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Temperature dependence and temperature limits of magnetic shape memory effect

Oleg Heczko and Ladislav Straka
Laboratory of Biomedical Engineering, Helsinki University of Technology, P.O. Box 2200, Espoo 02015 HUT, Finland

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We study the temperature dependence and low and high temperature limits of the magnetic shape memory effect (MSME) in five-layered tetragonal Ni–Mn–Ga martensite. Using a simple model we show that, additionally to the limits posed by transformation to austenite or an intermartensitic transformation, the temperature dependence of the magnetic anisotropy, tetragonality of the lattice, and twinning stress play important role when considering the temperature limits of the MSME. With decreasing temperature, the lattice distortion and magnetic anisotropy increase, but saturate in a low temperature region. The twinning stress does not saturate and its temperature dependence has exponential-like character that increases rapidly in the low temperature region. The model predicts that the low-temperature limit of the MSME is 165 K for Ni_{42.3}Mn_{28.9}Ga_{31.2} composition. This agrees very well with the value of 173 K determined from direct measurements. The high temperature limit is transformation to austenite at 315 K. The interval of the MSME existence is therefore 173–315 K. Quasistatic measurements of the MSME in the range 203–313 K up to the 1.15 T magnetic field show that the onset of the MSME shifts to a higher field and that a maximum field-induced strain increases with decreasing temperature. © 2003 American Institute of Physics.

I. INTRODUCTION

Some ferromagnetic off-stoichiometric Ni–Mn–Ga alloys exhibit giant magnetic-field-induced strain called magnetic shape memory effect (MSME) owing to a particular martensitic twinned structure. The effect is due to a reorientation of the crystal structure via magnetically induced twin boundary motion.\textsuperscript{1} The MSME was also found in Fe–Pd and Fe–Pt martensitic alloys.\textsuperscript{2,3}

The parental high temperature phase of Ni–Mn–Ga alloys close to the stoichiometry is L2\textsubscript{1} cubic and during cooling it transforms to a twinned martensitic structure. This twinned structure consists of domains with the same crystal structure but with different crystallographic orientation, called martensitic variants, separated by twin boundaries.

The martensitic structures so far observed in Ni–Mn–Ga alloys are five-layered modulated tetragonal with $c/a < 1$ (5M), seven-layered modulated orthorhombic with $c/a < 1$ (7M), and tetragonal with $c/a > 1$ (T).\textsuperscript{4,5} Magnetic-field-induced strain can reach up to about 6% in the 5M structure\textsuperscript{6,7} and up to about 10% in the 7M structure.\textsuperscript{8} The maximum macroscopic strain is determined by a lattice distortion. No MSME has been observed in the T structure.

Thus, the intermartensitic transformation to the T structure, which often occurs in Ni–Mn–Ga alloys,\textsuperscript{4,5,9} is an obvious limit for the MSME existence at low temperature. At higher temperature the limit is the transformation to the parental cubic phase in which no MSME exists.

According a simple model\textsuperscript{10,11} the MSME occurs at a given temperature $T$ when difference of magnetic energy $\Delta E$ of differently oriented martensitic variants exceeds the elastic energy needed to move twin boundaries between these variants

$$\Delta E > \epsilon_0(T) \cdot \sigma_{TW}(T, \epsilon),$$

where $\epsilon_0(T) = (a-c)/a$ is the tetragonal distortion of the lattice. Twinning stress, $\sigma_{TW}(T, \epsilon)$, is defined as an external stress necessary to reorientate structure or to move the twin boundaries to produce macroscopic strain $\epsilon < \epsilon_0$. This strain $\epsilon$ is defined as $\epsilon = (l - l_0)/l_0$ where $l$ is the length of the sample and $l_0$ is the initial length.

When a sample is magnetized to saturation perpendicularly to the easy magnetization axis of one variant and along the easy axis of the adjoining variant, the difference of the magnetic energy is equal to the difference of the magnetic anisotropy energy of these variants and we can rewrite the condition (1) as

$$\frac{K_1(T)}{\epsilon_0(T)} > \sigma_{TW}(T, \epsilon),$$

where $K_1(T)$ is magnetic anisotropy constant.

In Eq. (1) the temperature dependence of the MSME originates from an interplay between the magnetic energy and the energy necessary to move the martensitic twin boundaries. The saturation magnetization and magnetic anisotropy increase with decreasing temperature but saturate,\textsuperscript{13} whereas the twinning stress apparently does not.\textsuperscript{14} In general we may speculate that the monotonous increase of twinning stress with decreasing temperature will ultimately block the movement of the twin boundaries and the MSME ceases to exist. At high temperatures the sharp decrease of the magn...
netic anisotropy close to Curie temperature can have the same effect, i.e., the MSME may not occur close to Curie point.

Below magnetic saturation the difference of Zeeman energy, $\mathbf{M} \cdot \mathbf{H}$, between the variants is a considerable part of the difference of magnetic energy $\Delta E$. When the condition (1) is satisfied and the sample is not magnetically saturated the magnitude of the saturation magnetization is one of the parameters which determines at which field the MSME occurs. This field is called switching field, $H_{SW}$.

The evolution of the structural parameters of Ni$_2$MnGa in the range 10–290 K was studied by Ma et al., for the stoichiometric alloy and by Glavatska et al., for off-stoichiometric alloy showing MSME. The tetragonality of the martensitic lattice $c_0(T)$ increases with decreasing temperature but saturates at low temperature. This increases the magnetic energy needed for reorientation of the structure. Also the maximum MSME can be larger at low temperature.

Although there are many reports about the MSME in Ni–Mn–Ga alloys at one particular temperature, only some of them deal with temperature dependence. Glavatska et al. and Pasquale et al. measured the MSME in a quite narrow temperature range of about 20 K. Glavatska showed that the MSME increases with decreasing temperature. Using the shape of magnetization curves as an indirect evidence of the difference of magnetic energy needed for reorientation of the structure. The prediction of the low-temperature limit from the relation (2) is confirmed by a direct measurement of the MSME. We concentrate on the 5M martensite, as the MSME occurring in 7M is very particular to individual samples.

II. EXPERIMENT

Single crystalline samples, prism-shaped approximately $5 \times 5 \times 9$ mm$^3$, were cut along $[100]$ planes of the parental cubic structure from a nearly single crystalline ingot produced by a modified Bridgman method. The ingot was heat treated at 1273 K for 46 h and at 1073 K for 72 h in an evacuated quartz ampule. The composition of the Ni$_{10}$Mn$_{29}$Ga$_{11}$ alloy was determined using energy dispersive spectroscopy. The structure of the samples was checked by x-ray diffraction using a Philips X’pert texture diffractometer. The parent phase is $L_2_1$, cubic with lattice constant $a_L = 0.584$ nm (measured at 323 K). It transforms during cooling to a martensite. The transformation is completed at $T_M = 308$ K. The structure of the martensite is approximately tetragonal with a five-layer modulation (5M) and lattice constants $a_M = b_M = 0.595$ nm, $c_M = 0.561$ nm (measured at 293 K).

The reverse transformation from martensite to austenite starts at about $T_A = 317$ K. The transformation temperatures were determined by low-field susceptibility measurements. No other transformation was detected down to 120 K. Additionally, the magnetization measurements using vibrating sample magnetometer indicates that the 5M structure persists at least down to 10 K. Magnetic anisotropy constant $K_1$ and saturation magnetization were determined from the magnetization curves measured in the range 10–400 K up to a 2 T field.

Simultaneous quasistatic measurements of the field-induced strain (MSME) using a contactless laser dilatometer and magnetization by a vibrating coil magnetometer were conducted in the temperature range 203–313 K up to 1.15 T. The sample was placed inside a cylinder and compressed by a piston driven by compressed air. The force acting on the sample was determined from the pressure of the compressed air and the cross section of the piston. The whole apparatus was placed inside a 12 in. magnet. See inset in Fig. 1 for details of the experimental arrangement. A nitrogen flow was used for cooling, while electrically heated coils were used for heating of the measured sample. A small 0.2 MPa compressive stress was applied during the measurement of the MSME and of magnetization in order to hold the sample in the right position. After the magnetic field induced strain and magnetization measurements, the compressive stress was increased from 0.2 to 14 MPa and then decreased to 0.2 MPa while measuring the strain of the sample. In this way we obtained the stress-strain curves. Our procedure is different from a typical compression test, where strain is increasing linearly and stress is measured. From the measured stress-strain curve at a certain temperature the twinning stress value
can be directly determined. The 14 MPa compression causes reorientation of the martensitic structure and a full detwinning of the sample. Then the sample consists of only one martensitic variant with the c-axis oriented along the axis of the compression (detwinned state), and this state is maintained after releasing the stress. At room temperature, the detwinned state can be also achieved by application of a 1 T field. To obtain the stress-strain curve at low temperature the detwinned sample was prepared at room temperature, then cooled down and the stress-strain curve was measured.

We could not measure the MSME using quasistatic measurement at very low temperature due to the inability to keep the temperature constant. To determine low temperature MSME we cooled the sample down to 79 K, then we set the magnetic field to 0.9 T and measured the strain and magnetization with increasing temperature. The sample was heated by natural heat convection. The large increase of the strain and small increase of the magnetization indicate the occurrence of the MSME in the sample at a particular temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the simultaneous measurements of the strain and magnetization of the sample at ambient temperature 301 K. The applied magnetic field along the [100] direction, perpendicular to the easy axis, causes a twin boundaries motion due to the difference of magnetic energy $\Delta E$ of the variants. The twin boundary motion leads to a reorientation of the crystallographic structure. When the reorientation is complete, the [001] direction lies along the field. The twin boundary motion is accompanied by a large strain (MSME) and by changes of the magnetization curve shape. The first quadrant hysteresis in the magnetization curve is the typical mark of the MSME.6 Observations in polarized light, the value of strain 6% and also the square shape of the magnetization curve after the MSME shows that almost whole volume of the sample reorients and the fraction of other variants is negligible. To repeat this result it is necessary to change the structure back to the initial [100] orientation along the field. This was achieved by applying 14 MPa compressive stress perpendicular to the magnetic field after the measurement.

The observations by polarized light microscopy confirmed the existence of a twin boundary motion during a mechanical compression and also in magnetic field. Figure 2 shows the development of a surface morphology of the sample during the mechanical compression. Figure 2(a) shows nearly a fully detwinned state after magnetizing in a 1 T field. Figures 2(b) and 2(c) show two states containing two variants after application of small and larger stresses, respectively. The light bands in Figs. 2(b) and 2(c) are growing variants which broaden with an increasing compressive stress. Application of a 14 MPa stress leads to nearly fully detwinned state as shown in Fig. 2(d). The effect of a magnetic field applied perpendicular to the previous direction of magnetization was very similar. There were few bands in the sample, which broadened with an increasing magnetic field. The low amount of observed bands suggests that nucleation of new twin variants may require higher energy than the energy needed for twin boundaries motion resulting in the growth of existing variants.

An example of the stress-strain curve is shown in Fig. 3. We defined a twinning stress $\sigma_{TW}$ as a value of the external stress necessary to induce strain $\varepsilon = -3\%$ due to the twin boundaries motion. The temperature dependence of the twinning stress in the range 113–307 K is shown in the inset of Fig. 3 and also in Fig. 8. The temperature dependence of the twinning stress has an exponential-like character and strongly increases at low temperature. The increase of the twinning stress was noted before,14 the data suggested that the twinning stress increases linearly but the measured interval of temperatures was relatively narrow, about 70 K. The large nonlinear increase of twinning stress measured by Sooshenko et al.22 was attributed to the vicinity of the intermartensitic transformation. In our alloy the large increase of twinning stress cannot be attributed to intermartensitic transformation since the same SM martensite persists down to 10 K.

The determined values of the twinning stress (Fig. 3) have a relatively large spread of values at low temperature. It
may be ascribed to a slightly different initial configuration of the twins inside the sample for each measurement. As suggested earlier, the energy needed for the new variant nucleation can be quite high, and existence or nonexistence of additional twin boundaries can affect the growth of the existing residual variants and thus strongly influence the twinning stress.

We discussed the temperature dependence of magnetic anisotropy in Ni–Mn–Ga alloys in Refs. 13 and 23. Magnetic anisotropy in a 5M martensite is uniaxial with an easy axis along the [001] direction. The temperature dependence of the first anisotropy constant follows the third power of magnetization. The temperature dependence of magnetic anisotropy and of saturation magnetization is shown in Fig. 4. The Fig. 4 inset shows the magnetization curves of the sample at 143 K measured along the [100] and the [001] directions. These curves clearly show that there is no MSME at this temperature, since there is no first quadrant hysteresis (see Fig. 1 for comparison).

We measured the MSME directly using quasistatic measurements of the strain and magnetization as a function of magnetic field in the range 203–313 K. The MSME was observed in the whole temperature interval. Examples of the MSME measurements are shown in Fig. 5. The character of the curves is similar in the measured range, the MSME occurs in one or two large jumps and then slowly saturates in higher field. The large jumps of the strain are accompanied by the large jumps of the magnetization (see also Fig. 1). The magnitudes of the jumps suggest that the twin boundaries move freely over large volume of the sample without hindrance. It is noteworthy that at 307 K the MSME is observed already at 0.15 T.

Figure 6(a) shows the temperature dependence of the maximum measured strain \( \epsilon_{\text{MAX}}(T) \) (see Fig. 1 for definition). Despite the large spread of the measured values the maximum strain or the MSME apparently increases with decreasing temperature in agreement with the increase of the tetragonal distortion \( \epsilon_0(T) \). The increase is not as large as the increase of the tetragonal distortion taken from Ref. 16. This suggests that the larger volume of residual variants persists in the sample during magnetizing in lower temperatures. The persisting residual variants can markedly affect the maximum strain, switching field, and twinning stress.

Figure 6(b) shows the temperature dependence of the switching field \( H_{\text{SW}}(T) \) defined as the field when the strain reach \( \epsilon=1\% \) (see Fig. 1 for definition). The switching field \( H_{\text{SW}}(T) \) increases with decreasing temperature. This is caused by the increase of the elastic energy \( \epsilon_0(T) \cdot \sigma_{\text{TW}}(T, \epsilon) \) needed for the twin boundaries motion. Large spread of \( H_{\text{SW}}(T) \) can be ascribed to the different initial twin configuration as discussed earlier.

From magnetization curves (Fig. 4) is evident that there is no MSME at 143 K. To determine experimentally the low temperature limit of the MSME we measured the strain and magnetization in a constant 0.9 T magnetic field during heating from 100 K. The measurement is shown in Fig. 7. Very steep change in strain (6.5%) accompanied by a jump in magnetization during heating indicates the structure reorientation and thus the MSME at 173 K. No significant changes of the strain or the magnetization were detected at lower temperature. Since the 5M persists down to 10 K we can be
sure that the large changes of the strain and the magnetization are not caused by an intermartensitic transformation.

Note that magnetization at 0.9 T differs slightly for the [001] and [001] directions, as discussed above.

Additional distinctive click was possible to hear at 173 K. We repeated the experiment a couple of times and a different initial configuration of the twins inside the sample as discussed above.

The results are summarized in Fig. 8, which is a graphical expression of Eq. (2) for the experimentally determined parameters. The figure shows temperature dependence of $K_r(T)/\varepsilon_{0}(T)$ and of the twinning stress $\sigma_{TW}(T)$. The MSME can occur only in the area where the 5M martensite exists and where the twinning stress $\sigma_{TW}(T)$ is lower than $K_r(T)/\varepsilon_{0}(T)$. The area is marked in the figure. The high temperature limit of the MSME is the transformation to austenite at 315 K. The low temperature limit, determined as a temperature where rapid growth of the hardening stress exceeds $K_r(T)/\varepsilon_{0}(T)$, is 165 K. This agrees quite well with directly measured low temperature limit of the MSME, which is 173 K. The rapid, exponential-like, increase of the twinning stress with decreasing temperature may hinder the utilization of the magnetic shape memory effect of Ni–Mn–Ga alloys at very low temperature.

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