Production and characterization of large single crystals made of ferromagnetic shape memory alloys Ni-Mn-Ga

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Abstract

Ferromagnetic shape memory alloys (MSMA) are well-known smart materials for actuation applications, due to their large shape change in applied magnetic fields. Off-stoichiometric Ni-Mn-Ga single crystals of MSMA exhibit a magnetic-field induced strain of about 10%. In the past decade a lot of effort has been put into understanding and optimizing the properties of Ni-Mn-Ga alloys in terms of the magnetic shape memory effect, starting with the production of single crystals and going all the way to heat treatment and magneto-mechanical training.

Here we focus on and present the production and characterization of single crystal Ni-Mn-Ga alloys with off-stoichiometric composition. The molten material was cast into preheated ceramic shells and directionally solidified in a Bridgman-type process. Cylindrical single crystal bars of diameters up to 48 mm and a length of 110 mm were obtained by using suitable grain selectors. Only small misorientations between the single crystal c-axis and the bar axis were found in these bars. The crystals were characterized in terms of composition, segregation, crystal orientation and microstructural features by means of SEM/EDS, EBSD and light microscopy.

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1. INTRODUCTION

Ferromagnetic Ni-Mn-Ga shape memory alloys (MSMA) display the largest shape changes of all known magnetic Heusler alloys, with magnetically field induced strains (MFIS) reaching 10% [1]. The magnetic shape memory effect is accompanied by a rearrangement of the low-temperature twinned martensite under the magnetic field. The twin structure is formed in a structural transition from a high-temperature austenitic cubic phase to a martensitic low-temperature phase with orthorhombic or tetragonal crystal structure, depending among other things on composition [2]. The large MFIS combined with elevated transition temperatures (>50°C) and fast change
frequencies make these materials promising candidates for actuator and sensor applications. Single crystalline materials were reported to display higher magnetically field-induced strains than polycrystalline materials [3]. Obtaining oriented, or single crystals from Ni-Mn-Ga alloys was attempted by directional solidification using zonemelting [4] and Bridgman techniques [5, 6], but was limited to laboratory scale production and to small sample size. Here we report on the production of large single crystals from Ni-Mn-Ga alloys using an industrial-scale Bridgman furnace and adequate melting, investment casting and solidification conditions. We describe the microstructure of the as-solidified and heat treated material in terms of solidification morphology, segregation and crystal orientation.

2. BRIDGMAN SOLIDIFICATION FOR PRODUCTION OF SINGLE CRYSTALLINE NI-MN-GA

Ni-Mn-Ga alloys were molten, cast and directionally solidified in a Bridgman furnace type VIM-IC 5-S build by ALD Vacuum Technologies. The process encompasses inductive melting of the elemental mixture, casting into a ceramic shell mould and directional solidification at constant withdrawal velocity, as described below:

Ceramic shell moulds were custom-made using the lost wax method, common to investment casting. They consist of alumina and encompass a feeding system as well as cavities to be filled with the liquid alloy. Different shell mould designs were used, aiming to realize four to six cylindrical cavities of different diameter in the range of 20 to 48 mm, while keeping the height constant at 110 mm. Each cavity had a grain selector at the bottom. Depending on the shell mould design, the amount of melt required varied between 3 and 6 kg, resulting in individual bar volumes between 35 and 200 cm³ and corresponding weights between 0.27 and 1.6 kg. Fig. 1a displays a ceramic shell mould equipped with thermocouples type B ready for mounting on the chill-plate of the Bridgman furnace. Fig. 1b shows an example for an as-solidified single crystal bar as extracted from the cavity after processing.

For inductive melting, weighted amounts of Ni, Mn and Ga (with purities >99.9%) were introduced as small pieces into a clean alumina crucible that is placed inside the induction coil system of the Bridgman furnace. After several cycles of vacuum pumping and Argon flushing (Ar4.8) inductive melting was performed under Argon atmosphere of 0.6-0.7 bar. This allowed minimizing evaporation of elements from the superheated liquid. The temperature of the melt was monitored at the top surface of the melt pool by a pyrometric system. After a sufficient homogenization time the superheated melt was cast directly into the preheated ceramic shell mould. When pouring the melt into the preheated shell mould a small amount of liquid solidified directly on the chill plate, leading to a thin, polycrystalline layer present at the onset of the directional solidification process.

Fig. 1: (a) Example of a custom-made ceramic shell mould for directional solidification of six cylindrical bars (three of them are visible) with diameters from 20 to 40 mm. The shell mould was equipped with thermocouples type B for temperature recording. (b) Ni-Mn-Ga single crystal bar with 25 mm diameter.
To achieve directional solidification of the liquid alloy, the shell mould was withdrawn from the heating zone with a constant velocity of typically a few mm/min within an axial gradient of some K/cm. The polycrystalline solidification front of the austenitic primary phase starts from the chill-plate layer, enters the grain selector and ideally leaves the selector as a single grain. This single austenitic grain ideally grows with dendritic morphology throughout the entire cylindrical bar. Further cooling of the as solidified material leads to a multivariant martensitic microstructure. The temperature profile in a bar during directional solidification was obtained by means of thermocouples, inserted into the bars edge (Fig. 1a).

3. MATERIALS CHARACTERIZATION

Each solidified bar was marked with a small groove, engraved by spark erosion along the entire length. The groove serves as position marker throughout subsequent processing steps. From both ends of the bars slices of some millimeter thickness were cut by water jet or spark erosion for materials characterization. The slices were metallographically prepared for macro- and microsegregation measurements by energy dispersive x-ray analysis (SEM/EDS) and for crystal orientation measurement by electron backscatter diffraction (EBSD). EDS was performed in an SEM type Gemini 1550 equipped with the INCA Oxford analysis system. EBSD measurements were carried out in an SEM type 1540 XB equipped with a Nordlys detector and INCA-Crystal. Finally, the slices were etched for microstructure observations using light microscopy.

3.1 CRYSTAL ORIENTATION

With few exceptions all solidified bars were single crystals, with a multivariant (2-4 variants) martensite microstructure in the as-solidified condition. If present, grain boundaries are easily detected on the surface of etched metallographic specimens. Indeed, if the diameter of the bars exceeds 40 mm, few additional grains are likely to occur at the bottom end of the bars (Fig. 2a/b). In most cases they are outgrown during the directional solidification process, as shown in Fig. 2c.

Fig. 2: As-solidified grain- and microstructure of 40 mm diameter Ni-Mn-Ga sample showing mostly single-crystalline structure (90%) within bottom slices (a/b) with additional small grains at the edges. (c): During Bridgman growth a complete single crystal is resulting from the bar, as shown in Fig. 2b.

The single crystalline solidification structure, common to $\varnothing$ 20 up to $\varnothing$ 30 mm bars is shown in the transverse section through an as-solidified bar (Fig.3a). The solidification morphology is dendritic and the primary dendrite arm spacing ranges around 540 µm. The growth direction of the primary solidification phase cannot be measured as such; one can however measure the crystal orientation of the martensite variants. This was done by EBSD for a series of six bars with 7M modulated martensite, using the orthorhombic crystal structure, close to [7] (space group Fmmm, no. 69, lattice parameters $a=6.14\,\text{Å}$, $b=5.79\,\text{Å}$, $c=5.51\,\text{Å}$). Figs. 3b shows \{100\} pole figures obtained by...
EBSD-mapping on transverse sections through the bars. Colours represent the different martensite variants identified within the mapping areas of about 500x500 µm², each. Taken together, the variants from one map represent the orientation of the cubic, parent phase. The six pole figures allow concluding that the cubic parent phase grows fairly well aligned to the longitudinal axis of the bars (sample normal), with inclination angles between [001] and the sample normal being smaller than 10°.

Fig. 3: Transverse section through a directionally solidified bar with 25 mm diameter showing the dendritic solidification morphology revealed by etching (a). The crystal orientation of orthorhombic martensite variants was measured by EBSD in six different bars. The measurements were performed on transverse sections, with the sample normal being parallel to the longitudinal axis of the bars. The {100} pole figures of the orthorhombic martensite variants (b) demonstrate the good axial alignment of the cubic parent phase.

3.2 MACROSEGREGATION

EDS measurements were performed along the diameter of directionally solidified bars, aiming to check, if macrosegregation is present. EDS spectra were acquired from measurement areas of 3 mm², successively placed along the diameter of the bars. The spectra were quantified using pure element standards. The measured concentration profiles for Mn and Ga are displayed in figs. 4 for bars of 20, 30 and 40 mm, respectively.

Fig. 4: Concentration profiles of Mn and Ga along the diameter of directionally solidified bars of different diameter. Ni-content is given by the difference of both Mn- and Ga-content to 100 at%.

In ⊙ 20 mm diameter sample no significant macrosegregation is observed, while a deviation from average is found for bars with diameter larger than 30 mm. This local segregation on the mesoscale (some mm) is most prominent in the Mn-profile. While its origin is not clear, heat treatment is able to reduce the differences largely, as shown in the next section. The average chemical composition throughout the complete series of bars from this batch reads Ni49.8Mn28.8Ga21.4 at%. Differences between element contents in bottom and top slices of the as solidified
material are within ± 0.6 at.%.

3.3 MICROSEGREGATION

To capture the microsegregation inherited from solidification, a statistic analysis method was chosen, known as grid measurement technique [8,9]. This method involves point-wise EDS measurements from a statistically significant number of individual measurement points. Commonly, these points are spaced within a measurement grid. Fig. 5a shows the grid used here, covering several dendrites in an area of about 750×700 µm, the grid spacing being 25 µm. Figure 5b/c shows the statistic evaluation of microsegregation for both, the as-solidified and heat treated material, represented as composition plots vs. the cumulative fraction of measured data-points. To obtain these plots, all EDS data were ranked following weighted interval rank sorting [9]. The plots show that Mn and Ga segregate inversely, e.g. areas with low Mn-content show high Ga-content and vice versa. The Mn-poor and Ga-rich compositions correspond to former dendrite core regions, while Mn-rich and Ga-poor compositions are found in former interdendritic regions.

![Grid Measurement Technique](image)

Fig. 5: Microsegregation was measured for material in the as-solidified and heat treated condition using the grid measurement technique. An EDS grid (a) contained 400 to 800 single measurement points. Heat treatment is carried out using a high temperature homogenization period, followed by an ordering process at approximately 750°C.

The microsegregation in the as-solidified material is pronounced, but heat treatment leads to an effective homogenization.

4. SUMMARY AND CONCLUSIONS

An industrial scale Bridgman furnace was used to produce single crystalline bars for different NiMnGa alloys. Alumina-based ceramic shell moulds with integrated grain selectors were used to cast and solidify cylindrical bars of different diameter, ranging from 20 to 48 mm. The analysis of the solidified material encompassed light microscopy observations as well as EDS and EBSD measurements and allowed concluding:

- Up to diameters of 30 mm the bars solidify as single crystals and transform to multivariant martensite during cooling to room temperature. During solidification, the cubic primary phase grows with the [001] direction well aligned to the longitudinal axis of the bars. The misorientation angles are below 10°, independent on the bar diameter.
- For diameters larger than 40 mm, small additional grains form at the bottom end, mainly at the periphery of the cylindrical samples. In most cases they were observed to be outgrown during directional solidification.
Axial or radial macrosegregation is negligibly small, irrespective of the bar diameter. The meso- and microsegregation that develops at the scale of the (several) dendrites is significant, but it can be homogenized during heat treatment. No detrimental effects of microsegregation on the evolution of the martensitic structure have been observed so far.

No differences could be observed between as-solidified and heat-treated material concerning average composition and grain orientation.

To our knowledge these bars are the largest single crystals produced so far from Ni-Mn-Ga alloys. The results are more than encouraging. The Bridgman process offers room for further optimization, as to reliably eliminate additional grains even in bars with diameter larger 40 mm. The process is robust and well suited for production of MSMA material for actuator applications.

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