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The behaviour of Ni-Mn-Ga martensitic alloys in magnetic field

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Abstract. Some of the Ni-Mn-Ga alloys exhibit a large shape change in magnetic field. This phenomenon occurs in their martensitic state and it is called the magnetic shape memory (MSM), since these materials can change their dimensions when the direction of the magnetic field varies. This kind of behaviour can be utilised in actuators and sensors. In the present work, three different polycrystalline Ni-Mn-Ga alloys are studied. The transformation temperatures together with the ferromagnetic Curie temperatures are determined by the magnetic susceptibility measurement and confirmed by the optical differential scanning calorimetry. The structures of the alloys are investigated with the optical microscopy and the X-ray θ–2θ–method. The sample behaviour in magnetic field is studied both by the vibrating sample magnetometer and by measuring magnetic-field-induced strain. Also, the effect of thermal, static and dynamic magneto-thermal cycling on the behaviour of the alloys in magnetic field is studied.

1. INTRODUCTION

Ferromagnetic Ni-Mn-Ga alloys have been recently subjected for intensive investigations, because their excellent shape memory properties and their ability to produce quite large strains in magnetic field [1-4]. Ullakko et al. [5,6] has presented the possibility to obtain a large shape change in magnetic field by rearranging of the martensitic twin structure; this magnetic shape memory effect (MSM) together with the magnetic properties of some Ni-Mn-Ga alloys has been studied in [7-9]. The effect of thermal and magneto-thermal cycling on the structure of these alloys was studied in [10-11]. In this investigation, these previous studies are carried on with one of the original alloys and two others in which the transformation temperatures are different but Curie temperature approximately the same. The aim of this study is to investigate the structures and the magnetic induced straining in these polycrystalline alloys after different treatments.

2. EXPERIMENTAL

In the present study, three different non-stoichiometric polycrystalline Ni-Mn-Ga alloys are studied. Their compositions together with the transformation and Curie temperatures are given in Table 1. The textured non-stoichiometric Ni-Mn-Ga polycrystalline alloys were manufactured in Outokumpu Research Center (Finland). Specimens were homogenised in evacuated quartz capsules for 72 h at 1273 K and then

ordered at 1073 K for 48 h followed with cooling in air. Specimens were ground and electropolished and etched in 25 % HNO_3 – ethanol –electrolyte at ambient temperature.

Table 1: Transformation temperatures and Curie-temperature of the alloys after heat treatment. (* = obtained with DSC instead of magnetic susceptibility).

	M_s (K)	M_f (K)	A_s (K)	A_f (K)	T_c (K)
$Ni_{48}Mn_{33}Ga_{19}$ (Alloy A)	384*	370*	376*	398*	371
$Ni_{55}Mn_{21}Ga_{24}$ (Alloy B)	372	358	363	379	372
$Ni_{48}Mn_{31}Ga_{21}$ (Alloy C)	301	299	310	312	369

The measurement of temperature dependence of low field AC-magnetic susceptibility was used to determine Curie and martensite transformation temperatures. These results were confirmed and completed with differential scanning calorimeter Linkam DSC 600 measurements.

Magnetic properties were measured at ambient temperature using conventional vibrating sample magnetometer (VSM). The magnetic field induced straining was measured with samples of approximately 10 mm x 5 mm x 5 mm. This was carried out in a load cell equipped with a capacity sensor. Compressive stress was applied to the sample by piston driven by pressurised gas from the cylinder. This design permits to accommodate large strain associated with MSM effect without apparent change of applied load. All the magnetic measurements were carried out at the ambient temperature.

The θ–2θ–analysis was carried out at ambient temperature with Philips X-ray diffractometer using $Co_{K\alpha}$ and $Cu_{K\alpha}$ radiation without rotation of the sample. The sample was clamped to the special specimen holder in such a way that its position remained unchanged during all measurements.

Thermal and static magneto-thermal cycling in 0.4 T field was carried out with Linkam DSC600 using heating/cooling speed of 2 K/min. Also, dynamic magneto-thermal cycling with rotating field of 0.3 T was studied, but this could not been carried out in DSC600 because of high background effect. The thermal cycles exceeded the transformation and Curie temperatures. In all the measurements, specimens were clamped to prevent their moving in the magnetic field.

3. RESULTS AND DISCUSSION

In Fig. 1, the magnetisation curves of the studied three alloys are presented. The magnetic properties and magnetic field induced strain of single crystalline Alloy **C** is described in [8]. Its peculiar behaviour during the first magnetisation cycle is presented in the Fig. 1c. Here, a large transient hysteresis is obtained in the first quadrant, since the originally nearly linearly increased magnetisation is suddenly risen at 280 kA/m up to saturation and staying saturated also while decreasing the field again towards the lower field, [8]. In Fig. 1a and 1b, this behaviour does not exist. Since the magnetisation jump in Fig. 1c is according to [8] connected to the rearrangement of the twins and thus the reorientation of the easy magnetisation axis along to the magnetic field, polycrystalline Alloys **A** and **B** should not be suitable for MSM. Further information obtained from these magnetisation curves is the coercivity that for Alloy **A** is higher (0.02 T) than for Alloy **B** (0.006 T). Also, the magnetic anisotropy constant of martensite (K_u) can be estimated for Alloy **B** to be between 1.5-2 $\times$ 10^5 J/m^3, as for Alloy **C** it was given to be 1.7 $\times$ 10^5 J/m^3 in [8].

The results of the straining in the magnetic field are presented in Fig. 2. The curve for Alloy **A** (Fig.2 a) is measured after three cycles of dynamic magneto-thermal cycling while the martensitic structure of the sample is quite random in optical study (Fig. 4). Here, the specimen starts to change at 0.4 T while being perpendicular to the field and it reaches the maximum shape change of 0.09 % while the field is approaching 1 T. The total shape change remains in the structure even when the field is removed. The same kind of behaviour occurs in Alloy **B** after three cycles of dynamic magneto-thermal treatment though the shape change is only 0.04 % (Fig. 2b). When the dynamic magneto-thermal treatment is continued till 13 cycle, the full recovery of the strain is obtained as the field is removed, even though the maximum shape change is then decreased to 0.02 % with 0.25 T field (Fig. 2c). However, odd behaviour occurs as the field is increased and the shape change recovers up to approximately 0.004 %. These small

values are connected to the polycrystalline structure of the studied alloys, while in single crystalline Alloy **C** even 5.1 % MSM-strains can be obtained (Fig. 2d, [12]). However, even Alloy **C** presents strains approximately 0.5 % in polycrystalline state, [13].

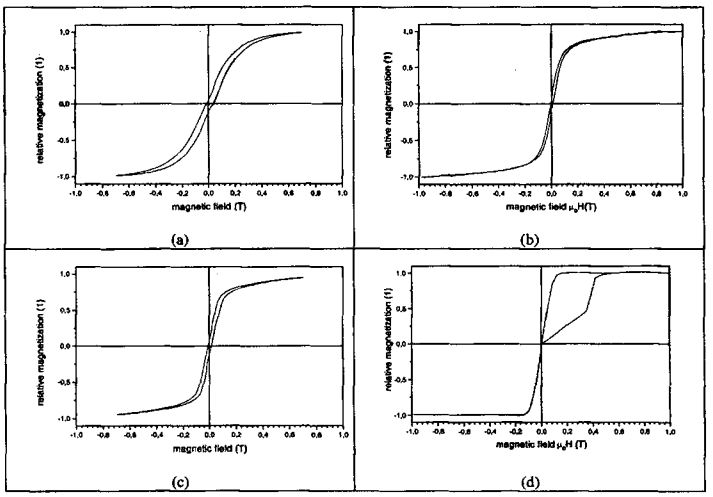

Fig. 1.
Magnetisation curves of the studied alloys.
(a) polycrystalline Alloy **A**,
(b) polycrystalline Alloy **B**,
(c) the same after 13 cycle and
(d) single crystalline Alloy **C**.

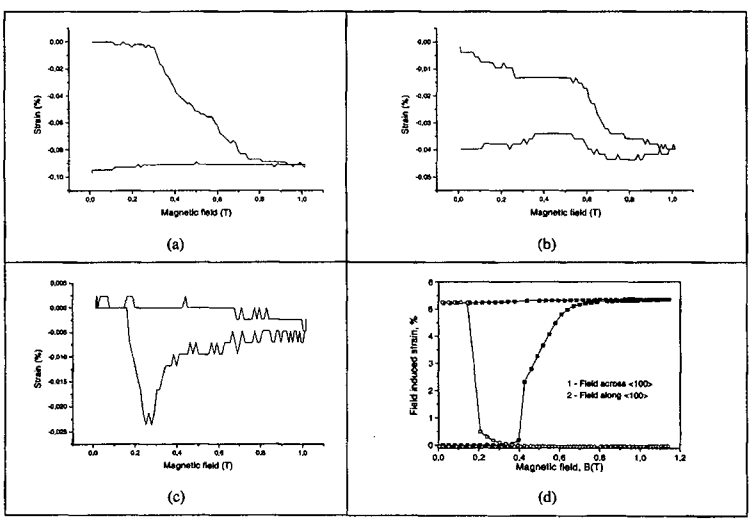

Fig. 2.
Straining of the alloys in the magnetic field:
(a) polycrystalline Alloy **A**,
(b) polycrystalline Alloy **B** after three cycle of dynamic magneto-thermal treatment,
(c) the same after 13 cycle and
(d) single crystalline Alloy **C**.

In Fig. 3, the θ–2θ-curves it is shown the structures of alloys in different stages. In Alloy **A** (Fig. 3a), the magneto-thermal cycling does not lead to increase of the martensite variant (004), instead this peak is decreased by the cycling. In Alloy **B**, the dynamic magneto-thermal cycling has changed the original martensite variants, {113} and {331}, to {220} and {333}, (Fig. 3b). In Alloy **C** after thermal (Fig. 3c) and magneto-thermal cycling (Fig. 3d), the clear change after cycling can be observed and especially the magneto-thermal cycling favours one martensite variant. The favouring of one martensite variant on the expense of the others leads to well oriented structure and better strains in magnetic field, [11].

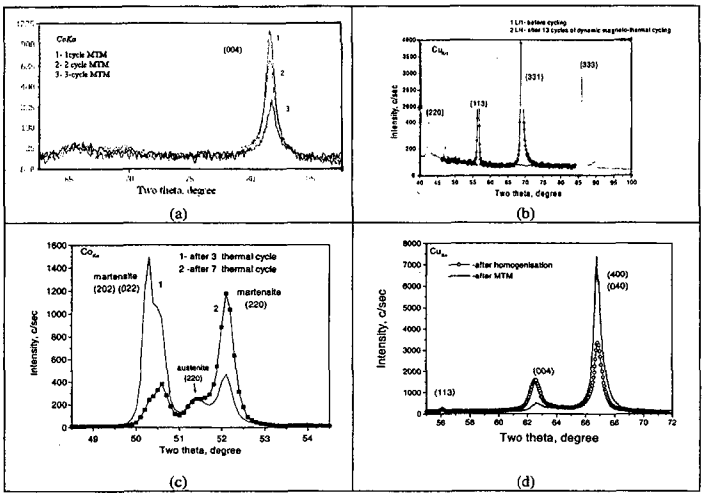

Fig. 3. θ–2θ-measurements:
(a) Polycrystalline Alloy **A** in magneto-thermal cycling,
(b) polycrystalline Alloy **B** in dynamic magneto-thermal cycling,
(c) and **(d)** polycrystalline Alloy **C** in thermal and magneto-thermal cycling.

Since the static magneto-thermal cycling did not have so profound effect to Alloys **A** and **B**, the dynamic magneto-thermal cycling was applied to them. However, even the dynamic magneto-thermal cycling is not really effective in Alloy **A** though some local oriented martensite areas could be spotted after three cycles and even after 35 cycle no greater improvement in the structure (Fig. 4) nor in the straining behaviour in applied magnetic field could be observed. This is in good agreement with the results of θ–2θ-measurement. In Alloy **B** already after two cycles the some martensite orientations become more favoured and after three cycles this structure produces the first macroscopic twin through the specimen (Fig. 4). But this very narrow twinned area does not give to the material desired reversible strain properties in magnetic field (Fig. 2b) and thus the dynamic magneto-thermal training was carried on up to 13 cycle. After this treatment, the width of the big twin area is approximately one third of the sample length. This area consists out of thin martensite structure (Fig. 4) which is also observed in [13] with Alloy **C**. Now, Alloy **B** is able to change its shape in applied magnetic field reversible (Fig. 2c).

The evolution of the transformation temperatures is observed during the thermal and static magneto-thermal cycling while they are carried out with the DSC. Transformation temperatures are chancing only little during the cycling. The major change occurred in thermal cycling of Alloy **B** where the martensite finish temperature is increased in such degree that the length of the martensitic transformation is diminished from 14 K down to 4 K.

Table 2: Effect of cycling to the transformation temperatures and the width of transformation. Values for cycling are the average values of different cycles (the temperatures remained quite stable after the first cycle).

		Without cycling (K)	Thermal cycling (K)	Magneto-thermal cycling (K)
Alloy **A**	M_s	384	384	384
	M_f	370	369	370
	A_s	376	376	376
	A_f	398	393	392
	M_s-M_f	14	15	14
	A_f-A_s	22	17	16
Alloy **B**	M_s	372	371	364
	M_f	358	367	354
	A_s	363	376	363
	A_f	379	381	371
	M_s-M_f	14	4	10
	A_f-A_s	16	5	8
Alloy **C**	M_s	301	301	302
	M_f	299	298	298
	A_s	310	308	308
	A_f	312	312	311
	M_s-M_f	2	3	4
	A_f-A_s	2	4	3

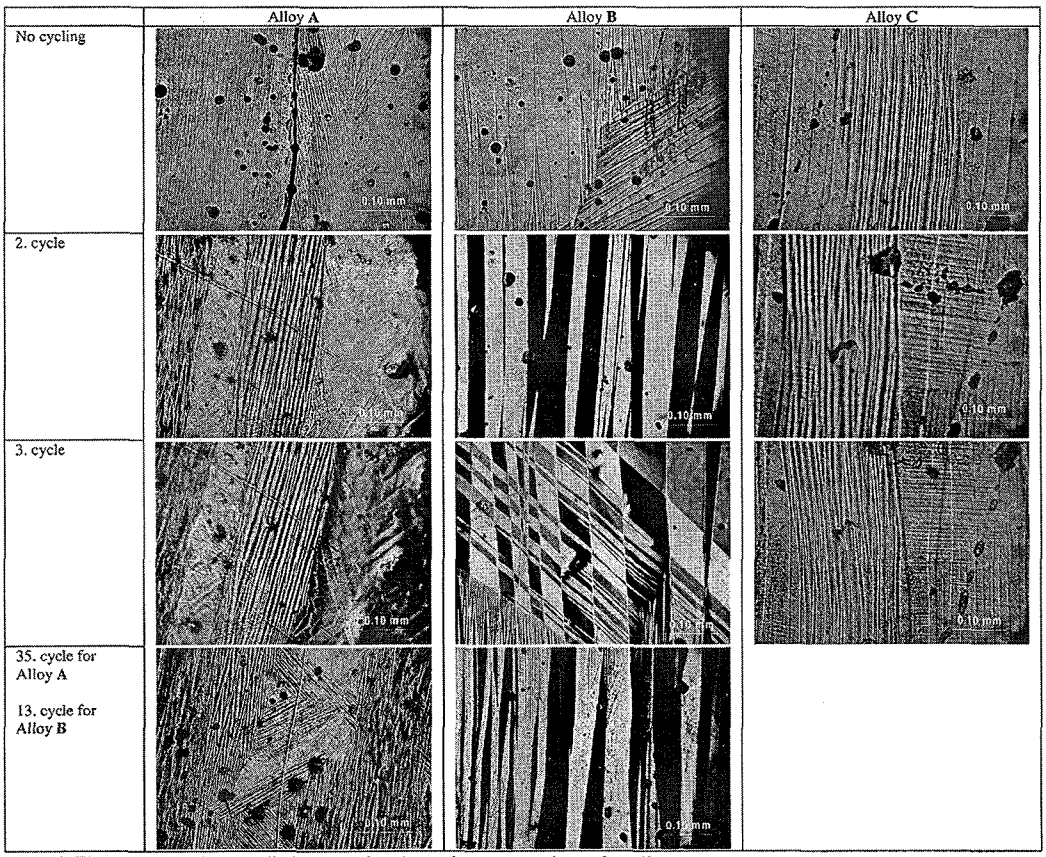

Fig. 4. The structure of the studied alloys after dynamic magneto-thermal cycling.

4. CONCLUSIONS

In the present study, three polycrystalline Ni-Mn-Ga alloys with different transformation temperatures and approximately the same Curie temperature are studied. One of the alloys, Alloy **C**, is used as a reference material as it has proved to be a good MSM-material already in the previous studies. In this alloy, the transformation temperatures are clearly below Curie point.

Here, it is presented that also Alloy **B** can show reversible, though small shape change in the magnetic field at ambient temperature. This is obtained after the dynamic magneto-thermal cycling where the transformation temperatures and Curie point are exceeded. In this alloy, these temperatures are very close to each other. It is also shown that the thermal cycling of this alloy decreases the length of the transformations from 14-16 K down to 4-5 K.

However, with Alloy **C** having transformation temperatures above Curie point, any reversible shape change in magnetic field could not be obtained even after different cycling procedures.

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