Influence of grain size and training temperature on strain of polycrystalline Ni$_{50}$Mn$_{29}$Ga$_{21}$ samples

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Abstract. The alloy Ni-Mn-Ga aroused great interest for application as a magnetic shape memory (MSM) material. This effect is caused by reorientation of twin variants by an external magnetic field. So far, most of the experiments were concentrated on single crystals. But, the MSM effect can also be realised in polycrystals which can be prepared much more efficiently. Here, polycrystalline samples were prepared by directional solidification with a <100> fibre texture of the high temperature cubic austenitic phase parallel to the heat flow. Afterwards, a heat treatment was applied for chemical homogenisation and stress relaxation in the austenitic state. Then the samples were heated up to the austenitic state and cooled down under load. The microstructure was analysed by Electron Back Scatter Diffraction (EBSD) before and after that treatment. Mechanical training at room temperature and 40°C was tracked by recording stress-strain curves. By increasing the number of training cycles the strain also increases. The influence of different training temperatures was investigated on samples with different grain sizes.

1. Introduction

In recent years Ni-Mn-Ga magnetic shape memory alloys with a chemical composition close to the stoichiometric composition Ni$_2$MnGa have attracted increasing attention due to their large magnetic-field-induced strain (MFIS) of up to 10%. This strain which is produced by twin boundary motion in the martensitic phase due to a magnetic field was demonstrated for the first time in 1996 by Ullakko et al. [1]. These materials can be used in sensors and actuators [2, 3]. Most studies reporting on MFIS in such alloys were performed on single crystals [4 - 7]. Polycrystalline samples are of great interest because they can be produced easier and for this reason they are cheaper. Usually polycrystalline samples have a low strain and a high twinning stress because of their differently oriented grains with varying microtwin orientation. The twinning stress is defined by the start of the movement of twin boundaries under load. Polycrystalline samples with a highly textured microstructure and coarse grains are close to single crystals. Such highly textured polycrystalline Ni-Mn-Ga samples were achieved by directional solidification in previous work [8]. Recently a residual strain of 2% was achieved after a maximal load of 40 MPa [9]. Polycrystalline Ni-Mn-Ga with addition of Si, In, Co or Fe was used to vary the transformation temperatures. But single crystals were prepared for investigation of the MFIS [10]. However, polycrystalline Ni-Fe-Ga samples...
show a residual strain of more than 2.4% after a load of about 300 MPa. But no MFIS is reported for these alloys [11].

In order to find MFIS by twin boundary motion, the magnetically induced shear stress must be larger than the twinning stress [7]. The magnetically induced stress is given by \( \sigma_{mag} = m \cdot K_u \cdot s^{-1} \), with the Schmid factor \( m \), the magnetocrystalline anisotropy constant \( K_u \) and the twin shear \( s = 0.5 \left( \frac{a - c}{c} \frac{a}{c} \right) \), where \( a \) and \( c \) are the lattice parameters of the martensite [4, 12, 13]. Mechanical training is effective to increase the strain and to reduce the stress for twin boundary motion in polycrystals. The influence of mechanical training on the stress – strain relationship in martensitic polycrystalline Ni\(_{50}\)Mn\(_{30}\)Ga\(_{20}\) has been shown by Gaitzsch et al. [14]. The influence of the magnetic field on the stress – strain behaviour was reported by Gaitzsch et al. [13].

The structure of Ni\(_{50}\)Mn\(_{29}\)Ga\(_{21}\) alloys is pseudo tetragonal in the martensitic state (5M) at room temperature and cubic in the austenitic state above the \( A_f \) – temperature (~60°C) [15]. The Curie temperature is approximately 100°C.

This paper presents stress-strain curves from samples with different grain sizes (hot mould cast samples and Bridgman samples). Furthermore stress-strain curves with training at 20°C and 40°C will be shown. The microstructure of samples with different grain sizes will be evaluated for the initial state and after compression along the solidification direction. The orientation of the c-axes of the various twins will be investigated for the initial state and after compression.

2. Experimental

The polycrystalline shape memory alloy Ni\(_{50}\)Mn\(_{29}\)Ga\(_{21}\) was melted inductively and cast into a hot cylindrical ceramic mould with a cold copper plate at the bottom. With this method it is possible to achieve a coarse-grained and a textured microstructure by directional solidification [8]. To achieve homogenisation the samples were annealed for 48 h at 1000°C under Ar/5 % H\(_2\) atmosphere. Cubic samples with an edge length of 5 mm were cut by spark erosion. One edge of the cube is parallel to the direction of solidification which is preferably a [100] axis of the cubic high temperature phase (austenite). Afterwards, the samples were annealed for 14 h at 600°C to relieve stress. This procedure had been shown to be effective by Gaitzsch et al. [16]. The next step was grinding and polishing to achieve plane and parallel surfaces. Besides the production of these hot mould cast samples, we also produced polycrystalline samples using a modified Bridgman technique. The alloy was withdrawn from the heat zone with a growth rate of 100 mm/h. The drawing direction defines the growth direction. The ingot has a diameter of 10 mm. Samples with a size of 5x5x5 mm³ were cut out erosively. The grains of the Bridgman samples and the hot mould cast samples have a diameter of 1 to 3 mm and 0.2 to 0.5 mm perpendicular to the solidification direction, respectively. The grains extend along the whole sample parallel to the direction of solidification. These polycrystalline samples were compressed along the 3 principal axes of the cube (3 compressions are 1 cycle). The properties of the samples with different grain sizes were investigated.

The microstructure was analysed by scanning electron microscopy (SEM) and the orientation of the grains was determined by electron backscatter diffraction (EBSD) with a step size of 18 \( \mu \)m.

3. Results and discussion

The microstructure of a hot mould cast and a Bridgman sample is shown in Fig. 1 for the initial state and after compression. The microstructure was characterised by EBSD after grinding and polishing. Fig. 1(a) shows the microstructure of a typical hot mould cast sample in the initial state. The orientation distribution of the c-axes of a hot mould cast sample after compression is shown in Fig. 1(c). Both figures show the same area of the sample. The grain diameter of the columnar grains is about 0.2 to 0.5 mm of the hot mould cast sample. For comparison the Bridgman sample has a grain diameter of 1 to 3 mm. The red lines in the EBSD image (colour online) indicate the grain boundaries of the parent austenitic phase. The grey scale symbolises the orientation of the c-axes in the grains and
variants. The angles between the c-axis and the growth direction are indicated by the shade of grey from black (c-axis parallel to growth direction) to light grey (c-axis perpendicular to growth direction) as given in the legend. White areas are not indexed. The relative frequency versus deviation of the angle between the c-axis and the solidification direction is shown in Fig. 1(b). The amount of variants with c-axes within a cone of 30° around the solidification axis was calculated from the area under the histogram curve (marked red in Fig. 1(b) and (d)). For the hot mould cast sample the fraction of the c-axes in this cone is 4.9 % in the initial state. Afterwards, the sample was compressed with 20 MPa along the growth direction (Fig. 1(c)). This compression was realised by cooling under load (c.u.l.) which means heating up the sample to the austenitic state, compressing with 20 MPa and cooling down to room temperature and then releasing the stress. The view is along the growth direction which is also the compression direction. The relative frequency versus deviation (Fig. 1(d)) shows that after c.u.l. 46.5 % c-axes are orientated within this cone. During this procedure variants with c-axis close to the compression axis grew at the expense of others.
Fig. 1: hot mould cast sample (grain size 0.2 to 0.5 mm): a) Microstructure of the initial state. c) Microstructure after cooling under load with 20 MPa load along solidification direction. e) Microstructure of the initial state. g) Microstructure after cooling under load with 20 MPa load along solidification direction. b), d), f) and h) Histogram of c-axes deviation from 0° to 90°. The amount of c-axes within a cone of 30° around the solidification (=compression) direction is marked red (colour online). The angle between the c-axes and the growth direction is indicated by the shade of grey from black (c-axis parallel to growth direction) to light grey (c-axis perpendicular to growth direction) as given in the legend. Bridgman samples (grain size 1 to 3 mm):

The microstructure of the Bridgman sample in the initial state with a grain size of 1-3 mm is shown in Fig. 1(e). The relative frequency as a function of the deviation (Fig. 1(f)) shows that only 4.5 % of the c-axes align within a cone of 30° in solidification direction. Thus, the c-axes fraction in solidification
direction is equal and low in the initial state for the hot mould cast sample and the Bridgman sample. The sample from Fig. 1(e) was compressed by cooling under load (c.u.l) with 20 MPa in solidification direction (Fig. 1(g)). Fig. 1(e) and (g) show nearly the same area of the sample. Also in this case the view is along the growth direction which is also the compression direction. After compression, 89.4 % c-axes align in compression direction (0°-30° in Fig. 1(h)). The fraction of the c-axes in solidification direction increases significantly after compression in solidification direction.

Fig. 1(c) and Fig. 1(g) illustrate the effect of a compression which occurred with cooling under load at the same temperature and with the same stress of 20 MPa. The important difference between both samples is the grain diameter. With larger grains more c-axis can be aligned in compression direction.

![Stress-strain curves](image)

**Fig. 2:** Stress-strain curves of: a) hot mould cast and Bridgman samples at room temperature without cooling under load (c.u.l). b) Bridgman samples at room temperature with and without c.u.l. c) Bridgman samples with c.u.l. at room temperature and at 40 °C. The maximal stress that can be achieved with a magnetic field is 2.6 MPa.

The comparison of the stress-strain curves of the hot mould cast and Bridgman samples, with and without cooling under load and at room temperature or at 40 °C is shown in Fig. 2. These stress-strain curves are measured after the 5th training cycle along the solidification direction. Here, successive compressions along the 3 principal axes of the cube are one cycle. Fig. 2(a) shows stress-strain curves of a hot mould cast (black) and a Bridgman sample (grey) at room temperature without cooling under load. The residual strain of the hot mould cast sample and the Bridgman sample was determined to be 1.8 % and 2.7 %, respectively. That means larger grains result in higher strain. Fig. 2(b) shows stress-strain curves of Bridgman samples at room temperature without cooling under load (black) and with
c.u.l. (grey). Because of cooling under load the residual strain is 5.6 % compared to 2.7 % for without c.u.l. The use of cooling under load at the beginning of the training process results in a larger residual strain and a lower slope. This c.u.l. was applied only once at the beginning and only along solidification direction. The grey curve shows a pronounced plateau which is due to twin boundary motion. Fig. 2(c) shows stress-strain curves of Bridgman samples with cooling under load at room temperature (black) and at 40 °C (grey). During training at 40 °C a smaller residual strain of 4.0 % is observed than during training at 20 °C with a residual strain of 5.6 %. But the level of the plateau of the stress-strain curve is much lower at 40 °C than at 20 °C. The maximal stress that can be achieved with a magnetic field is 2.6 MPa, therefore a MFIS of ~4.5% could be expected in the Bridgman sample with c.u.l. and trained at 40°C. That means the use of c.u.l. at the beginning of the training process and training of the sample at 40 °C results in a lower stress level. This corresponds to the results of Heczko and Straka who found that the stress to move twin boundaries and the strain decrease with increasing temperature below the martensitic transformation in single crystals [17]. This effect is due to the temperature dependence of the c/a ratio which increases with increasing temperature [18, 19]. Larger grains cause higher strain because of easier twin boundary movement which results in preferred orientation of the c-axes in compression direction.

4. Conclusion
Polycrystalline Ni$_{50}$Mn$_{29}$Ga$_{21}$ samples with good MSM properties were achieved by directional solidification. The fraction of the c-axis in growth direction before and after compression were analysed by EBSD. The stress-strain curves give the following conclusions:

- Larger grains and cooling under load (i.e. heating up the sample to the austenitic state, compress the sample and cool it down to RT while compressed) result in a longer plateau of the stress-strain curve. Thus, higher MFIS can be expected for such samples.
- At higher temperatures a lower twinning stress is achieved, which is necessary to obtain high MFIS. Furthermore, training at higher temperatures is expected to reduce the risk of cracks.

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