Publication 4

Ge Y., Jiang H., Sozinov A., Söderberg O., Lanska N, Keränen J., Kauppinen E. I., Lindroos V. K. Hannula S.-P. Crystal structure and macrotwin interface of five-layered martensite in Ni-Mn-Ga magnetic shape memory alloy. Materials Science & Engineering A, **438-440**, (2006), 961-964.

.

ELSEVIER

Materials Science and Engineering A 438–440 (2006) 961–964

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

Crystal structure and macrotwin interface of five-layered martensite in Ni–Mn–Ga magnetic shape memory alloy

Y. Ge [a,*], H. Jiang [b], A. Sozinov [a], O. Söderberg [a], N. Lanska [a], J. Keränen [c], E.I. Kauppinen [b,d], V.K. Lindroos [a], S.-P. Hannula [a]

[a] *Laboratory of Materials Science, Helsinki University of Technology, P.O. Box 6200, FI 02015, Finland*
[b] *VTT Processes, Aerosol Technology Group, P.O. Box 1602, 02044 VTT, Finland*
[c] *Centre for Electron Microscopy, Tampere University of Technology, P.O. Box 589, 33101 Tampere, Finland*
[d] *New Materials Center, Helsinki University of Technology, 02044 VTT, Finland*

Received 7 May 2005; received in revised form 21 October 2005; accepted 20 December 2005

Abstract

The crystal structure of the five-layered (5M) martensite and the martensite to martensite interface in the alloys $Ni_{48.9}Mn_{30.8}Ga_{20.3}$ and $Ni_{49.5}Mn_{28.6}Ga_{21.9}$ (numbers indicate at.%) were investigated by the X-ray diffraction as well as by the conventional and by the high resolution transmission electron microscopy (HRTEM). The martensite to martensite interface arises from meeting of growth fronts of two microtwin sequences with the twin planes (1 1 0) and (1 $\bar{1}$ 0), respectively. The interface was found to consist of two different configurations, the crossing and the step type. The HRTEM images reveal that the martensitic structure is not a perfect five-layered structure, but there are also other periodic structures (seven-layered and ten-layered), together with aperiodic structure and the irregular plane faults.

Keywords: Ni–Mn–Ga; Microtwin; HRTEM; X-ray diffraction

1. Introduction

The off-stoichiometric Ni–Mn–Ga alloys have drawn intensive attention due to the giant magnetic-field-induced-strain, so-called magnetic shape memory (MSM) effect [1,2]. This alloy system undergoes a ferromagnetic transition and an austenite-to-martensite transformation during cooling. The high-temperature austenitic phase is an $L2_1$ ordered cubic structure [3,4]. The low temperature martensitic phase can be a layered tetragonal structure with $c < a$, a layered orthorhombic structure or a non-layered tetragonal phase with $c > a$ (NM martensite) depending on the composition of the alloy [5].

The five-layered (5M) martensite has been demonstrated to produce a 6% magnetic-field-induced-strain [2]. The crystal structure of 5M martensite is a modulated tetragonal structure with the basal plane (1 1 0) periodically displaced along [1 $\bar{1}$ 0] direction [6]. When viewed at the atomic level, the modulated structure can be considered to be consisting of microtwins with their twin plane parallel to the basal plane (1 1 0). The microtwin sequence, which determines the modulation structure, and the interface between these microtwin sequences having the different twin planes are investigated in the present study in macroscale, mesoscale and nanoscale in 5M martensite.

2. Experimental

The 5M martensite is studied in two Ni–Mn–Ga alloys. The alloy $Ni_{48.9}Mn_{30.8}Ga_{20.3}$ was manufactured using a modified Bridgman method at Outokumpu Research Oy and the alloy $Ni_{49.5}Mn_{28.6}Ga_{21.9}$ was produced in AdaptaMat Ltd. The ingots were cut with spark cutting to samples that were annealed at 1273 K for 72 h, and at 1073 K for 48 h in vacuum quartz ampoules. The chemical compositions of the heat treated alloys were analyzed by the scanning electron microscope (SEM) LEO 1450 equipped with an INCA 300 energy dispersive spectroscope (EDS).

The single-variant state was created in the samples by compression along one of cubic axis, then this axis became [0 0 1] axis of martensite. A sample with edges approximately parallel to <1 0 0> direction of the cubic lattice axis was stud-

* Corresponding author. Tel.: +358 9 4512688; fax: +358 9 4512681.
E-mail address: Yanling.Ge@tkk.fi (Y. Ge).

0921-5093/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2005.12.057

ied by the X-ray diffraction using Philips X'pert diffractometer. For the TEM studies, the originally 2 mm thick plate samples which surface was normal to the [0 0 1] direction, were wet ground to the thickness of approximately 80 μm. From these films, the thin foil specimens were prepared with the window method applying the electropolishing with 25% HNO_3–ethanol electrolyte at 243 K. The conventional TEM observations were carried out by a JEOL 2010 and the HRTEM observation by a Philips CM-200FEG transmission electron microscope equipped with a Gatan 1 k × 1 k multi-scan CCD-camera.

3. Results and discussion

In order to observe the 5M structure, the surface normal to [0 0 1] direction was investigated with X-ray diffraction by scanning along both $[1\,1\,0]^*$ and $[1\,\bar{1}\,0]^*$ directions in reciprocal space. The typical X-ray scattering intensity distribution is shown in Fig. 1a obtained for $Ni_{48.9}Mn_{30.8}Ga_{20.3}$. The 5M structure is confirmed by the four extra spots, which equally divide the distance between the main spots into five parts. These extra spots appear along both $[1\,1\,0]^*$ and $[1\,\bar{1}\,0]^*$ directions. Based on the electron diffraction studies it has been reported that the 5M structure is formed by the shuffling of (1 1 0) plane in $[1\,\bar{1}\,0]$ direction [6]. Thus, it is reasonable to conclude that the two shuffling systems (1 1 0) $[1\,\bar{1}\,0]$ and (1 $\bar{1}$ 0) [1 1 0] leads to two kinds of domains and interface between them. These two shuffling systems are always present in X-ray measurements, but they have not been observed in the optical or SEM studies. Consequently, it is suggested that the domain structure appears at a very fine scale.

The domains suggested by the X-ray measurements were found in the low magnification TEM image. The two domains are shown in the bright field image of $Ni_{48.9}Mn_{30.8}Ga_{20.3}$ (in Fig. 1b, marked with A and B). The selected-area electron diffractions (SAED) taken from the A and B areas indicate that the crystal structure in both cases is the 5M martensite. However, the basal planes of these layered structures and the direction of modulation are orthogonal to each other, indicating that these two domains are derived from two shuffling system (1 1 0) $[1\,\bar{1}\,0]$ and (1 $\bar{1}$ 0) [1 1 0], respectively. The wavy interface between A and B domains is apparently not a planar boundary. The internal twins are visible as strips in the upper A domain and these strips cause corresponding steps in the interface. Anyhow, the interface between B domain and lower A domain is smoothly curved.

The nature of the interface is revealed in images at higher magnification. Fig. 2a shows the bright-field TEM image and the corresponding electron diffraction patterns, which are taken from $Ni_{49.5}Mn_{28.6}Ga_{21.9}$. It is shown in Fig. 2a that the studied domains consist of microtwins. The electron diffraction patterns from both side of interface reveal the crystal structure is that of the 5M martensite. The electron diffraction pattern of the interface area (top-right SAED pattern in Fig. 2a) is similar to the X-ray diffraction in Fig. 1a with extra spots from layered structure appearing both in $[1\,1\,0]^*$ and $[1\,\bar{1}\,0]^*$ directions. The main diffraction spots from the two domains fit to each other very well. If the two electron diffraction patterns from the upper and lower domains are added together, the resultant pattern is the same as the diffraction pattern taken at interface area. It indicates that the basic structure in both domains is identical. The interface between these two microtwin sequences can be called as a macrotwin boundary or a macrotwin, since the areas separated by the interface are also twin related. The SAED patterns clearly shows that the structure of two domains posses a mirror symmetry. Similar interface, macrotwin boundary, has been found for a NiAl alloy [7]. The macrotwin boundary consists of two constitutive elements, which are referred to as "crossing" type and "step" type elements. The *step* type element refers to the configuration, in which one set of microtwins ends at a

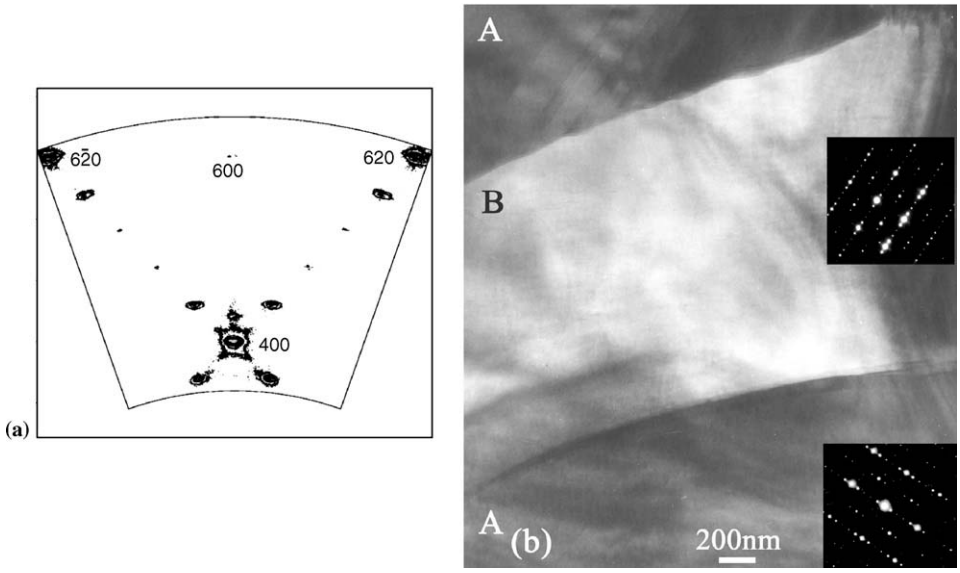

Fig. 1. (a) X-ray scattering intensity distribution with additional spots along the conjugate $[1\,1\,0]^*$ directions obtained by using two-dimensional scan and Epitaxy 3.0 software in $Ni_{48.9}Mn_{30.8}Ga_{20.3}$. The diffraction is indexed based on the tetragonal structure. (b) The bright-field image of $Ni_{48.9}Mn_{30.8}Ga_{20.3}$ and the inset is the selected-area electron diffraction (SAED) patterns from areas A and B, respectively.

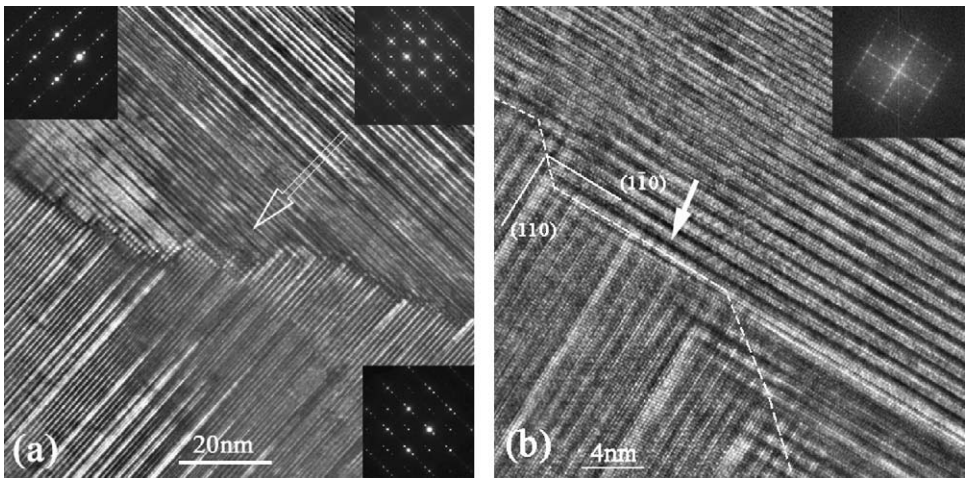

Fig. 2. (a) Bright-field image of the alloy $Ni_{49.5}Mn_{28.6}Ga_{21.9}$ and the insets are the SAED patterns from both side of interface and the interface area. (b) The atomic-scale image of macrotwin boundary in alloy $Ni_{49.5}Mn_{28.6}Ga_{21.9}$ and the inset is FFT of whole image.

twin plane of the other domain and this forms one step with several microtwins. In the *crossing* configuration two domains have similar microtwin widths and the deformations of one domain are seen to penetrate to some extent in the other domain.

In general, when the microtwin width changes in one domain the microtwin sequence of other domain will end at the twin plane of this microtwin. One such *step* is shown in Fig. 2b (indicated by an arrow). In this case the macrotwin plane is a coherent interface and parallel to the former (1 1 0) plane of cubic phase. The alternative twin plane of (1 1 0) and (1 $\bar{1}$ 0) will result in the average macrotwin boundary parallel to former (1 0 0) or (0 1 0) plane. Except one *step* in macrotwin boundary in Fig. 2b, the *crossing* type elements constituting the rest part of macrotwin boundary. The *crossing* type element seems to serve as a transition part between the *steps*. The macrotwin boundary with the *crossing* type is a 3–5 nanometer transition layer and approximately parallel to the former cubic (0 1 0) or (1 0 0) plane. Thus, the combination of two elements will explain the diversity of the macrotwin boundary, for example the curved interface in Fig. 1b. In both configurations, the step and the crossing part of macrotwin boundary, the two families of the microtwins smoothly intersect each other and no visible stress accommodation or lattice distortion is observed at the applied magnification. The fast Fourier transformation (FFT) of image Fig. 2b confirms the 5M martensite structure.

The microtwinned feature of the martensite is known for Ni–Mn–Ga alloys [8]. The width of microtwins changes with the periodicity of stacking sequences in the both studied alloys. Fig. 3 shows the existence of the variety of periodic stacking sequence which can be determined from its FFT. On the left side of interface the seven-layered structure (the top-left FFT) smoothly transits to the ten-layered one (the bottom-left FFT). The streaked spots in corresponding FFT indicate that neither the seven- nor the ten-layered structure is perfect: the high density plane faults are mixed in the both areas. On the right side of interface, the structure is five-layered structure including, also, a high density of irregular plane faults (the top-right FFT). The bottom-right FFT, made from whole image, shows that the main structure

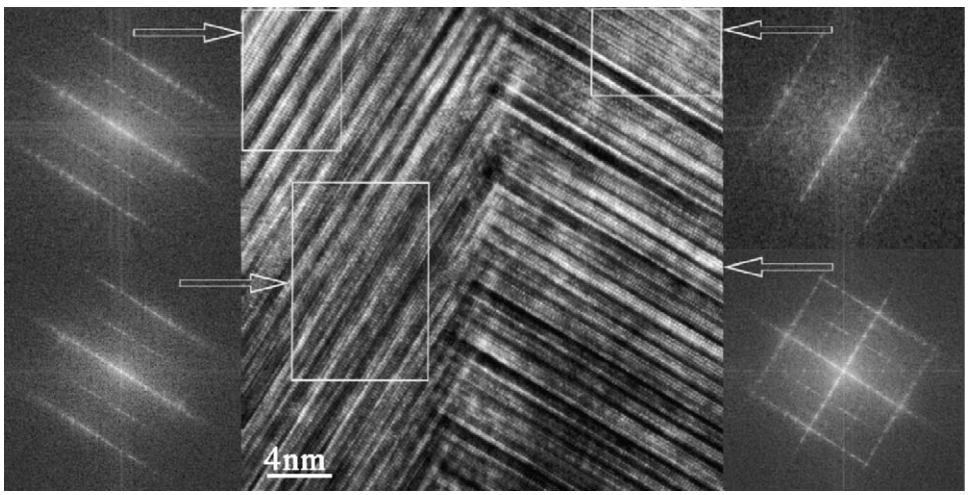

Fig. 3. The macrotwin boundary with irregular microtwin sequence. The microtwin sequence is determined from its FFT as seven-layered and ten-layered from top to bottom in on the left part of HRTEM image and five-layered in the top FFT in right of HRTEM image. The bottom FFT in right of HRTEM image is the FFT of whole HRTEM image. The arrows indicate the area where the FFT is made.

on the left side of interface is seven-layered and on the right side five-layered. The similar SAED pattern was also obtained in other zone. It should be noted that the basic structure of whole area is the same as the one with the perfect five-layered structure, i.e. the microscale seven-layered structure does not change the basic structure. As observed regularly with other Ni–Mn–Ga TEM studies for example in Ref. [8], the non-modulated areas were present also in the present sample. It is demonstrated in Ref. [9] that the periodicity of layered structure is stress dependent. The aperiodic and periodic layered structure is formed to accommodate the different stress situation during martensitic transformation or variant transition.

It is pointed out in Ref. [10] that the $\{1\,0\,0\}$ type interface does not appear in the overall energy minimizing configurations. However, Ball and Schryvers showed that such interface can exist when two domains with $(1\,1\,0)$ and $(1\,\bar{1}\,0)$ microtwin planes are forced to be compatible during the growth [11]. Thus the extra stress accommodation is needed near the $\{1\,0\,0\}$ macrotwin boundary, which causes the angle between microtwin plane – the former $\{1\,1\,0\}$ planes – to deviate from 90°. This angle is measured in all the SAED patterns and FFTs for two studied alloys. The deviation $(1\,1\,0)$ and $(1\,\bar{1}\,0)$ plane is less than 1°. The deviation applies at the macrotwin boundary as well as the area far away from the macrotwin boundary. It means the basic structure has orthorhombic distortion, i.e., *a* is slightly different from *b*. Furthermore, since there is no lattice distortion at the macrotwin boundary, it suggest that the macrotwin boundary may have high mobility.

4. Conclusions

The HRTEM and X-ray methods were applied in the study of the crystal structure and macrotwin interface of two Ni–Mn–Ga alloys. The majority structure in the studied alloys was of the five-layered martensite, while also the seven-layered, ten-layered and the aperiodic stacking faults coexisted. The studied 5M structure was confirmed to be orthorhombic with slightly different values of *a* and *b*. The HRTEM images reveal that the macrotwin interface is made of the *step* and *crossing* type constitutive elements. These two elements can form straight or wavy macrotwin interfaces.

Acknowledgements

The authors would like to acknowledge the funding support of the National Technology Agency of Finland (Tekes) as well as the industrial research partners (Metso Corporation Oyj, Nokia Research Center and AdaptaMat Ltd.). Y. Ge is grateful to the Helsinki University of Technology for the postgraduate scholarship. Furthermore, the assistance of Mrs. Pirjo Korpiala and Mrs. Marjatta Aav is acknowledged.

References

[1] K. Ullakko, J.K. Huang, C. Kantner, R.C. O'Handley, Appl. Phys. Lett. 69 (1996) 1966–1968.
[2] O. Heczko, A. Sozinov, K. Ullakko, IEEE Trans. Mag. 36 (2000) 3266.
[3] P.J. Webster, K.R. Ziebeck, S.L. Town, M.S. Peak, Phil. Mag. B49 (1984) 295–310.
[4] Y. Ge, O. Soderberg, N. Lanska, A. Sozinov, K. Ullakko, V.K. Lindroos, J. Phys. IV: Proc. 112 (2003) 921–924.
[5] N. Lanska, O. Söderberg, A. Sozinov, Y. Ge, K. Ullakko, V.K. Lindroos, J. Appl. Phys. 95 (2004) 8074–8078.
[6] V.V. Martynov, V.V. Kokorin, J. Phys. III 2 (1992) 739–749.
[7] D. Schrybers, Ph. Boullay, R. Kohn, J. Ball, J Phys. IV France 11 (2001) Pr8-23-30.
[8] J. Pons, R. Santamarta, V.A. Chernenko, E. Cesari, Mater. Chem. Phys. 81 (2003) 457–459.
[9] M. Chandrasekaran, J. Beyer, L. Delaey, Scripta Metal. Mater. 27 (1992) 1841–1846.
[10] K. Bhattacharya, Acta Metall. Mater. 39 (1991) 2431–2444.
[11] J.M. Ball, D. Schryvers, Solid Mech. Appl. 101 (2002) 27–36.