Ni-Mn-Ga single crystals with very low twinning stress

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Abstract. Twinning stress or mechanical hysteresis associated with the twin boundary motion is one of the most essential parameters which determine the actuating performance of magnetic shape memory alloys. Recent effort at AdaptaMat Ltd. to decrease the twinning stress resulted in a consistent production of Ni-Mn-Ga magnetic shape memory single crystals with the twinning stress of about 0.1 MPa, which is much lower than previously reported. In this work, the mechanical and magnetomechanical response of the developed crystals is discussed in detail and the importance of adjustment of the twin microstructure for obtaining an optimal actuating behavior is illustrated.

1. The MSM effect and importance of twinning stress

The magnetic-field-induced rearrangement of (ferro-)magnetic twinned martensite microstructure accompanied by a large macroscopic deformation, or magnetic shape memory (MSM) effect is a phenomenon which has attracted attention since its first demonstration on a Ni-Mn-Ga single crystal in 1996 [1]. Fast actuation seems to be one of the potential practical exploitations of the phenomenon as magnetic shape memory effect with large strains up to 10% was already demonstrated many times starting from 1999 [2–9] and the possibility of actuation in kHz range was also clearly shown [10]. Applications based on reverse mechanism were also suggested including sensing [11–13], energy harvesting [14,15], damping [16], etc. Ni-Mn-Ga alloys have been so far most studied and can be considered as a “prototype” magnetic shape memory material.

One way how to employ the MSM effect for linear reversible actuation is to apply a constant external compressive stress $\sigma$ along one principal axis and variable magnetic field $H$ perpendicularly along an other principal axis of a prismatic single crystalline Ni-Mn-Ga MSM element, Fig. 1 [13,17]. The overview of the other possible arrangements can be found in [18]. The MSM element is typically cut along $\{100\}^P$ faces and contains a simple two-variant twin microstructure as this type of microstructure seems to exhibit the best performance [19]. One twin variant (yellow or light in Fig. 1) is favored energetically by the external stress while the other one (red or dark in Fig. 1) is favored by the magnetic field. When the magnetic field is increased to a certain magnitude, the variant favored by the magnetic field (red) starts to grow on the expense of the variant favored by the stress (yellow). When the magnetic field is decreased, the reverse process takes place during which the external stress induces the growth of twin variant favored by the stress (yellow) on the expense of the twin variant favored by
Figure 1. Reversible several percent actuation of a crystal showing magnetic shape memory effect can be achieved by the combined application of a magnetic field and a constant external compressive stress (orientation of short c-axis inside twin variants is indicated by arrows). a) In zero or small magnetic field $H_1$, the twin variant favored by the applied external stress $\sigma$ (initial variant, yellow or light) occupies most of the crystal volume. b) With increasing magnetic field, the twin variant favored by magnetic field (red or dark) grows on the expense of the initial variant, which is accompanied by a several percent deformation ($\Delta L/L$) at final large field $H_2$. When the field is decreased back to zero or $H_1$, the twin microstructure rearranges to the initial state shown in (a) due to the effect of external stress which favors the initial (yellow or light) variant.

The c-axis and a-axis of the two discussed twin variants point along the two different principal directions of the MSM element. Thus, by growth or consumption of one or other variant, the orientation of c-axis is changed from one principal direction to the other principal direction. This is the reason why magnetic shape memory effect is sometimes called magnetic-field-induced reorientation, or MIR. Exchange of c-axis and a-axis by growth or consumption of twin variants results in a large deformation as the axes differ considerably in length. The maximum possible macroscopic linear strain occurs when the whole volume of the element transforms from one variant to the other variant and it is given by the relative difference between the lattice parameters $a$ and $c$. This is typically about 6% for 5M (five-layered, approximately tetragonal) Ni-Mn-Ga martensite studied and discussed in this article.

Figure 2. Apparatus for the investigation of MSM effect and of mechanical properties. Magnetic field and compressive stress were applied perpendicularly. Spring was not installed during compression tests but it was installed for measurement of magnetic-field-induced strain. Applied magnetic field was determined by a Hall probe without specimen installed.
Slow (≈1 Hz) and quasistatic actuation by the magnetic shape memory effect can be easily demonstrated and investigated using a simple magneto-mechanical apparatus as the one shown and described in Fig. 2. Using this apparatus with 20 mm long single crystals, MSM effect with strain close to 6% can be clearly visually observed by unaided eye. The same apparatus was used for determining the response of the studied crystals under compressive loading and in magnetic field. The twin microstructure, individual twin domains or variants, and twin boundaries were observed using polarized light optical microscopy. The microstructure was well observable by an optical microscope from certain faces of the specimen even without polarized light. X-ray diffraction was an additional tool which we used to confirm the observed or created twin configurations.

Twinning stress, $\sigma_{\text{TW}}$, as a measure of mobility of twin boundaries, is a crucial material parameter determining the existence of the MSM effect and the efficiency of the actuators based on the phenomenon [4, 21]. Twinning stress can be experimentally evaluated from the stress-strain curves [22] as the level of applied compressive (or tensile) uniaxial stress which causes the twin boundary motion. More specifically, it is often determined as the position of the detwinning plateau on the stress-strain curve, or it can be determined as the stress level at half transformation strain [19], or, two stress levels can be recorded – one near the beginning and the second near the end of the plateau on the stress-strain curve [4]. Such determinations, however, may not fully cover more general consideration of the twinning stress for which the stress level at which twinning initiates (i.e., twin variants nucleate) must be distinguished from the stress level at which twin variants grow [22,23]. This is discussed more below.

There is a common agreement that the lower twinning stress results in a better actuating performance of the MSM material. From the model of MSM effect introduced by Likhachev and Ullakko [4] it follows that to obtain a reversible MSM effect, the twinning stress must be less than half of the magnetic stress [24], i.e. less than about 1.5 MPa as the maximum magnetic stress, $\sigma_{\text{MAG}}$, is about 3 MPa for 5M Ni-Mn-Ga martensite at room temperature (e.g. [24]). How low below the above determined limit 1.5 MPa is satisfactory for practical actuation can be answered when considering the coupling factor, or efficiency of the MSM effect determined as the ratio of obtained mechanical work and work spent on the magnetizing of the material during one magnetizing (actuating) cycle.

Table 1 summarizes the calculated efficiencies for selected magnitudes of twinning stress using $\eta = (\sigma_{\text{MAG}} - 2\sigma_{\text{TW}})/\sigma_{\text{MAG}}$ [13, 21] and $\sigma_{\text{MAG}} =3$ MPa. As the generation of the magnetic field is typically costly and bulky, one would like to avoid unnecessary losses and keep the efficiency.

| Twinning stress $\sigma_{\text{TW}}$ MPa | Efficiency $\eta$ % | Note |
|----------------------------------------|---------------------|------|
| >3                                     | —                   | No MSM effect |
| 1.5–3                                  | —                   | Irreversible (one way) MSM effect |
| 1.4                                    | 7                   | Reversible MSM effect |
| 1                                      | 33                  |      |
| 0.5                                    | 66                  |      |
| 0.2                                    | 87                  |      |
| 0.1                                    | 93                  |      |
| 0                                      | 100                 | Ideal MSM material |
Figure 3. Illustration how nickel content of the studied alloys was selected. To avoid any problems with other martensitic phases, composition was selected to be in the region of 5M phase (green or dark) as far as possible (marked by circle) from intermartensitic transformations (IMT). This gives optimum nickel content of about 50% for the shown case with $e/a = 7.643$. 7M – seven-layered martensite, NM – tetragonal martensite with $c/a > 1$, $T_C$ – Curie temperature, $T_M$ – martensitic transformation, $T_A$ – reverse transformation to austenite.

not far from 100%. Using Table 1, it seems that this can be assured only if the twinning stress is not far from 0.1–0.2 MPa, where the efficiency is around 90%. It is noteworthy that 1 MPa twinning stress may seem low, when directly comparing to 3 MPa magnetic stress, but gives only 30% efficiency and, thus, may be too high for the practical usage of the MSM alloys.

2. Development of Ni-Mn-Ga single crystals

Our development of the crystals with a low twinning stress is based on the idea that the twin boundary mobility can be considerably increased by an efficient elimination of the obstacles for twin boundary motion from the lattice [25, 26]. As obstacles we consider chemical impurities from raw material and from the process resulting in inclusions and precipitates [25] and also inhomogeneities in composition, second phases, cell boundaries, etc. An example of the selection of nickel content for electron per atom ratio $e/a = 7.643$ is demonstrated in Fig. 3. The nickel content was selected to be close to 50 at. % of Ni, as this composition is far from other phases and a possibility of occurrence of the other martensitic phases than 5M (five-layered modulated, approximately tetragonal, with $c/a = 0.94$) in the crystal is minimized. The actual composition of the tested alloys was Ni$_{50.2}$Mn$_{27.8}$Ga$_{22.0}$ ($\pm 0.2$ atomic percent).

3. Properties of the developed crystals and effect of twin microstructure

Additionally to the obstacles in the crystal, the twin microstructure also influences the twinning stress [27–29]. In other words, the twin boundaries themselves can present obstacles for the twin boundary motion [30]. Due to that the stress-strain response of the crystal depends on the twin microstructure, and, thus, attention must be paid to the twin microstructure when determining the twinning stress from the stress-strain curve. We created well defined twin
Figure 4. a) Twin microstructures investigated in this study (schematically on the left, polarized light microscopy observations on the right): i) single variant, ii) single boundary, and iii) fine twins. b) Illustration how the fine twins were created by bending of a single variant.

microstructures in the studied crystals using an external stress and magnetic field prior to the testing. The morphology of the created twin microstructures is demonstrated in Fig. 4a. How the microstructure with fine twins was created by bending of a single variant crystal is illustrated in Fig. 4b [31].

Mechanical testing using compressive stress and measurement in a quasistatic magnetic field under zero stress were performed for each microstructure presented in Fig. 4a using the apparatus demonstrated in Fig. 2. For a single twin boundary and for fine twins, magneto-mechanical testing under nonzero external stress was also performed. The results are shown and discussed below for each microstructure separately.

3.1. Single variant

The main feature observed on the stress-strain curves determined for the single variant, i.e., for an initially detwinned crystal, is large load drop at the beginning of loading by which the initial stress peak was formed on the stress-strain curve, Fig. 5. The load drop can be ascribed to the nucleation of the new twin variant [22,27,28]. The large height of the stress peak indicates that the nucleation barrier is rather high in Ni-Mn-Ga (detailed discussion on the topic was presented in [32]). High nucleation barrier had been confirmed also by a generally small amount of twin boundaries observed in Ni-Mn-Ga single crystals [20].

The height of the stress peak corresponds to the stress initiating twinning (nucleating new twin variants) in a single variant (detwinned crystal) and we will refer to the height of the stress peak as the initial twinning stress. The average height of the stress peak, or the initial twinning stress, in our experiments was about 2 MPa.

After the twinning was initiated and some twin boundaries were clearly observed in the crystal, the deformation of the crystal progressed by motion of twin boundaries (with only occasional nucleation of additional twin domains). Stress required for this motion was much smaller (0.2–1 MPa) than the initial twinning stress and we will refer to it here as the conventional twinning stress, or just the twinning stress.
From the above observations we can conclude that to achieve actuation with a reasonable efficiency, some twin boundaries must be always present in the crystal. Otherwise, a high barrier (i.e., initial twinning stress) would have to be overcome by the magnetic stress and also by the external counterstress to achieve actuation. This was pointed out also in Ref. [32], where it was stated that the homogeneous magnetic field-induced nucleation of twin boundaries is not likely. It means that the twin boundary motion in the magnetic field may proceed only from the preexisting twin boundaries. In agreement with this statement, the observed response of a single variant in the magnetic field was unsteady and often no MSM effect was observed [33]. Note also that the initial twinning stress of 2 MPa is too high (>1.5 MPa) to allow a reversible MSM effect in the arrangement with the external counterstress, Fig. 1.

The stress-strain curves varied considerably between individual experiments made on single variants, Fig. 5. This can be ascribed to the different twin microstructure nucleated during each experiment with the different mobilities of twin boundaries. Nonetheless, as demonstrated also in Fig. 5, the stress necessary to move the twin boundaries often decreased to about 0.2 MPa. We concentrated on these cases, and after additional training of the crystal by repeated compression and extension we obtained crystals with a single highly mobile twin boundary described below.

3.2. Highly mobile twin boundary
The developed crystals showed tendency to nucleate only a pair or a few twin boundaries under compression and further deformation progressed by propagation of these nucleated twin boundaries [28]. The single twin boundary was formed from the nucleated pair when the pair was nucleated near the end of a crystal and one boundary vanished at the end of the crystal. The remnant boundary showed very low twinning stress either immediately or after a few compression-extension cycles performed manually while holding the crystal from its two ends.

Compression tests of the crystal with a single highly mobile twin boundary are demonstrated in Fig. 6a. The applied deformation (strain) induces motion of the highly mobile twin boundary present in the crystal and, typically no other twin boundary appeared in the specimen until the whole crystal had c-axis along the stress. At this point, the loading started to be elastic, which was indicated on the stress-strain curve by a sudden sharp increase of stress at the strain of about 6%. From the position of the detwinning plateau on the stress-strain curve we determined that the twinning stress of the crystal was 0.05–0.1 MPa. This is considerably less than previously reported (e.g. 0.5 MPa in [34]).

The magnetic shape memory effect in the crystal with a single highly mobile twin boundary in the quasistatic magnetic field is demonstrated in Fig. 6b. The field-induced straining occurred
Figure 6. a) Response of crystal with single highly mobile twin boundary to compressive stress. b) Response of crystal with single highly mobile twin boundary to magnetic field for external stress 0 and 0.6 MPa (marked next to curves). All displayed measurements were performed on the same crystal.

at the applied fields of 0.12 T and 0.24 T (switching field) for the external stress of 0 MPa and 0.6 MPa, respectively. This difference in switching fields was present due to that for 0 MPa external stress only the twinning stress had to be overcome by the magnetic stress, but for 0.6 MPa external stress the twinning stress and external stress had to be overcome by the magnetic stress. This resulted in the higher magnetic field needed for field-induced straining of the crystal under load. In agreement with expectations, application of nonzero external stress made the effect reversible as the specimen contracted along the applied stress when the magnetic field was decreased.

Additional important factor influencing the switching field was the demagnetization factor of the crystal along the magnetizing direction. In the shown case, the field was applied perpendicularly to 2.5 × 20 mm² face of the 2.5 × 20 × 1 mm³ specimen, thus, the demagnetization factor was high. In spite of that, the observed switching field was rather low, which is in agreement with the observed very low twinning stress of the crystal. Magnetizing the crystal along direction with the low demagnetization revealed that the applied field as low as 0.03 T (300 Oe) was enough to achieve the MSM effect [35].

Figure 7. a) Due to twinning crystallography, a tilt of α = 90° − 2 arctan(c/a) is present at each twin boundary. b) This may cause problems when considering use of crystal with a single (or few) twin boundaries in an actuator with a narrow air gap. c) Creating many fine twins can eliminate the problem.
The demonstrated experiment and more detailed investigations (using tensile stress [28] and different temperatures [36]) show that a very low twinning stress can be achieved in Ni-Mn-Ga. However, the crystal with a single twin boundary does not seem to be the best candidate for practical usage in a magnetic actuator with a narrow air gap. One of the problems is demonstrated in Fig. 7. Due to 3.5° kink of the specimen on the twin boundary caused by the twinning crystallography, Fig. 7a, the specimen with only one twin boundary may be hard to operate in a “standard” magnetic actuator with a narrow air gap, Fig. 7b.

The stochastic nature of the single twin boundary motion [37] and the slower response of the crystals with small number of boundaries [32] may be listed as other reasons why to consider a twin structure with many twin boundaries or fine twins, Fig. 4, and Fig. 7c. Additionally, handling the large nontwinned volume of the crystal may not be trivial as in this volume twin boundaries with different orientations can appear. These can interfere with the existing highly mobile twin boundary and can hinder its motion.

The above mentioned reasons initiated the effort to create a fine twin structure in the material and to employ it in actuation. The effort, however, was only partly successful since the twinning stress of the crystal increased considerably when the fine twin structure was created. The response of the crystal with fine twins is described in more detail in the next chapter.

3.3. Fine twins

Fine twins with density about 80 twin boundaries/mm were created in the crystals by bending [31], Fig. 4b. When straight shape of the crystal was recovered, the twin boundaries persisted in the crystal and all were parallel, i.e., had the same twinning plane. The mechanical testing of the crystal with fine twins revealed that this type of microstructure exhibited about one order higher twinning stress, i.e. about 0.8 MPa, Fig. 8a, than the above described case with a single twin boundary (both twinning stresses were determined on the same crystal). Reason for this increase is under investigation. The response in the magnetic field under zero external stress, Fig. 8b, corresponded in its character to the observed stress-strain curves. Higher twinning stress resulted in the larger magnetic field necessary to induce the MSM effect and field-induced strain occurred more gradually in comparison with the case of single boundary due to the considerable tilt of the stress-strain curve, compare Fig. 6a and Fig. 8a.

The fine twins annihilated completely from the crystal by the compression of several MPa stress or by the large magnetic field. Thus, achieving the reversible MSM effect in the crystal...
with fine twins was not straightforward. A method for stabilization of the fine twins based on a minor modification of the material is under development in AdaptaMat Ltd. An example response of a crystal with fine twins which do not annihilate under stress is shown in Fig. 8b. Due to the relatively high twinning stress and considerable tilt of the stress-strain curve, Fig. 8a, the straining achieved in the periodic actuation was less than 3% and a relatively large magnetic field was necessary to achieve straining of reasonable magnitude. Note that hand in hand with the high twinning stress goes necessity to apply at least the same high external compressive stress to maintain the reversibility. This further increase the field necessary for achieving actuation with reasonable strain.

4. Conclusions

We demonstrated that the very low twinning stress (0.1 MPa and lower) is possible to achieve in Ni-Mn-Ga 5M martensite. Thus, in principle, magnetic actuators with a high efficiency can be constructed based on Ni-Mn-Ga single crystals. Prior to that, however, several issues should be considered.

The measurements demonstrated that it is necessary to distinguish between the initial twinning stress, i.e., stress initiating twinning in material and the conventional twinning stress or just the twinning stress, i.e., the stress inducing motion of existing twin boundaries. As the former is much higher than the latter, the microstructure configuration without twin boundaries (i.e., single variant or detwinned crystal) should be avoided completely, when using the material for magnetic actuation.

Even the crystal with the pre-existing twin boundaries can show one order variation in the twinning stress, since the twinning stress and consequently the MSM effect depend strongly on the twin microstructure of the crystal. Our experiments demonstrate that a crystal with a single twin boundary which exhibits a very low twinning stress and an excellent actuating performance can be transformed easily, e.g. by bending, to a crystal with fine twins, moderate twining stress, and reduced actuation. Twin boundaries may also annihilate by the action of the external stress or magnetic field, which makes the crystal a single variant with an unsteady or zero actuating response.

Due to the conclusions presented above, we now focus our efforts towards the development of the suitable twin structures with a low twinning stress, which will be resistant to twin boundary annihilation. We expect that such modification will considerably increase the potential of the material for applications requiring fast and efficient actuation.

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