A Novel Thermo-Mechanical Processing Route Exploiting Abnormal Grain Growth in Heusler-Type Co–Ni–Ga Shape Memory Alloys

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Heusler-type Co–Ni–Ga shape memory alloys attracted significant scientific attention owing to excellent superelasticity in single-crystalline state. However, due to pronounced anisotropy, polycrystalline Co–Ni–Ga suffers from transformation-induced constraints at grain boundaries and, thus, premature failure upon thermo-mechanical loading. The present study reports on a novel thermo-mechanical processing route. Hot rolling followed by solution-annealing promotes abnormal grain growth, eventually leading to high-performance single-crystalline structures. The procedure proposed offers great potential for a direct microstructure design.

HEUSLER-TYPE Co–Ni–Ga shape memory alloys (SMAs), undergoing martensitic transformation (MT) from cubic austenite (B2) to tetragonal martensite $(L1_0)$,[1] have gained attention due to their outstanding functional properties in single-crystalline state. A huge superelastic (SE) temperature range from ambient temperature up to 500 °C and excellent functional stability up to 100 °C have been reported in both compression and tension.[2,3] Polycrystalline Co–Ni–Ga, however, commonly suffers premature cracking upon thermo-mechanical processing and/or cycling,[4,5] eventually hindering any industrial application. In microstructures with random texture, the pronounced anisotropic transformation behavior leads to transformation-induced constraints at grain boundaries (GBs) between unfavorably oriented neighboring grains. Even a grain boundary engineering approach by precipitation of the highly ductile secondary γ-phase (A1) along the GBs is not capable to sufficiently accommodate such grain constraints upon MT and, thus, to fully prevent early fracture.[4,6]

Microstructures avoiding grain constraints are the key to decrease the susceptibility of anisotropic SMAs toward cracking. In two recent studies, a novel thermo-mechanical processing route[7] and fabrication via additive manufacturing (AM)[8] were proposed in the Co–Ni–Ga system for designing favorable polycrystalline microstructures with superior damage tolerance. Hot extrusion followed by a post-process heat treatment allowed introducing so-called bamboo-like structures, i.e., oligocrystals, being characterized by the absence of GB triple junctions and a minimal GB area.[7] In particular, GB triple junctions have been identified as the most detrimental microstructural feature, leading to transformation-induced stress concentrations and eventually crack formation.[9] Employing the directed energy deposition (DED) technique, in turn, a columnar grain morphology with a strong crystallographic texture was obtained.[8] The low degree of grain constraints in both microstructures was found to be vital to attain superior functional behavior in polycrystalline state.[2,3,10] In the present study, an alternative thermo-mechanical processing route allowing for a direct microstructure design in Co–Ni–Ga is reported. Polycrystalline material has been processed by hot rolling. Microstructural evolution upon forming and final post-process heat treatment as well as SE properties are investigated in detail.

Polycrystalline ingots of Co–Ni–Ga with a nominal chemical composition of 49Co-21Ni–30 Ga (in at.pct) were prepared via vacuum induction melting. The as-cast material is characterized by a globular microstructure with an initial average grain size of about 950 μm (Figure 1) and features no preferred orientation of individual austenitic grains, i.e., random texture, as shown in previous work.[5] Plates with 8 mm thickness were cut from the cylindrical as-cast ingots and subsequently hot rolled. Hot rolling was carried out at 1000 °C followed by slow air-cooling. The thickness

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was reduced to 5.5 mm (reduction ratio of approx. 69 pct). In order to minimize thermal gradients during processing, specimens were encapsulated in steel. Cuboidal samples with dimensions of $3 \times 3 \times 5$ mm^3 were machined from the hot-rolled material such that their longer axis was parallel to rolling direction (RD). Samples were mechanically ground down to 5 μm grit size to remove any residue from machining. After encapsulation in quartz glass tubes under argon atmosphere, the hot-rolled samples were heat treated. At first, samples were heated up to 1160 °C at a low heating rate of 0.3 °C s^{-1} and then solution-annealed for 12 h. Following solution-annealing and without preceding quenching, samples were directly transferred to another furnace and additionally aged at 700 °C for 0.5 h in order to induce a thin film of ductile γ-phase along the GBs.[11] Such secondary phase layer decorating the GBs has been proven to be vital for the structural integrity of polycrystalline Co–Ni–Ga samples upon cooling following solution-annealing and/or thermo-mechanical loading.[4]

Microstructure characterization was performed using optical microscopy (OM) as well as scanning electron microscopy (SEM) using electron backscatter diffraction (EBSD). Mechanical testing was carried out on a servohydraulic test frame equipped with a digital microscope and a tele-zoom objective for in situ OM analysis. Quasi-static uniaxial incremental strain tests (ISTs) were conducted at 100 °C under compressive loading in displacement control at a nominal strain rate of 1×10^{-3} s^{-1}. The test temperature was selected to allow for direct comparison with data reported in literature for the single-crystalline reference condition.[10,12] For details on the sample preparation for (in situ) microstructural analysis and the in situ experiments/ setup, the reader is referred to References 4, 8, and 12.
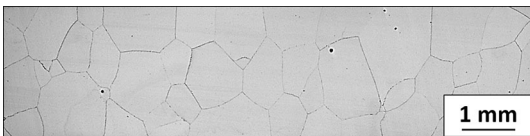

Fig. 1—Optical micrograph showing the microstructure of Co–Ni–Ga in the as-cast condition.

Figure 2 depicts the microstructure of a Co–Ni–Ga plate in the hot-rolled condition. Instead of equiaxed grains of about 1 mm in diameter seen in the initial as-cast state (cf. Figure 1), a deformed microstructure with elongated grains in the direction of hot rolling can be observed following thermo-mechanical processing (Figure 2(a)). The EBSD phase map with superimposed image quality (IQ) shown in Figure 2(b) clearly reveals minor volume fractions of a secondary phase (yellow) in the interior of the austenitic (blue) grains and at the GBs. While the austenite was indexed with a B2 cubic crystal structure (Pm-3 m) and a lattice parameter of $a = 0.2287$ nm, the secondary phase could be indexed as the ductile γ-phase using A1 cubic crystal structure (Fm-3 m) and a lattice parameter of $a = 0.3585$ nm. The presence of γ-phase is in line with results for $Co_{49}Ni_{21}Ga_{30}$ (at.pct) showing γ-phase formation after thermo-mechanical processing at 900 °C.[7] In addition, the EBSD grain reference orientation deviation (GROD) mapping of the austenite (Figure 2(c)) indicates an increase in local dislocation density and/or the formation of subgrain structures in the matrix, particularly, in the direct vicinity of GBs.

As can be deduced from the optical micrograph and the inverse pole figure (IPF) mapping in Figures 3(a) and (b), respectively, the microstructure significantly changes upon post-rolling heat treatment. A single-crystalline structure (indexed as austenite) being free of any GB is present in a heat-treated sample owing to abnormal grain growth (AGG). In previous work, hot extrusion followed by a solution-annealing treatment strongly promoted AGG and led to an bamboo-like microstructure in Co–Ni–Ga.[7] In general, two crucial pre-requisites for AGG have to be considered: A driving force for grain growth and a growth advantage of some grains over their neighboring competitors.[13] In the present study, even if recovery processes took place during hot rolling, internal stresses in the hot-rolled condition are supposed to be relatively high, as is indicated by the localized increase of misorientations and dislocation density, respectively (Figure 2(c)). Stress fields characterized by a preferred direction can be expected. In addition to the presence of process-induced internal stress fields, the GBs are decorated by the secondary γ-phase in the hot-rolled condition (Figure 2(b)). At this point, it should be emphasized
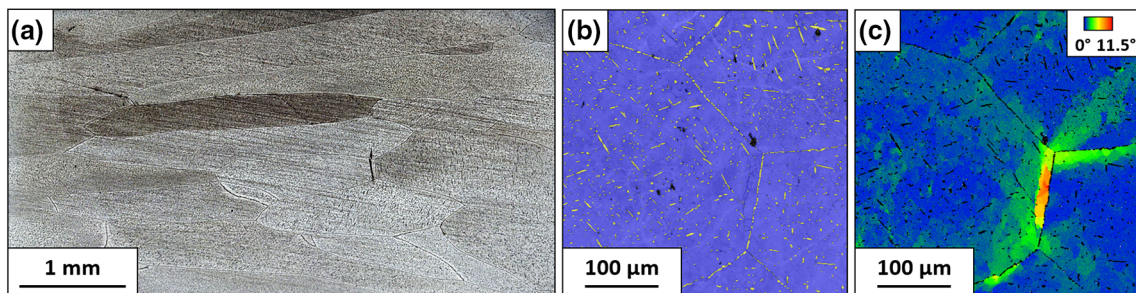

Fig. 2—Microstructure of Co–Ni–Ga in the hot-rolled condition: Optical micrograph (a), EBSD phase mapping with superimposed IQ (b), and EBSD GROD mapping of the austenitic matrix (c). In (b) austenite and secondary γ-phase are shown in blue and yellow, respectively. The misorientation angle of every pixel with respect to the average orientation of the same grain is highlighted in (c) by the color code given. RD is horizontal (Color figure online).
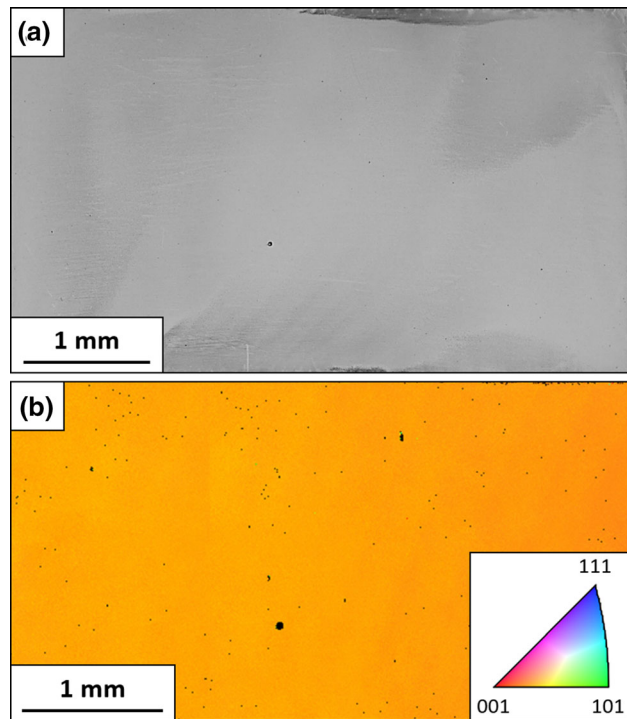
Fig. 3—Microstructure of a Co–Ni–Ga sample in the heat-treated condition: Optical micrograph (*a*) and EBSD IPF mapping plotted with respect to RD (*b*). The color-coded standard triangle is shown as the inset. RD is horizontal (Color figure online).
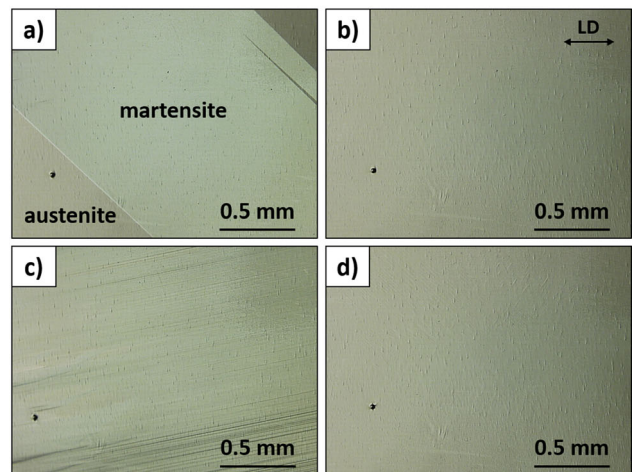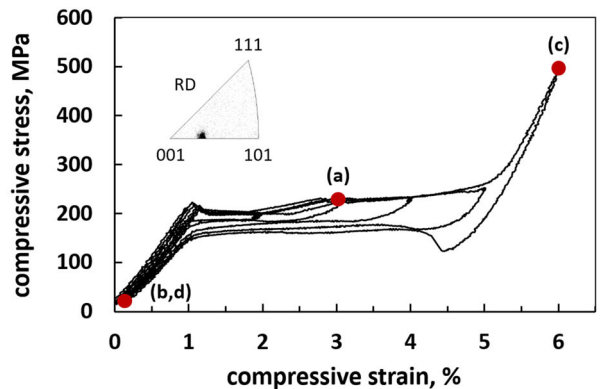

Fig. 4—*In situ* IST under SE compressive loading at 100 °C for the Co–Ni–Ga sample in heat-treated condition (shown in Fig. 3 in the initial state). The inset of the stress–strain diagram shows an IPF recalculated from the EBSD data of Fig. 3b. The IPF illustrates the crystallographic orientation of the single-crystalline sample with respect to RD. Micrographs (*a* through *d*) were recorded at specific points of the stress–strain curve marked by red points. Loading direction (LD) is horizontal and parallel to RD (Color figure online).

that in Co–Ni–Ga, a cyclic heat treatment is not able to induce AGG as reported for other SMA system like Cu–Al–Mn[14,15] and Fe–Mn–Al–Ni(–Ti).[16] Although Co–Ni–Ga features a single-phase and two-phase region at elevated temperatures, *i.e.,* basic requirements are met, preliminary results (not shown) reveal that the volume fraction and morphology of the secondary γ-phase are not appropriate to form subgrain structures during cyclic heat treatment and, thus, to provide the driving force (internal stresses) for AGG. However, such stress fields can be provided by the hot rolling procedure as detailed above. Consequently, based on these considerations and experimental results, microstructure evolution leading to the formation of the single-crystalline structure (Figure 3) during post-process heat treatment can be rationalized as follows: Upon slow heating to the solution-annealing temperature of 1160 °C within the furnace (cf. experimentals), the volume fraction of the secondary phase starts to decrease. The γ-phase should be fully dissolved when a given temperature is reached, *i.e.,* its solvus temperature. However, minor differences in local composition and/or in the initial thickness of the secondary phase layer along the GBs (cf. Figure 2(b)) can lead to distinct spatial differences. Upon heating a few GBs will be already free of γ-phase, whereas others are still decorated. It is well known from literature that GB movement and, thus, grain growth can be strongly hampered by GB phase decorations.[17] Assuming that the internal stresses are high enough throughout the entire microstructure after hot rolling, AGG is strongly

promoted according to the well-established grain growth theory, as long as a very low number of GBs is not pinned by the ductile secondary γ-phase during heating in the post-process heat treatment. Obviously, such conditions being beneficial for AGG seem to be perfectly met in the hot-rolled Co–Ni–Ga and by the time–temperature profile of the post-process heat treatment. The exact temperature for initiation of AGG (solvus temperature, at which the first GB is free of secondary γ-phase) as well as absolute values for internal stresses (affected by the choice of rolling parameters) cannot be distinguished. However, hot rolling can provide the driving forces for AGG as detailed above and the general mechanism leading to the formation of the single-crystalline microstructure can be derived from the findings presented here.

In order to reveal the potential of this novel thermo-mechanical procedure for optimization of the shape memory performance, an *in situ* IST was performed under compressive loading for the heat-treated sample shown in Figure 3. As can be deduced from the IPF in Figure 4 (cf. inset), the single-crystalline sample

features a near-$\langle 001 \rangle$ orientation with respect to RD. Figure 4 shows the corresponding stress–strain response and the *in situ* micrographs. The single-crystalline condition demonstrates an excellent SE behavior with perfect reversibility of the stress-induced MT up to a maximum applied compressive strain level of -6 pct. These superior functional properties are in excellent agreement with the SE behavior reported for (near)-$\langle 001 \rangle$ oriented and textured single- and polycrystalline Co–Ni–Ga, respectively.[8,10,12] Since significant grain constraints are known to be the most detrimental issue in this SMA system,[4,5,8] the thermo-mechanical procedure presented is thought to be highly promising for tailoring microstructures with excellent functional and structural stability. However, further research is needed to understand the full potential of hot-rolled Co–Ni–Ga, *i.e.*, maximum grain sizes being achievable for example.

In present work, a novel procedure is introduced promoting abnormal grain growth (AGG) in Heusler-type Co–Ni–Ga shape memory alloys (SMAs). Hot rolling followed by solution-annealing leads to the formation of a single-crystalline microstructure featuring excellent functional properties. It is thought that these results will be transferable to other SMAs. Thus, this processing route opens up new pathways toward property optimization in SMA systems being characterized by significant susceptibility to grain boundary-induced failure.

ACKNOWLEDGMENTS

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

FUNDING

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