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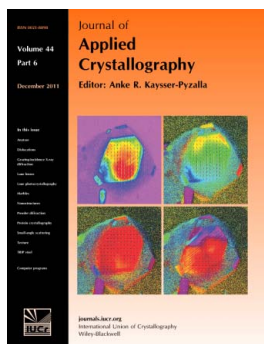
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Determination of the orientation relationship between austenite and 5M modulated martensite in Ni–Mn–Ga alloys

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The microstructural and crystallographic characteristics of 5M martensite in an Ni₅₀Mn₂₈Ga₂₂ alloy were investigated by electron backscatter diffraction (EBSD) analysis. The microstructure of 5M martensite observed at room temperature can be characterized by broad plates with alternately distributed fine lamellae (variants). With the accurate EBSD orientation measurements and by application of monoclinic superstructure information, four twin-related variants in one broad plate were identified. On the basis of the correct orientation data of martensite variants acquired from the EBSD measurements, the more favourable orientation relationship between austenite and 5M martensite was revealed to be the Pitsch relation with $(101)_A // (1\bar{2}5)_{5M}$ and $[10\bar{1}]_A // [\bar{5}51]_{5M}$ by detailed crystallographic calculation without residual austenite.

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1. Introduction

Ferromagnetic shape memory alloys have attracted much attention as a new type of smart material, ever since magnetic field-induced strain (MFIS) was discovered in the Ni₂MnGa alloy (Ullakko *et al.*, 1996). This effect, also termed a magnetic shape memory effect, originates from the magnetically induced variant reorientation through twin-boundary motion (O'Handley, 1998), which takes place solely in the martensite state and is closely related to the high magnetocrystalline anisotropy of the martensite. By this actuation mechanism, Ni–Mn–Ga alloys exhibit both a large output strain and a quick response during field-actuating events. To date, ~6 and ~10% large field-induced strains have been realized in off-stoichiometric Ni–Mn–Ga alloys with five-layered modulated (5M) and seven-layered modulated (7M) martensites (Murray *et al.*, 2000; Sozinov, Likhachev *et al.*, 2002), respectively. Thus, these types of materials have been viewed as attractive candidates for more efficient actuators and sensors.

The prerequisite for the realization of MFIS through variant reorientation is that the alloys must have the ferromagnetic twinned martensitic microstructure in the working temperature range. In Ni–Mn–Ga alloys, the high-temperature cubic phase has an $L2_1$ ordered structure (Brown *et al.*, 2002), also known as the Heusler structure. These alloys have a relatively high Curie temperature of around 376 K (Webster *et al.*, 1984), and the martensitic transformation temperatures are highly dependent on the chemical composition. Thus, they can be controlled by changing the chemical composition of the alloy (Chernenko, 1999; Jin *et al.*, 2002; Tillier *et al.*, 2011), which results in the formation of different types of martensite,

i.e. non-modulated (NM), 5M and 7M martensite. In general, martensitic transformation is a structural phase transformation of the diffusionless and cooperative type, and the formation of the martensite follows specific orientation relationships (ORs) between the lattices of the parent and product phases. The resulting transformation strain is accommodated by the formation of twinned variants. The redistribution of these variants through twin-boundary motion leads to macroscopic deformation.

Since large MFISs in Ni–Mn–Ga alloys arise mainly from the contribution of modulated structures (Sozinov, Likhachev & Ullakko, 2002), insight into the microstructural and phase transformation features of the modulated martensites is of fundamental significance for a deep understanding of the variant reorientation mechanism and further property improvement. This has motivated us to perform detailed microstructural characterization of the modulated martensites, *i.e.* 7M and 5M, with the application of electron backscatter diffraction (EBSD) measurements in previous investigations (Li *et al.*, 2010, 2011a), as the EBSD technique applied in a scanning electron microscope allows direct spatial correlation between the crystallographic orientation and the microstructure in a bulk sample. Using superstructure information for measurements, the precise crystallographic orientation of the martensite variants was obtained through automated acquisition and indexing of the EBSD patterns, which enables the twin relationships and twin interfaces between neighbouring variants to be fully determined. Furthermore, the most favourable phase transformation OR between austenite and 7M martensite was unambiguously

determined by EBSD measurements and crystallographic calculations (Li *et al.*, 2011b). Against this background, the transformation OR between austenite and 5M martensite was investigated in the present work. Without residual austenite, the most favourable phase transformation OR was fully determined.

2. Experimental

The off-stoichiometric Ni–Mn–Ga polycrystalline alloy, with nominal composition $\text{Ni}_{50}\text{Mn}_{28}\text{Ga}_{22}$ (at.%), was prepared by arc melting the pure elements. The alloy was homogenized at 1173 K for 24 h in a sealed vacuum quartz tube and then water quenched. The actual composition of the alloy was verified to be $\text{Ni}_{50.1}\text{Mn}_{28.3}\text{Ga}_{21.6}$ (at.%) by means of energy-dispersive X-ray analysis. As measured by differential scanning calorimetry, the martensitic transformation temperatures of the present alloy were above room temperature ($M_s = 316.8$ K; $M_f = 303.0$ K; $A_s = 314.1$ K; $A_f = 324.3$ K). The martensite at room temperature has a monoclinic crystal structure with 5M-type modulation, according to X-ray diffraction measurements (Li *et al.*, 2011b). The rectangular parallelepiped samples for microstructural observations and EBSD orientation measurements were cut out of the homogenized alloy. They were first mechanically polished, and then electrolytically polished with a solution of 20% nitric acid in methanol at room temperature. The microstructural examination and orientation measurements were performed in a field-emission gun scanning electron microscope (JEOL JSM 6500F) with an EBSD acquisition camera and *HKL CHANNEL5* software (Oxford Diffraction, Abingdon, UK). The beam-control mode was applied for automatic orientation mapping.

3. Results and discussion

Figs. 1(a) and 1(b) illustrate the lattice correspondence between austenite and 5M martensite. The high-temperature austenite possesses a cubic $L2_1$ Heusler structure ($Fm\bar{3}m$, No. 225) with the lattice parameter $a_A = 5.84$ Å (Brown *et al.*, 2002; Cong *et al.*, 2005). 5M martensite has a monoclinic super-

structure ($P2_1/m$, No. 10) (Glavatsky *et al.*, 2008) composed of five consecutive subcells along the c axis (denoted C_1 – C_5 in Fig. 1b). The monoclinic crystallographic axes of 5M martensite align along the $[\bar{1}10]_A$ (a axis), $[001]_A$ (b axis) and $[110]_A$ (c axis) directions of cubic austenite. According to the X-ray diffraction measurements, the lattice parameters of 5M martensite were determined to be $a_{5M} = 4.226$ Å, $b_{5M} = 5.581$ Å, $c_{5M} = 21.052$ Å and $\beta = 90.3^\circ$ (Li *et al.*, 2011b). This superstructure information for 5M martensite was used for subsequent EBSD measurements. If we ignored lattice modulation, the supercell could be further reduced into one subcell with mean lattice constants $a_{1M} = a_{5M} = 4.226$ Å, $b_{1M} = b_{5M} = 5.581$ Å, $c_{1M} = c_{5M}/5 = 4.2104$ Å, and $\beta = 90.3^\circ$, as shown in Fig. 1(c). Hereinafter, we will refer to this averaged subcell of the 5M martensite as the unit cell of a so-called 1M martensite, and denote the austenite, 1M martensite and 5M martensite by the subscripts A, 1M and 5M, respectively.

Fig. 2(a) shows a typical backscattered electron (BSE) image of the $\text{Ni}_{50}\text{Mn}_{28}\text{Ga}_{22}$ polycrystalline alloy taken at room temperature. It can be seen that the martensite is composed of

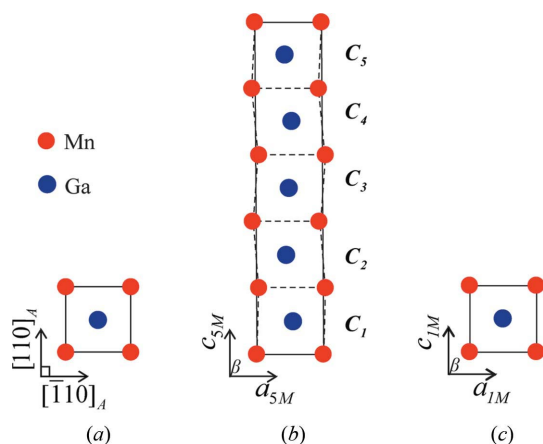
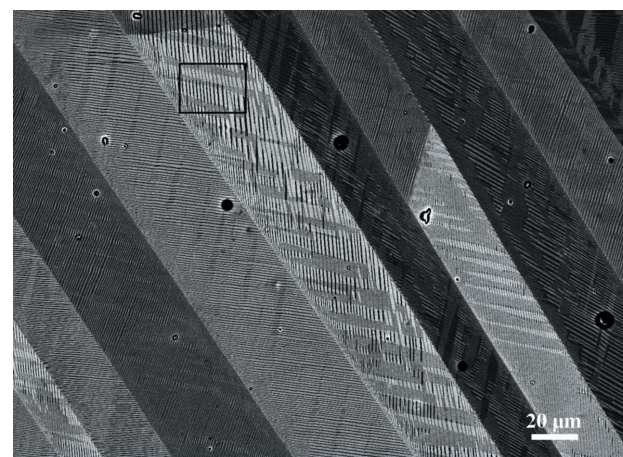
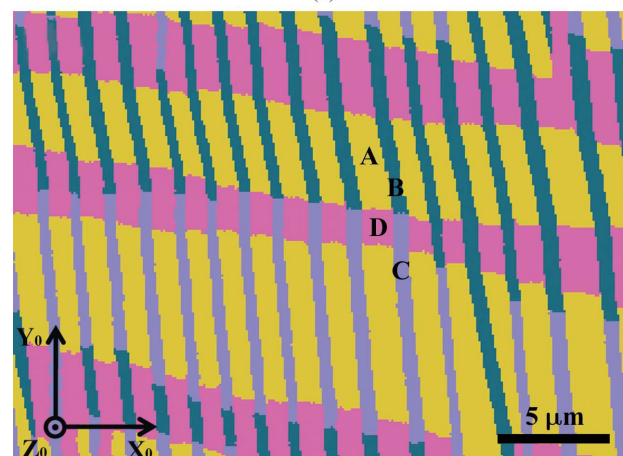


Figure 1

Schematic illustrations of (a) the unit cell of cubic austenite, (b) the supercell of monoclinic 5M martensite consisting of five subcells (outlined by dashed lines) and (c) the reduced average unit cell of 5M martensite (ignoring lattice modulation).



(a)



(b)

Figure 2

(a) A typical BSE image of the polycrystalline $\text{Ni}_{50}\text{Mn}_{28}\text{Ga}_{22}$ alloy. (b) Orientation micrograph of the framed region in (a). Four variants are denoted A, B, C and D. The coordinate frame ($X_0Y_0Z_0$) refers to the macroscopic sample coordinate system.

Table 1

A selection of possible ORs between austenite and martensite.

The Miller indices of the planes and in-plane directions for the product martensite with a monoclinic structure are referred to the average unit cell of 1M martensite illustrated in Fig. 1(c).

Transformation OR	Plane and in-plane direction parallelism
Bain relation	$(001)_A // (010)_{1M}$ and $[010]_A // [101]_{1M}$
K-S relation	$(111)_A // (011)_{1M}$ and $[101]_A // [\bar{1}11]_{1M}$
N-W relation	$(111)_A // (011)_{1M}$ and $[112]_A // [0\bar{1}1]_{1M}$
Pitsch relation	$(101)_A // (1\bar{2}1)_{1M}$ and $[101]_A // [\bar{1}11]_{1M}$

alternately distributed broad plates several micrometres wide. The plates are well self-accommodated and separated by interplate boundaries. Further observations at higher magnification show that the broad plates are composed of fine lamellae with thicknesses in the nanometre range (Li *et al.*, 2011b). Fig. 2(b) displays the orientation map covering the rectangular region marked in Fig. 2(a). The orientation map was reconstructed according to the structural model sketched in Fig. 1(b). In the map, the fine lamellae are coloured according to their orientation. Notably, there are four types of orientation variants distributed alternately in one broad plate and they are designated *A*, *B*, *C* and *D*, as shown in Fig. 2(b). Our previous study revealed that these neighbouring variants are twin-related to each other, and the twin relationships can be classified into three categories, *i.e.* a type I twin for *A* and *C* (or *B* and *D*), a type II twin for *A* and *B* (or *C* and *D*), and a compound twin for *A* and *D* (or *B* and *C*) (Li *et al.*, 2011b). The twin interfaces were also found to be coincident with the respective twinning planes (K_1 plane) according to indirect two-trace analyses (Li *et al.*, 2011b; Zhang, Esling, Zhao & Zuo, 2007; Zhang, Esling, Calcagnotto *et al.*, 2007).

Since the martensitic transformation is a diffusionless structural transformation realized by a coordinated displacement of the atoms, some specific ORs between the parent and product phases are required to minimize the lattice discontinuity across the phase boundary. In most cases, the determination of these ORs is rendered to find plane and in-plane direction parallelisms by making use of the coexistence of the retained parent austenite and the product martensite. However, for the present $\text{Ni}_{50}\text{Mn}_{28}\text{Ga}_{22}$ alloy, as the martensitic transformation is complete at room temperature, *i.e.* there is no retained austenite, it is not possible to make a direct determination of the OR between austenite and martensite. Therefore, verifying the austenite orientations that are calculated from the orientations of the martensite variants induced from the same initial austenite under an assumed OR could be an alternative solution to deduce the transformation OR (Humbert *et al.*, 1995). If the different sets of austenite orientations calculated from all individual martensite variants inherited from the same austenite grain share a common orientation, the assumed OR could be that which governs the martensitic transformation, and the resultant common orientation is the orientation of the initial austenite grain.

The austenite orientations (G_A^l) with respect to the orthonormal sample coordinate system can be calculated by the

following equation expressed in matrix notation (Li *et al.*, 2011a):

$$G_A^l = G_{5M}^k \cdot S_M^i \cdot T \cdot (S_A^j)^{-1}, \quad (1)$$

where G_{5M}^k represents the measured orientation of the k th martensite variant with respect to the orthonormal sample coordinate system; S_M^i ($i = 1, 2$) and S_A^j ($j = 1, 2, \dots, 24$) are the respective monoclinic and cubic symmetry elements; and T is the rotation matrix transforming the orthonormal crystal coordinate system fixed to the monoclinic martensite lattice to the austenite lattice basis under the given OR. From a survey of the literature, the widely addressed Bain (1924), K-S (Kurdjumov & Sachs, 1930), N-W (Nishiyama, 1934; Wassermann, 1935) and Pitsch (1962) ORs are presumed to be possible ORs between the parent austenite and the product martensite in the present work, as listed in Table 1. Moreover, the assumed plane and in-plane direction parallelisms are first used to specify the ORs between austenite and 1M martensite.

On the basis of the above considerations, we calculated the orientations of the parent austenite from the measured orientations of four local adjacent twin-related martensite variants, using the possible ORs listed in Table 1. Here, four twin-related variants in one broad plate that originate from the same austenite grain were treated as a variant group. To achieve statistical significance, the variant orientation data, expressed in Euler angles in Bunge's notation (Bunge *et al.*, 1980), measured from six different variant groups (denoted g1–g6) from different initial austenite grains were used as the initial input data. For easy visualization, the calculated austenite orientations under a given OR were plotted in the

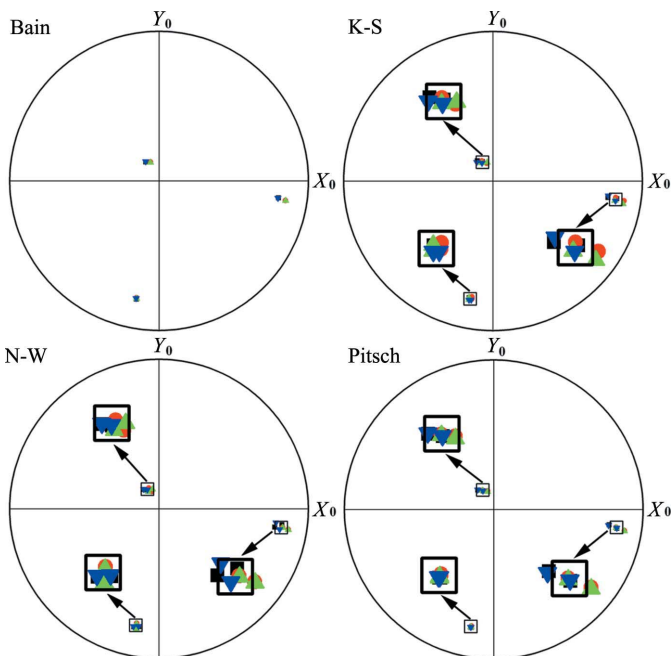


Figure 3 {001} standard stereographic projections of austenite orientations calculated from the martensite variants *A* (squares), *B* (circles), *C* (upward triangles) and *D* (downward triangles) in variant group g1 under the Bain, K-S, N-W and Pitsch relations, respectively. The common austenite orientations are enclosed in open squares.

Table 2

Minimum misorientation angles ($^{\circ}$) between the austenite orientations calculated from variant *A* and from the other three variants in the six variant groups under the Bain, K-S, N-W and Pitsch ORs.

Group No.	Variant pair	Bain	K-S	N-W	Pitsch
g1	A:B	3.45	0.75	2.09	0.75
	A:C	3.52	1.61	1.74	0.50
	A:D	0.44	1.58	2.44	0.25
g2	A:B	3.81	0.34	2.34	0.33
	A:C	3.30	1.89	1.86	0.66
	A:D	1.07	1.81	2.86	0.81
g3	A:B	3.33	0.66	1.80	0.66
	A:C	3.22	1.72	1.62	0.81
	A:D	0.41	1.90	2.66	0.20
g4	A:B	3.53	0.48	1.83	0.48
	A:C	3.42	1.44	1.50	0.70
	A:D	0.49	1.52	2.46	0.26
g5	A:B	3.20	0.79	1.81	0.79
	A:C	3.22	1.56	1.44	0.86
	A:D	0.84	1.38	2.38	0.40
g6	A:B	3.70	0.43	4.17	0.43
	A:C	3.66	1.90	3.94	0.36
	A:D	0.40	1.98	2.86	0.28

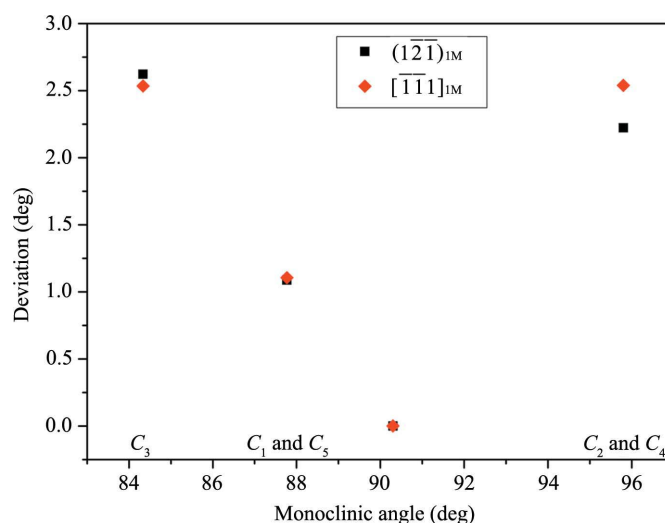
{001} standard stereographic projection in the macroscopic sample coordinate frame.

As an example, Fig. 3 displays the calculation results from variant group g1. In the figure, one austenite orientation is represented by three {001} poles. As there are 24 symmetry elements in the cubic and two in the monoclinic system, 48 austenite orientations from each martensite variant can be expected, of which several are distinct and the others are equivalent to the distinct ones depending on the OR selected. As displayed in Fig. 3, there is one distinct austenite orientation calculated from one martensite variant under the Bain relation, and two under the K-S, N-W and Pitsch relations. If the assumed OR is true for the transformation, all three {001} austenite poles from one martensite variant should correspond to those of the other three variants in the same variant group, *i.e.* the same named austenite poles from the four variants should overlap in the projection. It can be seen that the K-S and Pitsch ORs seem to give the smallest mismatch (dispersion) between the respective {001} poles for a common austenite orientation. To quantify the mismatch for an assumed OR, the minimum misorientation angles between two calculated austenite orientations were estimated, as shown in Table 2. Among all the selected variant groups, the Pitsch OR represents the smallest deviation angle. Further examination of the atomic correspondence between austenite and 1M martensite under the Pitsch OR indicates that Pitsch ORs may provide ideal lattice continuity if the crystal structure of the product martensite can be represented by the average unit cell. The respective planes, *i.e.* $(101)_A$ and $(1\bar{2}\bar{1})_{1M}$, have exactly the same atomic stacking sequences with very close interplanar spacing and consistent arrangements of the constituent atoms. Therefore, the Pitsch OR, *i.e.* $(101)_A // (1\bar{2}\bar{1})_{1M}$ and $[10\bar{1}]_A // [\bar{1}\bar{1}1]_{1M}$ between austenite and 1M martensite, or $(101)_A // (1\bar{2}\bar{5})_{5M}$ and $[10\bar{1}]_A // [\bar{5}\bar{5}1]_{5M}$ if referred to 5M martensite, should be considered as the more favourable transformation OR. Moreover, following the

Pitsch relation, the recalculated austenite orientations from different variant groups of four twin-related variants inherited from the same initial austenite grain also share a common austenite orientation.

As the resultant martensite of the present material possesses a modulated crystal structure, certain deviations of the subcells in the supercell with respect to the 'averaged unit cell' can be expected (Li *et al.*, 2011a). The structural modulation can be viewed as an atomic reshuffling in each subcell of the supercell with respect to the averaged unit cell. Clearly, this modulation results in certain angular deviations of the same indexed crystallographic planes and directions between each subcell and the average unit cell. The angular deviations corresponding to the Pitsch OR due to structural modulation are shown in Fig. 4. It is seen that the angular deviation for both the $(1\bar{2}\bar{1})_{1M}$ plane and the $[\bar{1}\bar{1}1]_{1M}$ direction increases with the difference in the monoclinic angle between the averaged unit cell and each subcell. The structural modulation generates angular deviations of ~ 1.0 – 2.6° for the corresponding plane and ~ 1.0 – 2.5° for the in-plane direction in each subcell.

On the basis of the determined Pitsch OR between the two phases, the theoretical number of martensite variants induced from the same austenite grain can be predicted. Because of the cubic symmetry of austenite and the monoclinic symmetry of martensite, there are at most 24 variants inherited from the same austenite grain under the Pitsch OR. As former EBSD analysis has revealed that only four variants appear in one variant group and they are twin-related to one another, these 24 variants can be divided into six groups. Thus, the formation of self-accommodated martensite in one initial austenite grain is realized firstly by a combination of four twin-related variants in a variant group and then by a combination of different groups over the entire grain. Such a configuration of the product microstructure should ensure a minimum lattice discontinuity between the parent austenite and the martensite.

**Figure 4**

Angular deviations of the $(1\bar{2}\bar{1})_{1M}$ plane and $[\bar{1}\bar{1}1]_{1M}$ direction (Pitsch OR) in each subcell from those of the average unit cell.

4. Conclusions

In summary, the microstructural and crystallographic characteristics of martensite variants in a polycrystalline $\text{Ni}_{50}\text{Mn}_{28}\text{Ga}_{22}$ alloy were investigated. The results show that 5M martensite is composed of alternately distributed broad plates. Each broad plate consists of four types of twin-related variants. On the basis of the local orientations of the individual martensite variants measured by EBSD, the orientations of the parent austenite were calculated using the assumed ORs between the cubic austenite and the monoclinic martensite. Considering the minimum misorientation angles between the calculated austenite orientations, the most favourable OR governing the transformation from austenite to 5 M martensite was revealed to be the Pitsch relation with $(101)_A // (\overline{1}2\overline{5})_{5M}$ and $[10\overline{1}]_A // [\overline{5}\overline{5}1]_{5M}$ without residual austenite. Under such an OR, at most 24 variants could be induced from the same austenite grain after martensitic transformation.

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