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Twin boundary nucleation and motion in Ni–Mn–Ga magnetic shape memory material with a low twinning stress

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The twin boundary motion in the Ni Mn Ga single crystal 10M martensite magnetic shape memory material was studied by mechanical twinning stress and magnetic measurements at ambient temperature. The compressive stress required to trigger the movement of the twin boundaries was higher in the sample with the single variant state than in that with the multivariant state. Magnetometer measurements confirmed that the energy needed to move the twin boundaries in a high quality single crystal 10M Ni Mn Ga is lower than that for the nucleation of a twin boundary.

Keywords: Twinning stress; Martensite; Ni Mn Ga; Ferromagnetic shape memory; Twinning

Magnetic shape memory (MSM) materials are readily applicable in magnetic-field-controlled actuators working in static to rapid (0.2 ms rise time) actuation in the temperature range up to about 333 K [1]. Characteristics of these materials is that they have highly mobile twin boundaries and high magnetocrystalline anisotropy energy, as in one of the most applicable MSM materials, Ni Mn Ga martensite single crystal with the 10M martensite structure [2 6]. The crystal structure of this material is generally referred to as five-layered martensite [7,8]. It has recently been analysed as being an orthorhombic structure, and can be considered an almost fivefold modulated structure [9]. The twin variant structure in these materials has been shown to be a multiscale structure, consisting of macroscopic twin variant boundaries and internal twin boundaries [10,11]; however, the actual structures of the different twin boundaries are still under discussion. The MSM effect has a basis in the motion of the martensitic twin boundaries of the magnetically aniosotropic twin structure [12], but, according to Ref. [13], no magnetic domain wall motion inside the structural twins is necessary for the twin boundary motion as the magnetic state alternates along a moving twin variant boundary. The strain has been associated with the motion of the macroscopic twin variant boundaries [5,21 23].

The macroscopic shape change of the 10M MSM materials, restricted by the crystal lattice parameters to about 6%, is allowed by reorientation of the twin variants. This MSM effect (MSME) takes place by motion of the variant boundaries induced by the applied stress or by a magnetic field, or their combination (see e.g. [1 6]). In order to trigger this magnetic-field-induced shape change, the field-induced stress must exceed the twinning stress, i.e. the stress threshold that must be exceeded to activate the movement of the twin boundaries. Therefore, it is possible to study the evolution of the twinning stress both by mechanical testing and from the behavior of the material in the magnetic field [14].

In Ref. [15] the threshold applied magnetic field needed to initiate the MSM effect in a Ni Mn Ga 10M material was larger in the first experiment (0.55 T) than in the subsequent measurements (0.3 T); the initial twinning stress was estimated to be 2.3 MPa, while that of the trained sample was 1.3 MPa. In Ref. [16], for the mechanical activation of high-purity Ni Mn Ga material, the initial stress maximum must exceed about 1.8 MPa for the twin boundaries to overcome an energy barrier. Meanwhile, the plateau connected to the twin boundary movement is 0.65 MPa [16]. When the material was trained thermomechanically, the initial stress maximum decreased but the plateau stress increased. In the present study, this effect is studied in further detail in order to reveal the possible general relationship between the stress ratio needed for the creation of the first secondary twin variant in the single variant structure and the movement of the twins in the two variant structure.

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The annealed single-crystal $Ni_{50.1}Mn_{27.7}Ga_{22.2}$ stick ($1 \times 2 \times 12$ mm^3) with the 10M modulated (e.g. five-layered) martensite structure was supplied by AdaptaMat Ltd., Finland. The surfaces of the stick were aligned essentially in the $[1\ 0\ 0]_p$ crystallographic direction (in the parent phase coordinates). The phase transformation (M_s, M_f, A_s, A_f) and the Curie temperatures (T_c) measured with low-field AC magnetic susceptibility were 306.8, 305.5, 310.6, 312.4, and 376.0 K, respectively. The single crystal structure, crystallographic orientation and microstructural phase of the sample material were confirmed by X-ray diffraction (X'Pert MRD, Co K_α radiation).

The mechanical compression tests were carried out uniaxially for a free-standing sample in a vertical tensile test machine (Lloyd 1000R) using the 20 N load cell and the internal displacement sensor. The compression tests were performed with displacement control, and were limited to a maximum load of 3 MPa. The systematic error of the equipment was established by measuring the strain of a high-stiffness reference sample (brass sample of 30 mm diameter) having a negligible strain at the force levels used. This error was subtracted from the measured values for the Ni Mn Ga sample. The single variant state, referring to the macroscopic variants for the compression experiment, was produced by a transverse applied field H_{appl} 1.0 T (after first compressing the sample longitudinally by 3 MPa), whereas the multivariant state was produced by H_{appl} 0.35 T. A laboratory-made vibrating sample magnetometer (VSM) was used for the magnetic measurements at 295 K. No external mechanical force was applied in the measurements. Before each VSM measurement, the twin structure of the sample was first oriented in a 1.2 T longitudinally applied field and then reoriented by a transverse magnetic field in a controllable electromagnet, holding the sample in a relatively loose ($1 \times 1 \times 0.5$ mm^3 slack) sample holder made of plastic and cardboard. The transverse magnetization was performed so that the field was first decreased to near zero, the sample was rotated 90° around its transversal axis and the field strength then increased to a defined value. The twin variant structure, and its amount of reorientation as a function of the applied magnetic field, i.e. the fractions of the different twin variants, were observed from the stick surfaces by a stereomicroscope (Euromex) with an oriented light source before the VSM measurements. The macroscopic twin variants and their fractions can be observed in situ by this technique [28]. The calibration value for magnetization in the VSM measurements was determined by measuring a pure-Ni reference sample similar in size to the test samples. The magnetization curves were corrected for demagnetization.

The results of the mechanical tests are collated to Figure 1. When the sample was in the single variant state, the onset stress needed to start the twin boundary motion is higher than the stress needed for the further reorientation of the rest of the twins (Fig. 1a). In the case of the two variant state (Fig. 1b), no such onset is present, implying that the pre-existence of the favorably oriented twin in the structure does not require any additional energy for formation of the new variant. After about 6% relative compression the twin variant structure is essentially reoriented. At this point, this mechanism does not allow

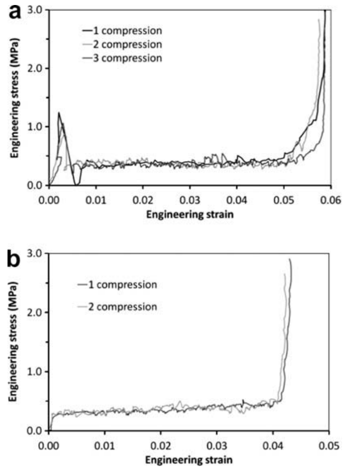

Figure 1. Compressive stress strain curves without an applied magnetic field for (a) three repeated compressions of the sample originally in the single variant state and (b) two repeated compressions of the sample originally in the two variant state.

for further deformation and the stress increases. The maximum strain of Figure 1a corresponds to that of the maximum lattice-dependent strain obtainable between two single variant states. The nearly horizontal plateau in Figure 1 suggests that only the existing boundaries are moving and there is no nucleation in this regime [17].

According to Figure 1b, the stress needed to initiate the reorientation of the twin structure in the two variant sample is 0.3 MPa. The fraction of the secondary (axially aligned c-axis) variant before the compression, calculated from the maximum strain, is f_2 0.28. It is worth noting that the applied stress must increase as reorientation proceeds, up to approximately 0.5 MPa. In the case of the single variant structure (Fig. 1a), the triggering stress for the formation of the first secondary twin variant is approximately 1.2 MPa. As this value is four times higher than the one connected to the two variant state, it is concluded that the formation of the new secondary twin variant requires more energy than growth of the existing secondary variant at the same temperature. In general, although not previously reported for Ni Mn Ga alloys, it is known that the nucleation of a deformation twin requires large local stress, but after overcoming this nucleation-related energy barrier, the twin growth occurs much more easily [18].

As the existing secondary twin variant has an influence on the start of the reorientation of the twin structure induced by mechanical stress, it is also interesting to determine the triggering magnetic field for the magnetic shape memory in a single and two variant states. In order to study this effect, different secondary variant amounts were created prior to the VSM measurement by applying a successively increased perpendicular reorienting magnetic-field H_{reo} after first orienting the sample in a 1.2 T longitudinal magnetic-field. The measured maximum magnetic field-induced strain, MFIS (between the transversally and longitudinally oriented single variant states) was 0.057, which corresponds to the reported values for the entirely reoriented macroscopic variant structure [28]. It agrees also within the accuracy of the measurement with the maximum strain 0.058 calculated based on the ratio of lattice parameters (*a*/*c*) determined by X-ray diffraction. The fraction *f* of macroscopic twin variants was determined based on the sum of the lengths of similar twin variants on the sample surface in relation to the length of the total sample. The twin structure consisted of two kinds of variants, i.e. $f_1 + f_2$ 1, such that the fraction of the secondary variant f_2 increased with the applied reorienting fields when H_{reo} was above 0.2 T. At H_{reo} 0.4 T, there were five macroscopic variant boundaries and f_2 was 0.17. At H_{reo} 0.5 T, approximately half of the variants were reoriented, resulting in many individual macroscopic variant areas and 37 variant boundaries observable on the specimen surface.

The magnetization curves for the sample are shown in Figure 2a. With f_2 0 at an applied H_{reo} 0.1 T, the magnetization curve is smooth and no clear anomaly due to the reorientation of the twin variant structure can be observed. When the reorienting field is H_{reo} 0.2 T (f_2 0.024), the magnetization curve shows a small alteration at H_{appl} 0.02 T. The same occurs at H_{reo} 0.3 T (f_2 0.05) and 0.35 0.4 T (f_2 0.085 0.17) at H_{appl} 0.03 and 0.02 T, respectively. The curve under a decreasing field (left) provides a reference for the fully reoriented twin structure, since the maximum applied field H_{appl} 1.2 T (f_2 1). In Figure 2b the switching field for triggering the MSM effect is shown as a steep step up in the magnetization curve for a single variant material, while for the multivariant sample it is smooth and gradual. This step-like behavior has been shown in a number of previous works [19 21], and the abrupt change in the single variant state has been correlated to the sudden reorientation of the large volume of twins. The smooth transition in the multivariant state has been also noted before [24].

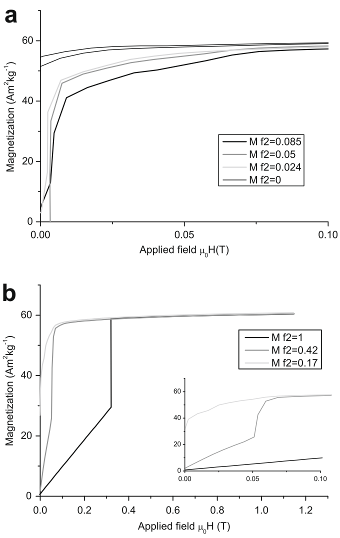

Figure 2. Magnetization curves measured by VSM at 295 K for (a) the sample with secondary variant fractions $f_2 < 0.1$, corresponding to H_{reo} (reorienting) below 0.4 T, and (b) the sample with secondary variant fractions $f_2 > 0.1$, or completely in a single variant state $f_2 = 1$, corresponding to $H_{reo} = 1$ T. The insert at the lower right shows the region 0 0.1 T in more detail.

Figure 2b shows that the applied magnetic switching field needed to move the twin boundaries was remarkably higher in the single variant state (f_2 1) than in the multivariant state (f_2 0.42). The single variant sample was magnetized in H_{reo} 1 T longitudinal applied magnetic field before the test, while the multivariant sample was pre-magnetized at H_{reo} 0.5 T (chosen according to the results in Fig. 2a). If the amount of the pre-reoriented twin variant f_2 is smaller, the change in the magnetization is more gradual, although the reorientation began at very low applied field. The magnetization of the single variant structure changed abruptly, which suggests that there was a period of accumulation and a sudden release of magnetization energy in the sample. The saturation of the studied MSM materials was at M_S 60.3 $Am^2\ kg^{\ 1}$. Thus, the magnetic anisotropy constant K_u for the studied sample was calculated to be 164 kJ $m^{\ 3}$, which corresponds to the values reported earlier for 10M martensite Ni Mn Ga [25].

It is obvious that the difference between the stress onset for the twin variant nucleation and that for the twin reorientation movement has hitherto been unnoticed because the less perfect crystals studied to date have exhibited considerably higher reorientation twinning stress levels, thus disguising the stress needed for twin nucleation.

Likhachev and Ullakko [26] have shown that the magnetic field-induced stress (σ_{mag}) induced by the magnetizations of the twin variants' per unit volume, $m_a(h)$ and $m_t(h)$, and the twinning transformation strain ε_0 can be obtained from:

$$\sigma_{mag} = \varepsilon_0^{-1} \int_0^h (m_a(h) - m_t(h))dh \qquad (1)$$

Eq. (1) was used to calculate σ_{mag} corresponding to the onset of the observed magnetic-field-induced twin reorientation. The switching field and the calculated magnetic-field-induced stress are shown in Figure 3 at various twin variant fractions, together with the measured onsets for mechanically induced twin variant nucleation or reorientation. It can be noted that the calculated σ_{mag} values for the single variant structure (f_2 1) are clearly higher than those for the multivariant structure ($f_2 < 1$) and are also about 40% above the mechanical onset stress values given in Figure 1. In the case of the two variant structure (f_2 0.42), the stress values derived from the mechanical and magnetic measurements are in good correspondence.

The high magnetic field onset for the twin boundary motion creates a high magnetic pressure on the domain walls, the Zeeman energy being equal to $-M_sH$ [27]. In this case, as can be seen in Figure 2b, the energy seems to accumulate in the material until it is released suddenly when it reaches a triggering level. When the previously calculated M_S is used, the Zeeman energy of the assumed single variant state is -18.7 J $kg^{\ 1}$, at the maximum switching field of Figure 2b. Using the model of Likhachev and Ullakko [28], it is also possible to calculate the magnetic driving force $f_{mag}(h)$ as the difference in the magnetization free energies in the axial ($g_a(h)$) and transverse ($g_t(h)$) directions, i.e.:

$$f_{mag}(h) = g_t(h) - g_a(h) \qquad (2)$$

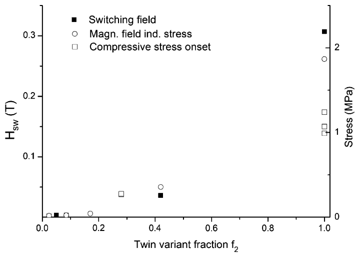

Figure 3. Change in the applied switching field (closed symbols) needed to start the twin reorientation with different secondary twin variant fractions (f_2). Calculated magnetic field induced stress values and the measured compressive stress values at the onset of the twin variant reorientation are shown by open symbols.

The magnetic driving force is obtained when the free energies calculated from the magnetization curves (Fig. 2a and b) are inserted in Eq. (2). Using the single variant measurement results of Figure 2 at the onset of twin boundary motion, f_{mag} 13.3 J kg ^{1} (or 108 kJ m ^{3} when expressed in terms of unit volume) is obtained. For the multivariant states, the f_{mag} at the onset of twin variant boundary motion drops to 20.7 kJ m ^{3} (f_2 0.42) and 1.2 kJ m ^{3} (f_2 0.05). Despite the possible inaccuracy in the measurements at low-field strengths, it is clear that the magnetic driving force needed for MSME is significantly higher for the single variant state than for the multivariant states. This is also in accordance with the mechanical compression results of Figure 1.

The varying internal stresses between the single and multivariant states suggests that the fatigue life and appearance of local stress-peak-induced microcracks or variant inhomogeneities may vary depending on the state of the crystal. For example, a large fatigue amplitude (i.e. strains likely to produce single variant states) has been found to reduce the fatigue life of MSM material [29], while a large number of cycles (over 2×10^6) has been reached with moderate amplitudes. Furthermore, in a constant rotating magnetic field at large amplitudes, the magnetic-field-induced strain MFIS decreases with cycling [30]. The observed high nucleation stress in the single variant structure should be taken into account for example in the actuator design or other applications, where the MSM material is used with the maximum straining.

It has been shown that in a low twinning stress 10M $Ni_{50.1}Mn_{27.7}Ga_{22.2}$ MSM material the stress onset needed to move the twin boundaries is clearly higher in the single variant state than in multivariant states of the same material. Also, the applied magnetic field onset and the calculated magnetic-field-induced stress for magnetic-field-induced twin boundary motion are higher for the single variant state than for multivariant states. The results suggest that the mechanism for a shape change of the MSM material may be different in different variant states. This can lead to corresponding differences in the performance of the crystals and must be taken into account, for example, in the actuator design.

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