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Stress- and magnetic-field-induced variant rearrangement in Ni–Mn–Ga single crystals with seven-layered martensitic structure

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Abstract

Ni–Mn–Ga alloys with different chemical compositions having cubic-7M martensitic transformation were studied. Despite of composition difference, low de-twinning stress (approximately 1–2 MPa) and magnetic-field-induced strain (MFIS) of approximately 10% at ambient temperature in a magnetic field order of 1 T were observed in 7M martensitic phase. The influence of magnetic field on stress–strain curves and temperature dependencies of de-twinning stress are also presented.

Keywords: Ni–Mn–Ga alloys; Martensite phase transformation; Magnetic shape memory; Twinning; Mechanical test

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1. Introduction

Giant magnetic-field-induced strain (MFIS) caused by the rearrangement of martensite variants in ferromagnetic alloys, has attained considerable attention during last years. Several ferromagnetic shape memory systems are under investigation now as promising candidates for practical applications.

The first observation of a large MFIS was reported in Ni–Mn–Ga [1]. Since then, intensive, detailed experimental and theoretical study during the last few years has been concentrated on this system. A giant strain response of about 6% was achieved in Ni–Mn–Ga five-layered martensite (5M) in a relatively small magnetic field, below 1 T [2].

A MFIS of approximately 10% was reported in a $Ni_{48.8}Mn_{29.7}Ga_{21.5}$ alloy at ambient temperature in a magnetic field order of 1 T [3]. It was confirmed by different experimental methods that the strain is related to a magnetic-field-induced rearrangement of the crystallographic domains (twin variants) [4]. The basic crystal structure of thermally-induced martensitic phase in this alloy was found to be close to orthorhombic in the temperature range of 245–333 K. The lattice parameters were $a = 0.619$ nm, $b = 0.580$ nm, and $c = 0.553$ nm (related to the cubic parent phase coordinates) at ambient temperature. More detailed X-ray studies revealed seven-layer shuffling-type modulation along $[1\,1\,0]$ and $[1\,\bar{1}\,0]$ directions. It was also found that this orthorhombic phase (7M) has a low de-twinning stress (approximately 1–2 MPa) and the energy of magnetic anisotropy is higher than in 5M martensite.

However, all these results were obtained with one particular alloy composition. The purpose of the present paper is to investigate in more detail the stress- and magnetic-field-induced martensite variant rearrangement in several Ni–Mn–Ga alloys with 7M phase. Furthermore, it is aimed to show that also a giant MFIS response exists in these alloys. Some new experimental evidences supporting our model for MFIS are also presented.

2. Experimental procedures

Single-crystal samples of Ni–Mn–Ga with different compositions were studied. Chemical compositions (Table 1) were determined by means of an energy-dispersive spectrometer (EDS) connected to a scanning electron microscope (LEO-SEM). The single crystal ingot of alloy Or1

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Table 1
Chemical compositions, transformation temperatures and Curie points of the studied alloys

Alloy	Content (at.%) (±0.5%)			M_S (K)	M_F (K)	A_S (K)	A_F (K)	$T^{7M\text{-}NM}$ (K)	$T^{NM\text{-}7M}$ (K)	T_C (K)
	Ni	Mn	Ga							
Or1	48.8	29.7	21.5	337	333	338	342	245	311	368
Or2	51.0	28.5	20.5	356	350	354	360	233	318	365
Or3	50.5	29.4	20.1	351	343	348	357	223	313	366
Or4	49.5	30.3	20.2	341	337	344	348	283	343	363

was manufactured at AdaptaMat Ltd. Polycrystalline ingots with big grain size of alloys Or2, Or3 and Or4 were manufactured at Outokumpu Research Center. After homogenisation at 1253 K for 20–70 h and aging at 1073 K for 30–70 h in evacuated quartz ampoules these bars were cooled in air to room temperature. Their orientation, the martensite crystal structure and lattice parameters (Table 2) were determined in a Philips X'Pert X-ray diffractometer equipped with Co-tube and parallel beam optics (X-ray lens and parallel plate collimator with a divergence of 0.3°). The lattice parameters are given in the coordinates related to the parent cubic phase. Samples with dimensions of 4 mm × 5 mm × 9 mm were cut with a spark-erosion machine in one single grain. The edges of these rectangular prismatic single-crystal samples were nearly parallel to the [1 0 0], [0 1 0] and [0 0 1] directions of the parent cubic phase. The specimens were wet ground and electropolished (12 V, 0.1 A/mm^2) at 273 K for 30 s in an electrolyte of 300 ml ethanol and 100 ml nitric acid. The compression tests were carried out in tensile machines Lloyd L1000R equipped with a heating-cooling thermostat (223–473 K) and Lloyd LRX Plus equipped with an electromagnet. In the latter one, a magnetic field (maximal value $\mu_0 H = 1.1$ T) was applied orthogonal to the compression direction. The speed of the cross head was 0.2 mm/min for Lloyd L1000R and 0.5 mm/min for Lloyd LRX Plus. Details of the twinning stress measurements and the compression measurements in a magnetic field are given in [5,6]. The Curie point T_C, the martensite transformation temperatures M_S, M_F, A_S, A_F and the intermartensitic transformation temperatures $T^{7M\text{-}NM}$ and $T^{NM\text{-}7M}$ (see Table 1) were measured by low field ac magnetic susceptibility (113–573 K) and a differential scanning calorimeter Linkam 600 (113–873 K). Microstructure studies were carried out using a Leica DMR polarized light microscope.

Table 2
Crystal lattice parameters of the studied alloys

Alloy	Lattice parameters (at 300 K) (nm)			Ratio (*a*/*c*)
	a	*b*	*a*	
Or1	0.6188	0.5804	0.5530	0.894
Or2	0.6198	0.5795	0.5515	0.890
Or3	0.6183	0.5801	0.5524	0.893
Or4	0.6165	0.5780	0.5500	0.892

3. Results and discussion

We have found only a few Ni–Mn–Ga alloys exhibiting a straight cubic-7M transformation. All these 7M alloys have the martensitic transformation temperatures 10–35 K below the Curie point (see Table 1). For all studied alloys, the 7M phase is unstable on cooling and it transforms to non-modulated (NM) tetragonal phase at low temperatures (see Table 1) similar to the results reported before for alloy Or1 [3]. In alloy Or4, the temperature $T^{NM\text{-}7M}$ of reverse intermartensitic transformation NM-7M overlaps the temperature of reverse martensitic transformation 7M-cubic.

Formation of a single-variant state in the 7M phase requires the compression of multivariant samples along different directions of the sample at the temperatures higher than $T^{NM\text{-}7M}$, but below the temperature of reverse 7M-cubic martensitic transformation. This procedure worked properly with other alloys except alloy Or4 in which NM-7M and reverse 7M-cubic martensitic transformations occurred at the same temperature region. Consequently, it was not possible to obtain a single-variant state in this alloy. Fig. 1 shows the stress–strain curves for the first, the second and the third compressions of a multivariant sample (alloy Or1). It should be noted that the de-twinning stress decreases remarkably from the first compression to the third one due to the change in the twinned structure. Similar results were reported for Ni–Mn–Ga non-modulated martensite in [7].

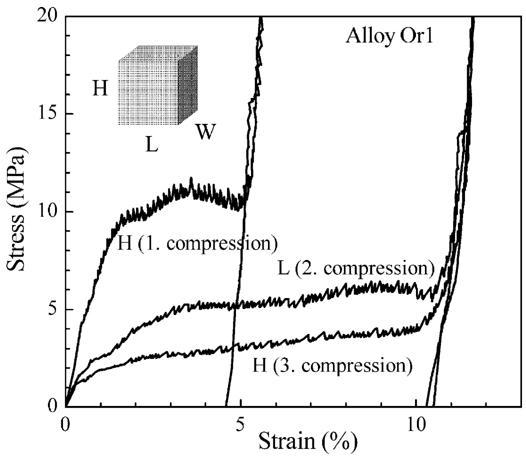

Fig. 1. Stress–strain curves at $T = 328$ K for compressions of martensitic multivariant samples of alloy Or1 along the *H* and *L* directions. Sample is shown schematically in the inset.

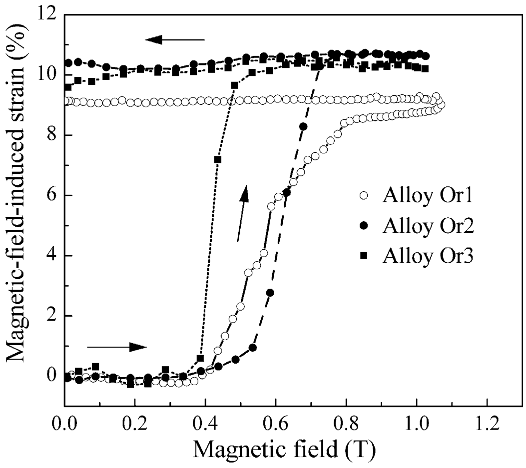

Fig. 2. Magnetic-field-induced strain in single-variant samples of Or1, Or2 and Or3 alloys measured perpendicular to the magnetic field applied along [1 0 0] (*a*-axis) at 300 K.

Fig. 2 shows a giant MFIS of approximately 10% at ambient temperature in a magnetic field order of 1 T, observed in the alloys Or1, Or2 and Or3 in which a single-variant state has been obtained. MFIS was not observed on multivariant samples of the alloys.

We studied de-twinning stress in single-variant samples compressed along [1 0 0] (*a*-axis) and [0 1 0] (*b*-axis) and found that it is lowest in [1 0 0] direction (Fig. 3). It confirms similar results obtained for the first time in [8]. The temperature dependence of the de-twinning stress measured under compression along [1 0 0] and [0 1 0] is also different (Fig. 4).

We confirmed experimentally that in the 7M martensite the effect of macroscopic force created by the applied magnetic field is close to the value predicted by our model [9]. According to it, the effect is equivalent to some uniaxial compressive stress applied directly to sample faces. The magnetic stress cannot exceed the saturation value of 1.6 MPa calculated as $\sigma_{\text{mag}} = K_u\varepsilon_0^{-1}$, where $\varepsilon_0 = (1 - a/c) \approx 0.11$ and $K_u = 1.6 \times 10^5\,\text{J/m}^3$ for 7M-phase in Ni–Mn–Ga [3]. The experimental confirmation was obtained by special experiments with magnetic field (Figs. 5 and 6). By compressing alloy Or1 (Fig. 5, dashed line) along the [1 0 0] direction and parallel to the long *a*-axis, the maximum twinning strain is approximately 10.6%. However after compression, the final 7M structure is having the long *a*-axis perpendicular to the compression direction, i.e. the original martensitic variant is transformed to another. When the sample was then rotated 90° before the next compression, the original structure was restored. After this, the compression

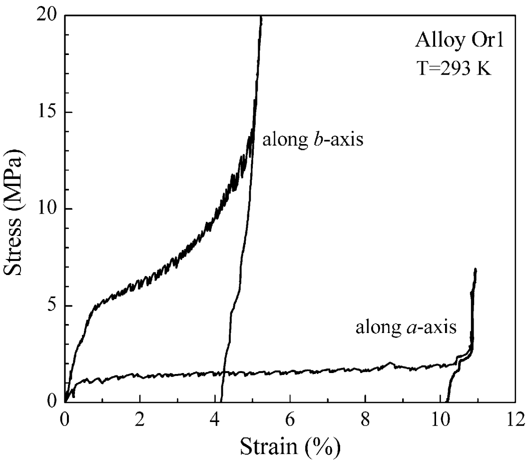

Fig. 3. Stress–strain curves for compression of a single-variant sample of alloy Or1 along [1 0 0] (*a*-axis) and [0 1 0] (*b*-axis) at 293 K.

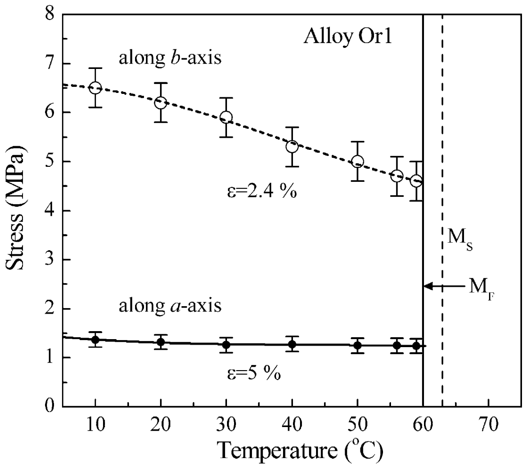

Fig. 4. Temperature dependencies of de-twinning stress (measured along [1 0 0] (*a*-axis) and [0 1 0] (*b*-axis) at strain value $\varepsilon = \varepsilon_0/2$) on single-variant samples of alloy Or1. Vertical lines indicate start and finish temperature (M_S and M_F) of the martensitic transformation.

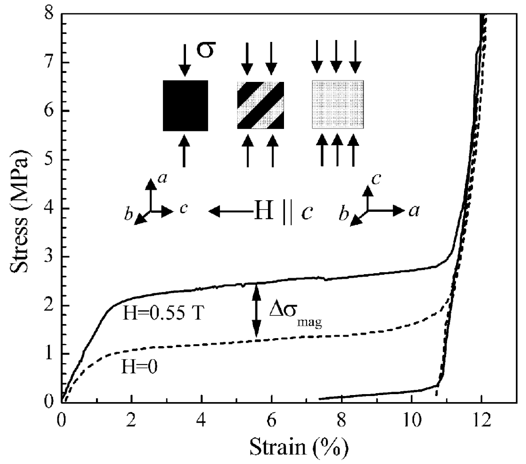

Fig. 5. Stress–strain curves for compression along [1 0 0] direction of a single-variant sample of alloy Or1 at 293 K without magnetic field (dashed line) and with a magnetic field $H = 0.55\,\text{T}$ (solid line) applied along the [0 0 1] direction. Microstructure change, orientation of the sample and field direction are shown schematically in the inset (vectors *a*, *b* and *c* are crystal lattice directions, *H* is magnetic field, σ is compression stress). Applied magnetic field results in increasing of the de-twinning stress $\Delta\sigma_{\text{mag}}$.

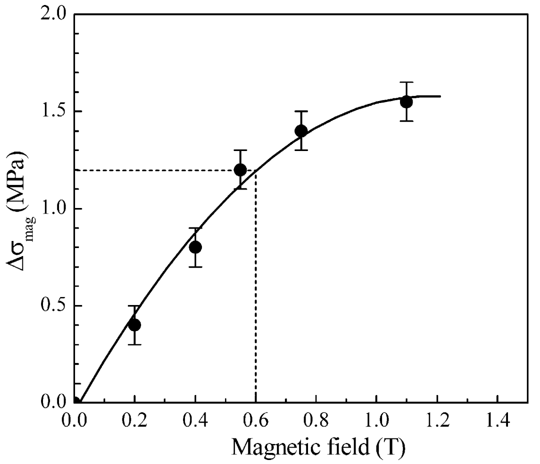

Fig. 6. Field dependence of the increase in twinning stress $\Delta\sigma_{\mathrm{mag}}$ (see Fig. 5) measured at 293 K and at the strain value $\varepsilon \approx \varepsilon_0/2$ for the alloy Or1. Vertical dashed line shows the field value at which $\Delta\sigma_{\mathrm{mag}}$ (horizontal dash line) becomes comparable with twinning stress of the alloy Or1 measured at $H = 0$ (see Fig. 5, dashed line).

was carried out in a magnetic field applied perpendicular to the compression direction (inset of Fig. 5). Now, the magnetic field retarded the reorientation of the sample (solid line) and the twinning stress increased by a value $\Delta\sigma_{\mathrm{mag}}$. The field dependence of $\Delta\sigma_{\mathrm{mag}}$ is shown in Fig. 6. There are two remarkable details. $\Delta\sigma_{\mathrm{mag}}$ at small field values is a linear function of H and it saturates at high field in accordance with our model. It can be supposed that if magnetic field is applied along the compressive direction, the twinning stress will decrease by a value $\Delta\sigma_{\mathrm{mag}}$. Moreover, one can see that $\Delta\sigma_{\mathrm{mag}}$ reaches a value comparable to the twinning stress of alloy Or1 approximately at $H = 0.6$ T. According to Fig. 2, approximately at this field value a sharp increase of MFIS is observed. This confirms additionally the validity of our model.

4. Conclusions

Several Ni–Mn–Ga alloys with seven-layered orthorhombic martensitic structure, showing giant MFIS of approximately 10% at room temperature in a magnetic field of 1 T, have been found. This confirms the suggestion that low twinning stress is an intrinsic property of the 7M phase in Ni–Mn–Ga.

It is shown that it is possible to obtain the martensitic single-variant state in 7M martensite via the compressions in certain temperature range, to different faces of the sample cut along ⟨1 0 0⟩ directions of the parent cubic phase.

We confirmed experimentally that the maximal macroscopic force effect of the applied magnetic field in 7M martensite is close to the value ~1.6 MPa, predicted by our model. This value exceeds the twinning stress for 7M martensite and it enables a large MFIS response.

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