Magneto-mechanical behaviour of textured Polycrystals of NiMnGa ferromagnetic Shape Memory Alloys

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Abstract. Textured polycrystalline NiMnGa alloys were prepared by directional solidification. Alloys were chosen to have either the 7M or the 5M modulated martensitic structure after proper heat treatment. Mechanical training allowed to reduce the twin boundary pinning stress to below the magnetically induced stress. Thus, magnetic field induced changes in the mechanical behaviour could be demonstrated. The conditions of preparation and mechanical training will be discussed together with their influence on structure, microstructure, and the magneto-mechanical behaviour.

Introduction

Single crystals of NiMnGa show magnetic-field-induced strain (MFIS) due to twin boundary motion [1]. This effect is found in low temperature martensitic phases, which form from a cubic L2₁ phase arising upon cooling at around 750 °C. Prerequisites for MFIS are a uniaxial magnetic anisotropy and highly mobile twin boundaries [2]. Both features depend not only on composition but also on structure details on all scales. The goal of the present paper is to investigate the conditions under which magnetic field induced twin boundary movement can be achieved in polycrystalline NiMnGa. There are three different types of martensite which may exist in NiMnGa: Nonmodulated (NM) martensite with tetragonal symmetry and c/a>0, modulated martensite with five unit cells modulation length (5M) with tetragonal symmetry and c/a<0, and modulated martensite with seven unit cells modulation length (7M) and orthorhombic symmetry [3]. Only the modulated martensites (5M and 7M) have a uniaxial magnetic anisotropy and are capable to show MFIS.

Experimental

Master alloy ingots with a diameters of 15 mm were prepared by induction melting of the pure elements (Ni 99.98, Mn 99.8, Ga 99.999) in Ar atmosphere followed by casting into a cold copper mold. The mass loss was negligible, hence the composition is assumed to be the intended one. Pieces of those master alloys were remelted and cast into a preheated ceramic mold with a heat sink at its bottom. Thus, the solidification front moves upwards and a coarse-grained columnar structure arises with the [100] direction preferred along to the solidification direction. The obtained ingots are of 10 mm diameter and 50 mm length. Finally, electro-discharge machining was used to cut samples of the desired shape, e.g. cubes of 5 to 7 mm edge length from the ingots. Magneto-mechanical behaviour was characterized by a mechanical testing machine which was additionally equipped with a magnetic yoke. Structure was determined by XRD and microstructure was characterised by optical microscope and SEM (scanning electron microscope) with EBSD (electron backscatter diffraction). All structural features depend on preparation conditions. It could be shown that magnetic field induced strain in polycrystalline textured NiMnGa can be achieved.
Selection of Structure

In the NiMnGa System besides the cubic high temperature phase (austenite) three types of martensitic structures exist so called nonmodulated martensite (NM), modulated martensite with a period of 5 lattice cells (5M), and modulated martensite with a period of 7 lattice cells (7M). The NM martensite is of tetragonal symmetry with c/a ≈ 1.2. Its magnetic anisotropy is of the type easy plane. Therefore, this type of martensite is not suited for showing magnetic field induced strain (MFIS). The structures of the other martensites are tetragonal with c/a ≈ 0.94 for 5M and orthorhombic with c/a ≈ 0.9 for 7M. The magnetic anisotropies of these martensites is of the easy axis type, which is one prerequisite for MFIS.

According to the phase sequence upon cooling (cf. Fig. 1) the NiMnGa alloys in the region of interest solidify in a B2 structure with the Ni atoms at the centre of the cube and the Ga and Mn atoms distributed randomly at the cube corners. At around 740 °C the B2 structure transforms to a L2₁ (Heusler type) structure where the Ga and Mn atoms are no longer randomly distributed. Each atom species tends to be neighboured by atoms of the other species. It is to be mentioned that nearly all means to influence the microstructure of the martensite have to be applied at higher temperatures because these alloys cannot be cold deformed.

Preparation of 7M Martensite.

From a series of annealing experiments, it turned out that a thermal treatment of the as-cast sample in the sequence 12 h at 900 °C, 2 h at 700 °C followed by water quenching and a third annealing step for 24 h at 530 °C leads to the formation of the desired 7M martensite in a bulk sample. Fig. 2 shows the XRD pattern recorded from a slice that had been spark-eroded from the sample and thermally treated according to the above mentioned procedure. It

![Fig. 1: Transformation sequence upon cooling for NiMnGa alloys of the Ni₅Mn₃Ga type](image1)

![Fig. 2: Influence of final annealing on the martensite type of Ni₅₀Mn₃₀Ga₂₀](image2)

![Fig. 3: XRD spectrum of Crushed Ni₅₀Mn₃₀Ga₂₀ in the as crushed state.](image3)

had turned out that neither the second annealing step at 700 °C nor the water quenching is essential for the formation of the 7M phase. Rather the last final annealing step had proven to be mandatory.
in order to promote the formation of the 7M phase. If the bulk sample is crushed to powder a transformation of the 7M martensite to NM martensite (Fig. 3) is observed. Recovery to practically single-phase 7M martensite was achieved after annealing at 600 °C for 14 h (Fig. 4). Therefore, we assume that the transformation of the 7M martensite to NM martensite is stress induced [4].

**Preparation of 5M Martensite.** According to Lanska et al. [5] a lower valence electron number per atom favours the formation of the 5M martensite (cf. Fig. 5). Therefore, we changed the composition from Ni₅₀Mn₃₀Ga₂₀ with e/a = 7.70 to Ni₅₀Mn₂₉Ga₂₁ with c/a ≈ 7.66. It turned out that the martensite is of 5M structure for this composition nearly independent on the thermal treatment.

**Preparation of Austenite.** As mentioned above nearly all technological means to influence the microstructure have to be applied in the austenitic state. Therefore, we prepared samples which are cubic at room temperature in order to be able study the influence of preparation on microstructure without passing the austenite – martensite transformation [6, 7]. The composition Ni₄₈Mn₃₀Ga₂₂ with T_{mart} ≈ -5°C fulfils these requirements.

**Changing the Microstructure**

**As cast Microstructure.** The principle of the experimental set up is displayed in Fig. 6. A hot mold is mounted on a cooling copper plate. To avoid heating of the cooling plate by the hot mold, an insulation ring is placed between the mold and the plate. When the melt is cast into the mold, a temperature gradient and thereby a heat flow through the melt toward the bottom is generated, which causes a directional solidification in opposite direction. The texture is supposed to occur along the direction of the heat flow,

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**Fig. 4:** Crushed Ni₅₀Mn₃₀Ga₂₀ after annealing at 600 °C for 14 h

**Fig. 5:** The relation between composition, c/a-ratio, and martensite type (data taken from [5]).

**Fig. 6:** Principle of directional solidification, q: direction of heat flow, d: direction of solidification

**Fig. 7:** Influence of the mold temperature on the as-cast microstructure. The given mold temperatures are at begin of the casting process.
preferentially in [100] direction [8]. The influence of various casting and annealing parameters was demonstrated in [9]. The influence of different mold temperatures on the as-cast microstructure can be seen from the optical micrographs in Fig. 7. Four different regions of the microstructure of the samples can be distinguished. In the first very narrow zone at the bottom of the mold fine almost globular grains are observed. This is due to the high cooling rate at the beginning of the solidification. In this region also a grain selection takes place. In the second zone columnar grains can be seen. The size of this zone depends on the casting parameters, especially the mold temperature. With increasing mold temperature the area of elongated grains becomes larger. At the top of this zone a conical region can be seen, where in the centre still columnar grains can be observed whilst globular grains are on the rim of the sample. There the solidification direction changes gradually from unidirectional (to the copper plate) to radial (to the mold). Above this cone in zone 3 all the grains are globular. In the fourth zone sink holes and other cavities due melt shrinkage are observed.

**Effect of Annealing.** Annealing at 1000 °C for 48 h in Ar-5% H₂ atmosphere causes grain coarsening and homogenization cf. Fig. 8. In the DSC curves in Fig. 8 the transformation peaks become sharper after the annealing process. This is due to homogenization, stress relaxation and possible ordering during cooling. Is to be mentioned that the martensite transition temperature does not vary for small samples taken along the direction of solidification [9]. This demonstrates, that the chemical composition of the ingot does not vary significantly along its length. EBSD measurements on annealed samples showed, that the columnar grains are preferably aligned along the direction of solidification with an [100] axis.

**Mechanical training and magneto-mechanical response**

**Mechanical training.** Plastic deformation of martensitic NiMnGa alloys by dislocation movement is not possible. Dislocation movement is hampered strongly due to atomic ordering and the low crystal symmetry of these alloys. Therefore, the main source of plastic deformation observed in such alloys is the movement of twin boundaries. Magnetic field induced strain (MFIS) in ferromagnetic shape memory alloys is also a result of twin boundary movement in the special case as a result of an external magnetic field. Thus, plastic deformation provides information about the mobility of the grain boundaries. Furthermore, it is expected, that cyclic plastic deformation increases the mobility of the twin boundaries.

Cubes of 5 to 7 mm edge length were cut from the columnar region of directionally solidified and annealed ingots. Such cubes were cooled through the martensitic transformation under 30 MPa load. A strain of typically 1–2% is achieved by this procedure which means that many twins remained in the sample, since a detwinned sample would cause a strain of $\varepsilon_{\text{trans}} = 5\%$ during the martensitic

![Fig. 8: Microstructure and DSC curves of the as-cast (left) and the annealed sample (right).](image-url)

![Fig. 9: EBSD picture of a sample (right) and histogram (left) with the orientations of grains of the marked area.](image-url)
transformation \((\varepsilon_{\text{trans}} = 1 - \frac{a_{\text{aust}}}{c_{\text{mart}}})\). The samples were successively compressed along all three axes in order to cause maximum deformation. This means a sample that was compressed along axis 1 is pressed along directions 2 and 3, before the next compression along axis 1 is performed. (Fig 10). The influence of successive training is given in Fig.11 for a 7M martensite [10]. For clarity, only the curves of compression along one direction are displayed in Fig. 11. A clear effect of the training can be observed. The residual strain increases to 8%, which is rather close to the crystallographic strain limit \(\varepsilon_{\text{max}} = 1 - c/a \approx 10\%\). It becomes also evident that most of the strain is produced at comparably small loads. However, the strain at 2 MPa, which is approximately the stress an external magnetic field can generate [11], is very low.

The effect of training a 5M martensite is given in Fig. 12. Training of the 5M martensite is much more efficient. It is possible to apply a large number of training cycles without any harm to the samples. The maximum stress which can be generated by a magnetic field is about \(\sigma_{\text{mag,max}} \approx 2.6\) MPa for the 5M martensite. This value is higher than the corresponding value of the 7M martensite due to the lower crystallographic strain of the 5M martensite which is \(\varepsilon_{\text{max}} = 1 - c/a \approx 6\%\). There is a considerable large amount of strain at stress values smaller than \(\sigma_{\text{mag,max}}\) for the 5M martensite. Therefore, we can expect an effect of a magnetic field on the stress – strain curve of such samples.

**Magneto-mechanical response.** Trained samples of the 5M martensite were subjected to mechanical testing with and without a magnetic field. The axis of the magnetic field was perpendicular to the axis of the mechanical load. The axis of the columnar grains was parallel to the load axis. I turned out, that there is a considerable influence of the magnetic field on the mechanical
behaviour. Fig. 13 shows unloading curves for a sample made from trained 5M martensite. The initial load was 2 MPa and the strain upon stress release was recorded. The strain observed during stress release with a magnetic field of 0.7 T is about 0.5 % larger than the strain observed when no magnetic field is applied. Thus, a MFIS of 0.5 % was found for the trained 5M martensite.

Summary

Magnetic field induced strain was demonstrated for a textured polycrystalline Ni_{50}Mn_{29}Ga_{21} alloy with 5M structure. In order to achieve this, structure and microstructure have to be adjusted. Furthermore, mechanical training was applied to reduce the twinning stress to a level which is lower than the stress which can be exerted by a magnetic field.

Texture was achieved by directional solidification. A large grained columnar microstructure with a fibre texture developed this way. Homogenization and stress relief was achieved during annealing at 1000°C/48 h. The bottom of the ingot had to be removed in order to prevent giant grain growth and loss of the texture.

Mechanical training of cubic samples was performed by compressing along all three axes successively with various loads. It was not possible to achieve magnetic field induced strain in NiMnGa with 7M structure.

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References