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Study of austenite-martensite transformation in Ni-Mn-Ga magnetic shape memory alloy

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Abstract. $Ni_{49.7}Mn_{29.1}Ga_{21.2}$ magnetic shape memory sample showing magnetic-field-induced strain of 5.7 % in the magnetic field 0.5 T was studied at different conditions during austenite-martensite and martensite-austenite transformations. Transformation temperatures T_A = 317 K, T_M = 308 K were determined by AC susceptibility measurement. Structure parameters obtained from X-ray measurement are a_A = 0.584 nm for austenite and $a_M = b_M$ = 0.595 nm, c_M = 0.561 nm for martensite which has five-layered modulated structure. Mechanical stress up to 4 MPa and magnetic field up to 1 T were applied in order to study their influence on the transformations. Totally 39 transformation cycles were measured. The thermoelastic strains during transformations vary from -3.6 % to +1.8 %. Simultaneous change of magnetization and strain has been observed. Thermomechanical and magnetic history of the sample seems to have no or only very weak influence on the character of austenite-martensite transformation and no clear trend emerges in our experiments.

1. INTRODUCTION

Ni-Mn-Ga alloys are a new kind of perspective active materials [1]. They can exhibit giant magnetic-field-induced strain (elongation) of up to 6 % in magnetic field less than 1 T - magnetic shape memory (MSM) effect [2,3]. One of the important conditions affecting the magnitude of MSM effect is a certain arrangement of martensitic variants in the structure. The largest MSM effect occurs in the samples being in single variant state and having low twinning stress [2]. One may expect that the martensitic structure can be influenced by the conditions applied to the sample during austenite-martensite transformation.

In this paper we study the effects of magnetic field and/or mechanical stress on the character of austenite-martensite transformation and on the final martensitic structure. Moreover we tried to establish a link between the thermomechanical and magnetic history of the sample and the character of transformation. The data about the transformations are obtained mainly by measuring the strain and magnetization during the transformation.

2. EXPERIMENTAL

Single crystalline samples (approx. 5x5x9 mm^3) were cut along {100} planes from off-stoichiometric Ni_2MnGa (with excess of Mn) nearly single crystalline ingot. The composition determined by EDS is $Ni_{49.7}Mn_{29.1}Ga_{21.2}$ (precision about 0.5 at. %). Crystalline orientation and structure studies were made by optical microscopy and X-ray X'Pert Philips diffractometer. AC low field susceptibility measurement was used to determine transition temperatures.

Behavior of single crystalline sample during transformations was studied by means of simultaneous measurement of dilatation using laser vibrometer and magnetization measurement using vibrating coil magnetometer (VCM). The sample was placed inside a cylinder between two heated (fixed and movable) copper pistons. The sample was compressed by the piston driven by compressed air. The cylinder was installed inside a 12 inches magnet. This arrangement allowed applying heat, stress and magnetic field simultaneously. The orientation of the magnetic field was perpendicular to the applied stress. The strain was measured along the axis of the compressive stress, the magnetization along the field direction. The same equipment was used to measure MSM effect.

3. RESULTS AND DISCUSSION

Figure 1 shows the susceptibility during heating and cooling within the range of 100 - 400 K. The sharp changes on the curves correspond to the transitions. The crystal structure determined by X-ray diffraction is cubic austenite Heusler phase $L2_1$ above T_A=317 K with lattice parameter a_A = 0.584 nm (at 323 K) and 5-layered tetragonal martensitic (5M) below T_M = 308 K with parameters a_M = 0.595 nm, c_M = 0.561 nm (at r.t). The hysteresis between direct and reverse transformation from cubic to tetragonal structure is T_A-T_M = 9 K. Curie temperature of the alloy is T_C = 374 K. No additional transformation was detected.

Simultaneous measurement of the strain and magnetization as a function of magnetic field under pressure 0.2 MPa at room temperature is shown in Fig. 2. The sample was pressed (4 MPa) before measurement. It shows MSM effect of value 5.7%. This value is close to the maximum theoretical value calculated from the lattice parameters (a_M/c_M-1) = 6.06%. The maximum value corresponds to change from one single variant with orientation of c-axis perpendicular to the magnetic field to the variant with c-axis along the field.

Prior any measurement of transformation-induced strain was made, the sample was put into magnetic field in order to check the existence of the MSM effect. It was then placed inside the cylinder and heated to austenite (318 - 320 K) under stress 0.2 MPa (this minimum stress was necessary to fix the sample). We chose the austenite as the initial and final point for transformation-strain measurements since the austenite structure is cubic and therefore exactly defined and consequently these points should coincide. Each cycle consisted of cooling of the sample to the martensite (303 -305 K) and then heating back to the austenite. In some cycles stress and/or magnetic field was applied during cooling and heating. The rate of cooling and heating was about 1-2 K/min. The conditions applied during the transformation and corresponding transformation-induced strains are listed in Table 1. The cycles are numbered in time sequence. The value of the strain in Table 1 is taken as the difference of the strains immediately before and after the austenite-martensite transformation in order to exclude the influence of dilatation of the equipment, which we were unable to remove fully.

The transformation from cubic austenite to tetragonal martensite should cause a change of the sample dimensions. According X-ray the crystallographic axes of 5M martensite are approximately parallel to the crystallographic axis of cubic austenitic structure. When the sample transforms from austenite to single variant martensite with short c-axis [001] in the direction of the strain measurement (called c-variant), the resulting strain is $(c_M-a_A)/a_A$ = -3.94%. The transformation from austenite to martensitic single variant with the a-axis [100] or [010] along the strain direction (called a-variant(s)) leads to strain $(a_M-a_A)/a_A$ = 1.88%. The value of the strain inside this interval signifies that the austenite transforms to a mixture of martensitic variants with different orientation of tetragonal c-axis. The short c-axis of tetragonal martensite is also the easy axis of magnetization [2]. Simultaneous measurement of

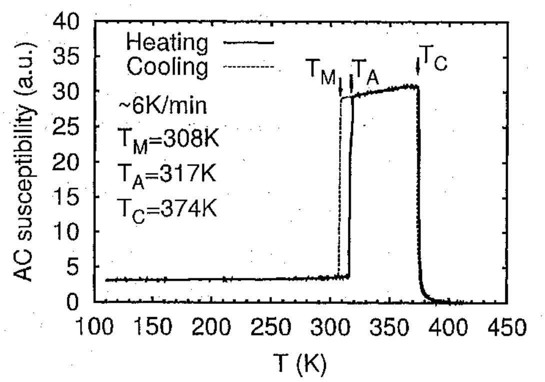

Fig.1. AC susceptibility as a function of temperature for $Ni_{49.7}Mn_{29.1}Ga_{21.2}$ alloy. Changes to martensite (T_M), austenite (T_A), and Curie point (T_C) are marked.

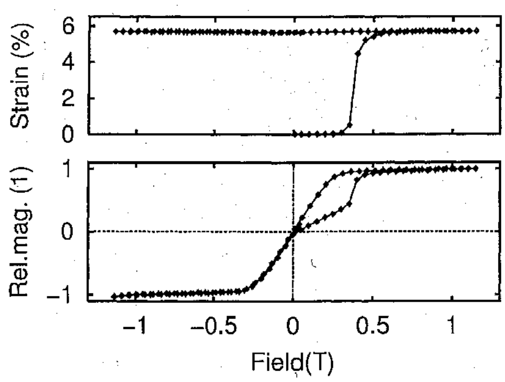

Fig. 2. Simultaneous measurements of the strain and magnetization of the sample. The sample was in single variant state initially.

Table 1. Conditions of austenite-martensite transformation and values of transformation induced strain

Cycle	1	2	3	4	5	6	7	8	9	10	11	12	13
Stress [MPa]	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	1	1
Field [T]	0	0	0	0	0	0	0	0	0	0	0	0	0
Strain [%]	-0.3	+1.7	-0.6	-0.4	-0.2	-0.3	+1.8	+1.8	+1.7	+1.7	+1.7	-2.6	-3.0

Cycle	14	15	16	17	18	19	20	21*	22	23	24	25	26
Stress [MPa]	1	2	2	4	0.2	0.2	0.2	0.2	0.2	0.2	1	2	2
Field [T]	0	0	0	0	0	0	0	0	0	0	0	0	0.5
Strain [%]	-3.2	-3.4	-3.5	-3.6	-0.3	+1.7	+1.7	+1.7	-2.6	+1.7	+0.4	-3.5	0.0

Cycle	27	28	29	30	31	32	33	34	35	36**	37	38	39
Stress [MPa]	2	2	2	2	2	2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Field [T]	0.5	0.5	0.5	1	1	1	1	1	0	0	1	1	0
Strain [%]	+0.4	-3.0	-3.0	+1.0	+0.9	+1.0	+1.7	+1.7	-0.2	-0.2	+1.7	+1.7	0.0

* Pressed 7MPa in martensite after the cycle 21.
** Optical observations after the cycle 36; pressed 5MPa and measured for MSM.

magnetization ascertains the transformation and helps to determine a distribution of martensitic variants in final structure.

Examples of the dilatation curves are in Fig. 3-5. Fig. 3 shows a comparison for different compressive stresses in zero magnetic fields. It is worth mentioning here that the stress needed to change single variant sample to another variant (twining stress) is about 2.2 MPa at room temperature. It is clear from the Fig. 3 that compression comparable to or higher than the twinning stress encourages, as expected, the growth of easy martensitic variant along the axis of its application. The measured strain suggests that for 2 and 4 MPa the resulting martensite phase is close to single variant state with c-axis (short) along stress direction (c-variant). For 0.2 MPa the sample transforms to the a-variant(s), while for 1 MPa a mixture of c-variant and a-variants occurs.

During heating, there is a drop (-0.3%) at strain curve for 1 MPa at 314 K. This drop appeared in three cases of four for 1 MPa (cycles 12, 13, 14), which transformed mainly to c-variant except one case which transformed to the mixture of variants (cycle 24, strain 0.4 %). The drop may be associated with the variants rearrangement induced by stress prior austenite-martensite transformation. The twin rearrangement in stress direction should lead to decrease of the magnetization. However, the magnetization curve shows small increase of the magnetization in that area (on the edge of our resolution), which might suggest existence of another phase. Further investigation to clarify this is needed. In the cases for 2 MPa and 4 MPa the influence is clear. The transformation to martensite takes place at a little higher temperature and larger part of transformation to austenite is shifted slightly to the higher temperature as well.

Fig. 4 shows the dilatation curves under small compressive stress (0.2 MPa) without and with magnetic field 1 T. During transformation in the field the strain increases very sharply. The magnitude of the increase indicates that the sample transformed to a-variants which may have two c- axis orientations - along and perpendicular to field direction. To determine the direction of c-axis, magnetization loop in martensite was measured. The measurement shows that only one variant with the c-axis in direction of the field is presented in the sample. This is an expected result as the c-axis is easy magnetization axis and this variant has lower energy in magnetic field. In contrast to transformation without magnetic field the strain change is the same for all cycles and, therefore, the transformation is determined unambiguously.
Additionally, the transformation to austenite in the field

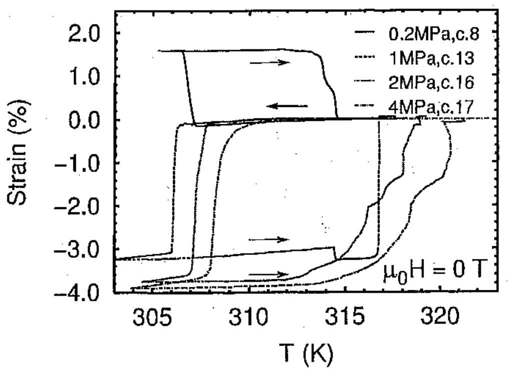

Fig. 3. Examples of strain curves for different stresses 0.2MPa, 1 MPa, 2 MPa, and 4 MPa in zero magnetic field. High pressure induces single variant state (cycles 16, 17).

takes place at a slightly higher temperature. In fact, we measured even bigger shift (2 cases to 316 K, cycles 37, 38; 2 cases to 320 K, cycles 33,34). A possible explanation of the shift could be that magnetic field induces very pure single variant state in which a nucleation of the austenite is more difficult than in mixed variant state with higher internal stresses.

Two 0.2 MPa curves shown in Figure 4 demonstrate that in the absence of strong external forces (field or stress) the distribution of the variants, i.e. the final martensitic structure, may be different from case to case (see also Table 1). We tried to control the character of the transformation by pressing the sample (7 MPa) in martensite. In the following cycle (22) the strain occurred in the direction of the stress but in next cycle (23) the transformation strain returned to the value measured before compression. The cycles without magnetic field and stress (35, 36) that followed after the cycles in magnetic field exhibited very small strain. After cycle 36 we took the sample out and the microscopy observations were done. Observed structure, as expected from the small strain, consists of a random combination of all three variants. Due to this the macroscopic strain is close to zero. We can conclude that the applied values of stress, field and the number of cycles do not show clear influence on the tendency of the sample to transform to certain variant(s) in the cycles without high external forces.

Combined effect of the field and stress is shown in Figure 5. Large field (1 T) and stress (2 MPa) make transformation faster than in cases with small pressure (0.2 MPa), but the field is not strong enough to initiate the growth of single variant state preferred by the field. Instead a mixed martensitic structure occurs. The structure is a combination of a-variants with c-axis along the field and c-variant with c-axis along the stress.

The value of 0.5 T of the field can yield different values and even signs of the strain. In the both cases shown in Fig. 5 the resulting structure is again a mixture with different ratio of a-variants and c-variant. For comparison the dilatation curve for 0 T and 2 MPa is also shown. These conditions encourage the growth of easy variant along the axis of the compressive stress (c-variant).

The remanent (0.005T) or the applied field of the magnet made it possible to measure magnetization as a function of temperature by VCM during every measurement. The value of magnetization is proportional to initial DC susceptibility (slope of the magnetization curve) in remanent field and to the saturated magnetization in the 1T field. In almost all cases we could identify a change in the magnetization during austenite-martensite transformation and reverse change to the original (austenitic) value of magnetization during reverse transformation. Magnetization changes coincide very well with the strain changes. Magnetization was lower in martensite than in austenite in the presence of remanent field (or 0.5 T) and higher in the presence of the field of 1 T when the sample is in saturation. This complies with the facts that the saturation magnetization is higher in the martensite than in the austenite and that the magnetic anisotropy of the martensite is much larger [3,4]. The only exception to this, where we cannot see any change in the magnetization are the cases with 0.2 MPa, H = 0.005 T and

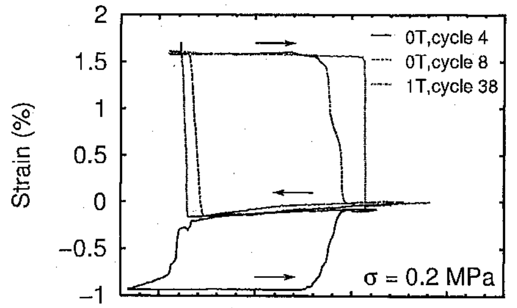

Fig. 4. Transformations under small stress 0.2 MPa with and without field. The field induces single variant state with exactly defined strain (cycle 38) while in the absence of the field the strain can be random (cycles 4,8).

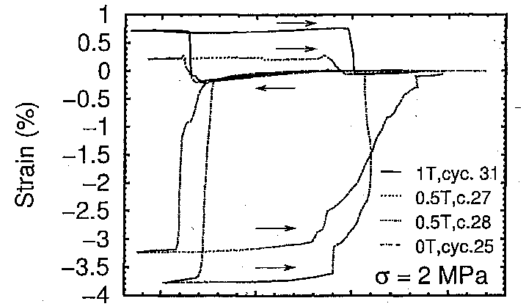

Fig. 5. Transformations under stress 2 MPa with different values of the magnetic field. Note difference between curves for the same conditions

having strain changes about 1.7 % (cycles 7-11, 19-21, 23). This suggests a presence of a variant with easy magnetization axis (c-axis) along the field direction (a-variant), because only in that case the initial slope of the magnetization curve for austenite and martensite is too similar to be recognizable with our resolution.

CONCLUSION

Our experiments show that one of the ways to establish the single variant state in Ni_2MnGa alloy with a five layered modulated structure is to apply high mechanical stress or high magnetic field during the austenite-martensite transformation.

Without external forces (field/stress) the character of the transformation and the resulting martensitic structure of the sample is in general unpredictable. Based on our data we can not establish any clear influence of the magnetomechanical and thermal history on the transformation and thus on the final martensitic structure.

Measured values of thermoelastic (reversible) strain during austenite-martensite transformation in different conditions vary in an interval (-3.6 %, 1.8 %), which corresponds well to the theoretical strain expected from the lattice parameters of martensite (-3.94 %, 1.88 %).

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