants correspond to the \textit{a-c} twins with their common \textit{b} axis perpendicular to the substrate surface, the so-called \textit{b}-variants in literature [12-14]. However, in the high relative contrast zone (Group 2), the variants Vₐ and Vₕ are with their (2\ 0\ -2\ 0)\textsubscript{mono} plane nearly parallel to the substrate surface (Fig. 3, middle), and the variants Vₐ and Vₐ with their (0\ 4\ 0)\textsubscript{mono} plane nearly parallel to the substrate surface (Fig. 3, right). Furthermore, the variants Vₐ and Vₐ and the variants Vₐ and Vₕ are of low brightness and high brightness, respectively. They correspond to the \textit{a-c} twins with their common \textit{b} axis parallel to the substrate surface, the so-called \textit{a}-variants for Vₐ and Vₕ and \textit{c}-variants for Vₐ and Vₐ [14].

![Fig. 3. Representation of individually measured orientations of 7M variants in Group 1 and Group 2 in the form of \{2\ 0\ 2\ 0\}\textsubscript{mono}, \{2\ 0\ -2\ 0\}\textsubscript{mono} and \{0\ 4\ 0\}\textsubscript{mono} pole figures.](image)

With the determined crystallographic orientations (represented with three Euler angles in Bunge’s
notation [18]) of the four 7M variants in each plate group, the orientation relationships between neighboring variants can be further evaluated. Detailed analysis has revealed that each pair of adjacent variants can be identified as either Type I or Type II or Compound twins. In the low relative contrast zone (Group 1), the variant pairs $V_1$ & $V_3$ and $V_2$ & $V_4$ belong to Type I twins, $V_1$ & $V_2$ and $V_3$ & $V_4$ to Type II twins, and $V_1$ & $V_4$ and $V_2$ & $V_3$ to Compound twins. The adjacent variants in the high relative contrast zone (Group 2) possess exactly the same twin relationships, where $V_A$ & $V_C$ and $V_B$ & $V_D$ belong to Type I twins, $V_A$ & $V_B$ and $V_C$ & $V_D$ to Type II twins, and $V_A$ & $V_D$ and $V_B$ & $V_C$ to Compound twins. The complete twinning elements - $K_1$, $K_2$, $\eta_1$, $\eta_2$, $P$ and $s$ - of the above three types of twins were derived using a general method [19, 20] and are shown in Table 1. The twinning modes are exactly the same as those in the bulk materials [6, 20].

### Table 1. Twinning elements of 7M variants represented in the monoclinic crystal coordinate frame.

| Twin elements | Type I twin | Type II twin | Compound twin |
|---------------|-------------|--------------|---------------|
|               | ($V_A$ & $V_C$; $V_B$ & $V_D$; $V_1$ & $V_2$; $V_3$ & $V_4$) | ($V_A$ & $V_B$; $V_C$ & $V_D$; $V_1$ & $V_2$; $V_3$ & $V_4$) | ($V_A$ & $V_D$; $V_B$ & $V_C$; $V_1$ & $V_2$; $V_3$ & $V_4$) |
| $K_1$         | (1 2 10)$_{\text{mono}}$ | (1.1240 2 8.7602)$_{\text{mono}}$ | (1 0 10)$_{\text{mono}}$ |
| $K_2$         | (1.1240 2 8.7602)$_{\text{mono}}$ | (1 2 10)$_{\text{mono}}$ | (1 0 10)$_{\text{mono}}$ |
| $\eta_1$      | [11.0973 10 0.8903]$_{\text{mono}}$ | [10 10 1]$_{\text{mono}}$ | [10 0 1]$_{\text{mono}}$ |
| $\eta_2$      | [10 10 1]$_{\text{mono}}$ | [11.0973 10 0.8903]$_{\text{mono}}$ | [10 0 1]$_{\text{mono}}$ |
| $P$           | (1 0.1161 11.1610)$_{\text{mono}}$ | (1 0.1161 11.1610)$_{\text{mono}}$ | (0 1 0)$_{\text{mono}}$ |
| $s$           | 0.2537 | 0.2537 | 0.0295 |

#### 3.2 Orientations of twin interfaces

Using the indirect two-trace method [21, 22], the planes of twin interfaces in the low and high relative contrast zones were further calculated with the measured crystallographic orientations of individual variants and the measured orientations of their interface traces on the film surface. Results show that the twin interface planes are coincident with the respective twinning planes, i.e. {1 -2 -10}$_{\text{mono}}$ for Type I twins, {1.1240 -2 -8.7602}$_{\text{mono}}$ for Type II twins, and {1 0 10}$_{\text{mono}}$ for Compound twins, as in the case for bulk materials. For easy visualization of the through-film-thickness orientations of twin interfaces in two relative contrast zones, the {1 -2 -10}$_{\text{mono}}$, {1.1240 -2 -8.7602}$_{\text{mono}}$ and {1 0 10}$_{\text{mono}}$ orientations are shown in Figure 1.
-8.7602} mono and \{1 0 10\} mono planes of the four 7M variants in Group 1 and Group 2 are represented in the form of stereographic projections, as displayed in Fig. 4a and Fig. 4b. In both figures, the interface trace directions on the film surface are indicated by the arrowed lines.

For the low relative contrast zone (Group 1), it is seen from the \{1 -2 -10\} mono pole figure (Fig. 4a, left) that two different Type I twin interfaces are oriented at +89.9° (V₁ and V₃) and -89.9° (V₂ and V₄) with respect to the substrate surface, although their interface traces on the film surface are both parallel to the [0 1 0] MgO direction. Similar cases can be found for the Type II twin interfaces. As shown in the \{1.1240 -2 -8.7602\} mono pole figure (Fig. 4a, middle), the two Type II twin interfaces that have parallel traces on the film surface intersect the substrate surface at +85° (V₃ and V₄) and -85° (V₁ and V₂), respectively. Apparently, the four Type I and Type II twin interfaces are oriented differently through the film thickness, but they have the same interface trace orientation on the film surface. As for the two compound twin interfaces, they are parallel to the film surface, as shown in the \{1 0 10\} mono pole figure (Fig. 4a, right). That is why no compound twin interfaces could be observed by examining solely the film surface microstructure in the present work. Such compound twin interfaces have been detected by the cross section observation using SEM [14].

![Fig. 4. Stereographic projections of \{1 -2 -10\} mono, \{1.1240 -2 -8.7602\} mono and \{1 0 10\} mono planes of 7M variants in (a) low relative contrast zone (Group 1) and (b) high relative contrast zone (Group 2). The macroscopic sample coordinate frame is set to the crystal basis of the MgO substrate. The arrowed lines represent the trace directions of twin interfaces.](image)
For the high relative contrast zone (Group 2), it is seen from the \{1 -2 -10\}_\text{mono} pole figure (Fig. 4b, left) that the Type I twin interface between variants \(V_A\) and \(V_C\) and that between variants \(V_B\) and \(V_D\) possess roughly the same orientation in the film. They incline at about 45° to the substrate surface and their traces on the film surface are along the [-1 1 0]_{MgO} direction. However, for the Type II twin interfaces shown in the \{1.1240 -2 -8.7602\}_\text{mono} pole figure (Fig. 4b, middle), although the twin interface between variants \(V_A\) and \(V_B\) and that between variants \(V_C\) and \(V_D\) incline at about 45° to the substrate surface, their interface traces on the film surface do not possess the same orientation. They are 37.3° (\(V_A\) and \(V_B\)) and 52.5° away from the [1 0 0]_{MgO} direction, respectively. The angle between the two differently oriented Type II twin interface traces on the film surface is about 15°, being in accordance with the results reported in the literature [23]. As for the compound twin interfaces, the twin interface between variants \(V_A\) and \(V_D\) and that between variants \(V_B\) and \(V_C\) possess roughly the same orientation (Fig. 4b, right). They are nearly perpendicular to the substrate surface and their traces on the film surface are nearly parallel to the [1 1 0]_{MgO} direction. It is found that the bending of martensite plates in the high relative contrast zones is associated with the orientation change from \(V_A\) to \(V_D\) or from \(V_B\) to \(V_C\), which results in the plate interface change from Type I twin interface to Type II twin interface or from Type II twin interface to Type I twin interface.

4. Summary

By means of the EBSD-based orientation characterization, a comprehensive analysis was made on the microstructural and crystallographic features of 7M modulated martensite in Ni\(_{50}\)Mn\(_{30}\)Ga\(_{20}\) thin films epitaxially grown on MgO(100) substrate. The plate-like microstructure of the 7M martensite is composed of two distinct kinds of plate groups. One refers to long straight strips with relatively homogeneous contrast in the SE images, running parallel to one edge direction of the substrate. The other refers to shorter and bent plates with relatively high relative contrast, being oriented with the plate length direction roughly in 45° against the substrate edges. Each 7M martensite plate contains one orientation variant. There are four orientation variants in one plate group. The inter-plate interfaces are either Type-I or Type-II twin interfaces.

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