Multiscale twin hierarchy in NiMnGa shape memory alloys with Fe and Cu

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Abstract—X-ray microdiffraction and scanning electron microscopy studies reveal 10 M martensitic structure with a highly correlated multiscale twin hierarchy organization in NiMnGaFeCu shape memory alloys. High compatibility is found at the twin interfaces resulting in a highly correlated twinned lattice orientation across several laminate levels. The lattice unit cell is described as monoclinic I-centered with $a = 4.28 \, \text{Å}$, $b = 4.27 \, \text{Å}$, $c = 5.40 \, \text{Å}$, $\gamma = 78.5^\circ$. The modulation is found parallel to the $b$ axis. Thin tapered needle-like lamellae and branching are observed near the twin boundaries.

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1. Introduction

Ferromagnetic off-stoichiometric Heusler-type NiMnGa-based (NMG) alloys recently attracted a lot of attention due to the unique combination of different properties, such as shape memory and magnetic memory, magnetoelastic effect, and large magnetoresistance [1–6]. These alloys have high potential for practical applications in actuators, sensors, and energy harvesters [5,7]. With a temperature decrease the NMG alloys undergo the 1st order displacive (martensitic) transformation from L21 structure to a tetragonal, orthorhombic or monoclinic martensitic phase [8–10].

In the first approximation, it was considered that martensite in NMGs can be described in tetragonal approximation [11,12]. However, soon it became clear that martensite in NMGs can be described in tetragonal approximation. In the first approximation, it was considered that martensite in NMGs requires a description beyond the tetragonal approximation [11,12]. Later several distinct martensite structures were observed in NMGs: seven (14 M) modulated martensite [3,13], five (10 M) modulated martensite [14–16], nonmodulated martensite [17]. It was suggested that the shape memory effect is largely determined by the arrangement, type and movement of the twin boundaries (TBs) in NMG alloys [18–22]. The minimal stress needed to move a TB determines the critical twinning stress. Two types of the TBs were reported in 10 M martensite: type I and type II TBs [15,23]. Type I TBs have a twinning stress $\sim 1 \, \text{MPa}$ at room temperatures, while type II TBs usually have a much smaller twinning stress $\sim 0.2 \, \text{MPa}$. The twinning stress for the type I TBs is strongly temperature dependent, while the type II TBs it is very weakly temperature dependent [23,24]. It was found that at least two levels of “lamination” are possible in the NMG crystals. There is still an open question “how such microstructures can be connected compatibly over a single interface?” [23].

Phase transition temperature in ferromagnetic NiMnGa-based alloys can be modified by the magnetic field, external strain field and alloy composition. It was noticed that off-stoichiometric alloys often demonstrate higher shape memory effect than stoichiometric Ni$_2$MnGa alloys [25–30].

Commensurate as well as incommensurate types of modulated martensite structures were derived from experimental data [31–33]. It was noted, that there is a controversy between the conclusions of [31] and the results of [33]. Specifically [31] emphasized that “The change of the composition from stoichiometry (Ni$_2$MnGa) could imply a different behavior of the modulation amplitudes of atomic sites differently occupied by chemical species.” These authors argue that: “The historical classification of martensitic modulated structures based on the number of observed satellites must be reconsidered”. For many applications the shape memory materials should be able to operate at elevated temperatures above 130 °C [34]. The operating temperatures of shape memory alloys are determined by their Curie and
structural phase transition temperatures. In the same time for different magnetocaloric applications the operating temperatures should be close to ambient. It was noticed that additional elements may essentially modify the transition temperature and enhance both shape memory and calorific effects. In particular, additions of Fe [34–37] and Cu [38,39] appeared very effective to shift the transition temperature and modify shape memory and magnetocaloric effects [40]. While in stoichiometric and off-stoichiometric ternary NMGs the martensite structures were studied relatively well, the structure of NMGs additionally doped with Fe and Cu is still poorly understood. Therefore several alloys with different additions of Fe and Cu were prepared and compared to ternary NiMnGa alloys with different Ni:Mn:Ga ratio [40]. The alloy with the highest martensitic transition temperature was chosen for this study.

In this letter we report the multiscale TB hierarchy in the martensite structure of the NMG alloy with additions of Fe and Cu with microdiffraction and scanning electron microscopy to explore the micromechanism of twinning effects.

2. Materials and experimental procedures

The polycrystalline Ni–Mn–Ga–Fe–Cu alloy composition corresponds to the following stoichiometry: 2.3/0.7/0.96/0.03/0.03. The martensite transition temperature of the alloy is 619 K. The ingot rod with 12.7 mm diameter and 19.0 mm length was prepared by arc melting in argon atmosphere. It was re-melted four times, annealed at 1100 K in evacuated quartz ampoules in high purity helium environment for 72 h. The sample is similar to the “sample #3” described by [41].

The martensite structure was studied by X-ray microdiffraction and Scanning Electron Microscopy (SEM). SEM measurements were performed using a Philips XL30 field-emission scanning electron microscope equipped with a DigiView camera. For SEM measurements the ingot was cut perpendicular to the growth direction of the rod. Sample surface was initially ground with 2400 grit SiC paper, and then vibrationally polished with a slurry of SiO2 

X-ray Laue micro diffraction was performed in transmission geometry in order to distinguish crystalline twin domains with a better angular resolution. White beam within the 5–70 keV energy range was focused down to ~10 × 10 μm2 using KB-mirrors. Diffraction patterns were recorded using MARCCD area detector with 16 bit read-out and 80 × 80 μm2 pixel size positioned at around 170 mm from the sample. Sample positioning was done with two horizontal and one vertical translational stage moving in directions perpendicular to each other. The horizontal stages were mounted on top of a rotational stage which made possible measurements at different angular positions. Precision of the sample positioning and eccentricity of the rotation stage were about 1 μm. An in-line Si 111 channel cut monochromator was used to provide a monochromatic beam of 0.3065 Å wavelength, which is readily exchangeable with the white beam setup. The monochromatic beam was exploited for calibration of sample to detector distance and detector tilt with CeO2 powder standard using Fit2d software [43]. Indices of Laue reflections were found from orientation matrix previously determined with this monochromatic beam. Finally orientation matrices of studied crystals have been found more precisely based on known indices and positions of white beam reflections using specifically developed software routines. Fit2d peak search feature was used to find centers of diffraction spots. Based on positions and indices of two strong reflections from each individual crystal its orientation matrix has been calculated [44,45], therefore coordinates of other reflections from the same grain were predicted in order to compare them with the experimentally determined ones which in turn allowed to recognize twin domains.

3. Results and discussion

Hierarchical twin microstructure in the Ni–Mn–Ga–Fe–Cu alloy is clearly demonstrated by SEM (Figs. 1 and 2). At the mesoscale, the twin structure consists of alternating, so-called, “compound” twins with an average thickness of ~10 μm (Fig. 1a). Higher magnification reveals the next structural level of twins within these compound twins – so called “laminate” (Fig. 1b). At the grain boundaries between two different laminates a lot of branching is observed with the formation of thin tapering needles (Fig. 1c and d). These structural peculiarities confirm the microstructural model for macro-twin interfaces that was recently suggested by [23]. Within the framework of their model, the “minor variant in each laminate forms thin, tapering needles ending at the interface”, which exactly corresponds to the features observed in Fig. 1c and d. The thin tapering needles are formed at the TB due to their higher energy for nucleation at the front of the moving TB, than at the side of the TB. According to [46] this “is leading to the long and narrow shape of lamellae. At the atomistic scale, the needle shape is formed by steps on the twin wall”. Fig. 2a and b show a compatible micro-twin boundary with continuity at the twin interface. Further increase of magnification reveals the next finer level of the twin colonies with the size of the twin lamellae below 100 nm (Fig. 2c and d). While [11,23] observed two levels of twin laminate at the scale higher than 10 μm, the next 4 higher levels of laminate reaching from 10 μm to 100 nm are found. This agrees with the comment by [23] that “the presence of fine laminates (possibly higher orders) close to the interface does not
contradict their concept”. The characteristic length scale of the laminate, starting from 10 μm and reaching up to 100 nm confirms the suggestion of the [46] that there may be some internal length scale of the energy landscape in the shape memory material which influences the motion of the TB.

Unit cell parameters were determined by X-ray diffraction. Using the monochromatic beam diffraction, about 100 reflections collected from a single grain yielded orthorhombic unit cell with the following parameters: $a = 4.276(5)$ Å, $b = 20.93(2)$ Å, $c = 5.397(7)$ Å. As the first approximation, the $b$-axis dimension indicates the formation of the 5 modulated martensite (M10) in the Ni–Mn–Ga–Fe–Cu alloy. Examination of the same grain of the sample with the white beam provided much better angular resolution of inter crystalline orientation and indicated that the beam was probing a twinned laminate consisting of colonies with two twin unit cell orientations and related to each other by a mirror plane (Fig. 3 left). The lattice is modulated along the $b$ axis of the above orthorhombic unit

![Fig. 1. SEM images demonstrate the multiscale character of the twinned structure of the NiMnGaFeCu alloy.](image1)

![Fig. 2. Compatible TB (a) and an enlarged region of the boundary (b) show continuity at the TB at the nanoscale. Twin colonies at different magnification show that the average thickness of the twin lamellae within the colony is below 100 nm (c, d).](image2)
cell (Fig. 3 right). If the crystal lattice of one colony is reflected by this plane, then the resulting lattice will deviate from the second colony lattice only by $\sim 0.3^\circ$ (calculated from the orientation matrices of the colonies). Angular step used for the diffraction measurements with the monochromatic beam was much larger than this deviation overlap of the reciprocal lattices, therefore the twinned colonies were always observed within mutual pseudo orthorhombic reciprocal space lattice. Unit cell parameters of the twinned lamellae have been calculated based on the pseudo orthorhombic cell. They turned out to be I-centered monoclinic lattice: $a = 4.28 \, \text{Å}$, $b = 4.27 \, \text{Å}$, $c = 5.40 \, \text{Å}$, $\gamma = 78.5^\circ$.

In Fig. 4, two indexed Laue diffraction patterns are shown. Average deviation between the predicted and observed positions of reflections is within 3 pixels limit. Only a few reflections exhibit such deviation up to 7 pixels which can be explained by the following reasons. First of all, unit cell of each separate colony in the pseudo orthorhombic setting may not have a precise orthorhombic matrix as it was assumed for the calculations of the reflection positions. Another possible reason is that the diffraction spots exhibit some broadening and diffuse tails which introduced some uncertainty to the determination of their positions. Some reflections were oversaturated, so their

![Fig. 3](image-url)

**Fig. 3.** Left: Observed reciprocal space projected onto (001) plane of the twin orientations. Circles denote reciprocal vectors, and numbers denote $l$ indices of observed reflections from orientation 1 (green), 2 (magenta) and overlapping reflections from both lattice orientations (black). $a^*$ and $b^*$ are basic vectors of the reciprocal lattices of orientation 1 (green), 2 (magenta) and both lattices in the pseudo orthorhombic setting (black). Basic vectors in the pseudo orthorhombic setting are shown the same for both lattices because angular shift between the orientations in this setting is very small: $\sim 0.3^\circ$. Right: Relations of basic vectors of the orientations 1 (green) and 2 (magenta) with their basic vectors in the pseudo-orthorhombic setting (black) and basic vectors of L2$_1$-like lattice (brown). $a^*$ vectors of both lattices coincide with their $-a$ in the pseudo-orthorhombic setting. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

![Fig. 4](image-url)

**Fig. 4.** Typical Laue patterns from a single crystal of NiMnGaFeCu collected at two angular positions of the sample shifted from one another by $9^\circ$. Reflections of twined orientation 1 are marked by green and those of the orientation 2 are marked by magenta. Precise predicted positions of selected reflections are shown on incertions. Predicted positions of reflections (732), (412) from orientation 1 and (732), (201) from orientation 2 are shown together with their predicted positions from the opposite orientation reflected in the plane of twinning (denoted by the corresponding color). Splitted reflections are denoted by white rectangles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
precise positions were not available. On the other hand, the predicted positions of reflections from the opposite twin orientation reflected in the plane of twinning exhibit much higher deviation from the observed positions; 7–9 pixels in average and up to 15 pixels. Four such predicted positions are exemplary shown in Fig. 4 in comparison with the predicted positions of the domains themselves. Reflections with \( h = 5 \) exhibit splitting because each of the twin orientations has such a reflection, which clearly indicates that all these reflections cannot be indexed assuming only one lattice orientation.

The observations from Laue microdiffraction are supported by the above SEM results, which show that the martensite structure consists of multiscale hierarchy of twin colonies (laminates). With the beam size of \( \sim 10 \) \( \mu \)m for Laue microdiffraction, being much higher than the thickness of the individual lamellae within the twinned lattices, the beam is always probing the multiscale twinned laminate within one grain (Figs. 1b and 2a and b). Therefore reflections from both twinned lattice orientations are always simultaneously present at the Laue pattern. In Laue diffraction, the position of the Laue spot at the pattern is determined by the lattice plane orientation. The fact that the whole colony of lamellae diffract almost in the same direction of reciprocal space demonstrates highly coherent orientation between lamellae within the twinned colonies laminate (as seen at the Fig. 2b). Results support the model of hierarchically twinned martensite, described by Mullner and collaborators [19–21] at the microscopic and mesoscopic scales.

4. Conclusions

X-ray microdiffraction and SEM study support the model of several levels of twin laminate within individual grain of the polycrystalline sample – “twins within twins”. Combination of X-ray microdiffraction and SEM shows that the nanolaminate structure is extended to much smaller length scales, than was previously assumed. Ref. [24] suggested that the laminate structure had a length scale up to 25 \( \mu \)m, and noted that a smaller probe size is needed to identify the features below this length scale. Our observations identify at least 4 levels of twinned laminates reaching from 10 \( \mu \)m to 100 nm. High compatibility is found at the twin interfaces resulting in a highly correlated twinned lattices orientation across several laminate levels, which addresses the problem raised by [23] on “how such microstructures can be connected compatibly over a single interface”. X-ray microdiffraction study confirmed the twin laminate structure: two twin orientations have been recognized with an I-centered monoclinic lattice: \( a = 4.28 \) \( \AA \), \( b = 4.27 \) \( \AA \), \( c = 5.40 \) \( \AA \), \( \gamma = 78.5^\circ \) corresponding to the 10 \( \bar{M} \) martensite with modulation direction along the \( b \) direction of the unit cell.

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