Microstructural evolution and magnetic properties of binder jet additive manufactured Ni-Mn-Ga magnetic shape memory alloy foam

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Abstract

This study investigated microstructural evolution, phase transformation and magnetic behavior of additively manufactured magnetic shape memory alloy foam. Pre-alloyed angular Ni-Mn-Ga ball-milled powder was binder jet printed and sintered at 1020 °C for 4 h in both vacuum and argon atmospheres. Porosity of the manufactured foams was studied using micro-computed x-ray tomography and it was found that the relative density of the sintered parts was about 50-60%. In the printed sample that was sintered in argon, electron microscopy with elemental analysis showed no compositional gradient. X-ray diffraction indicated that 10M modulated martensite was present in the pre-alloyed powder as well as the sample sintered in argon. Differential scanning calorimetry and thermomagnetic results showed that martensitic transformation of the sample sintered in argon was at 34 °C, while barely detectable in the sample sintered in vacuum. Saturation magnetization of the printed sample sintered in argon atmosphere was around 68.4 Am²/kg. Production of a magnetic shape memory alloy by printing would enable complex-shaped elements for demanding applications, and intentionally including porosity could allow these polycrystals to exhibit the magnetic shape memory effect. Therefore, a facile method for sintering of Ni-Mn-Ga printed parts has been presented for the first time.

Keywords:Additive manufacturing; Solid-state sintering; Porosity; Phase transformation; Magnetic shape memory; Ferromagnetic shape memory.

1. Introduction

Ni-Mn-Ga is a multi-functional ferromagnetic martensite material, and can exhibit both the magnetocaloric and magnetic shape memory effects [1]. Alternately, Ni-Mn-Ga is known as a magnetic shape memory alloy (MSMA) when it displays the magnetic shape memory effect. MSMA's have shown promise for applications such as long stroke, high precision, fast actuators with a long stroke and high precision, breaker switch/fuse, energy harvester, vibration damper and sensor [2,3], and also in micropumps for drug delivery[4,5]. Ferromagnetic Ni-Mn-Ga alloys are known as smart materials, showing a giant magnetic-field-induced strain (MFIS)[6,7]. The mechanism of MFIS is based on the reordering of crystallographic domains in an applied magnetic field which lowers magnetization energy[8,9]. Richard *et al.* [10] extensively studied off-stoichiometric Ni_2MnGa alloys. As room-temperature single crystals, these display large magnetoplastic strains (up to 10%) when optimally oriented to the magnetic field [11,12].

In general, polycrystalline bulk Ni-Mn-Ga alloys are brittle, costly and display moderate MFIS due to high twinning stresses limiting their practical applications. Therefore, various processing methods have been developed to modify microstructure and mechanical properties of the Ni-Mn-Ga alloys such as melt spinning[13], spark plasma sintering [14,15], composites[16–19] and thin films[20–22]. Another alternative to reach high MFIS is to manufacture a porous structure to reduce internal constraints. Chmielus *et al.* presented a Ni-Mn-Ga open-pore foam with a monomodal [22] and bimodal [23] pore size of 76% volume fraction and an MFIS of 0.12%. Müllner *et al.*[25] proposed that the main mechanism of reducing internal and external constraints via porosity and foam architecture is based on the reduction in twin-twin and twin-grain boundary interactions. It is expected that high saturation magnetization is favorable to the

MFIS[9]. The saturation magnetization of Ni-Mn-Ga single crystals may vary between 50 and 70 Am²/kg[26,27] and after ball milling, it may drop to 15-25 Am²/kg depending on the time and milling energy[28].

However, production of these foams by replication casting is time-consuming and requires the use of strong acids. Additive manufacturing is suitable for producing near-net shaped parts with controlled porosity, and this may be sufficient to overcome grain boundary constraints in polycrystalline Ni-Mn-Ga. Representing a new alternative, binder jet printing (BJP) is a fast, low-cost additive manufacturing method which enables complex geometries[29–31]. The ability to fabricate porous parts with complicated geometries could have broad applications in energy management, lightweight structures, and sensors[23]. In our previous studies on the BJP of Ni-based alloys[29–33], it was found that an irregular powder shape decreased “green” part density: spherical and irregular shaped powders led to ~55% and ~40% density, respectively. Subsequent sintering is necessary to strengthen these resulting “green” parts.

The main objective of this study is to introduce a reliable, easy to use and versatile method to produce magnetic shape memory alloy foams via binder jet printing and subsequent sintering without oxidation or composition change and gradients. Parts were produced using a custom-made binder jet printer for small volumes, developed in our lab. Microstructure evolution, phase formation temperatures and density of the manufactured foam were investigated. A sintering process is proposed in this work leading to the formation of a foam structure with microstructural, magnetic and thermal properties similar to the feedstock Ni-Mn-Ga powder and, in general, conventionally produced bulk samples.

2. Materials and methods

A Ni-Mn-Ga polycrystalline ingot was prepared by induction melting high purity elements of Ni, Mn and Ga under an argon atmosphere and cast in a copper mold for fast cooling. The ingot was crushed into powder by forging at room temperature. Powder with the appropriate particle size was obtained by sieving.

Figure 1 shows an SEM micrograph of the angular Ni-Mn-Ga feedstock powder. Higher magnification (Figure 1 inset) clearly showed the morphology and size distribution of the powder. Chemical composition of the pre-alloyed powder via EDS analysis was 49.6 ± 0.4 at.% of Ni, 30.8 ± 0.2 at.% of Mn and 19.6 ± 0.4 at.% of Ga.

A custom-made binder jet printer (BJP, optimized for very small volumes) was used to manufacture 15-layer green parts, where each layer was $200 \mu\text{m}$ and layers were bound together with a water-soluble binder made of ethylene glycol monomethyl ether and diethylene glycol. Titanium sponges (Alfa Aesar, 99.95%) were encapsulated with the samples to prevent oxidation during sintering. To reduce oxygen partial pressure in capsules, high vacuum was obtained using a rough-pump. Capsules were purged and back-filled with argon gas five times to dilute oxygen concentration. Two different methods of encapsulation were used – “argon” and “vacuum”. In the last step of encapsulation, tubes filled argon gas are called “argon sintering condition” and the ones vacuumed in the last step are called “vacuum sintering condition”. A Lindberg tube furnace was used for sintering with the following heating profile: heating at $5 \text{ }^\circ\text{C}/\text{min}$ from room temperature to $500 \text{ }^\circ\text{C}$, and $2.5 \text{ }^\circ\text{C}/\text{min}$ to the holding temperature of $1020 \text{ }^\circ\text{C}$; holding for 4 h and then cooling at $2.5 \text{ }^\circ\text{C}/\text{min}$ to $500 \text{ }^\circ\text{C}$; and finally furnace cooling to room temperature.

Density of the sintered samples was visualized with a Bruker SkyScan 1272 micro-computed tomography scanner (μCT) with square $0.2 \mu\text{m}$ pixels and 2×2 binning. Scanning parameters

were 100 kV and 100 μ A with a 0.11 mm Cu filter, averaging of 10 frames, and angular range of 0°–180° with 0.11° steps. For microscopy observation, sintered samples were mounted using epoxy and hardener, then progressively ground and polished to a final step of colloidal acidic alumina. Microstructural observation and elemental composition analysis were conducted with a ZEISS Sigma 500 VP scanning electron microscope (SEM) equipped with energy dispersive x-ray spectroscopy (EDS). Phase identification was carried out using an x-ray diffractometer (XRD, Bruker AXS D8 Discover) with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$, 40 kV, 40 mA) with a step of 0.02° and a scan speed of 0.5 sec/step at room temperature. Additionally, the diffractometer was configured with the general area detector diffraction system (GADDS), utilizing a 1.0 mm incident beam capillary and a 151 mm detector distance. 2D data was collected at $\theta=10, 20, 30$ and 40° for 240 s each, in a θ/θ geometry (incident beam and detector coupled). Integration was then performed with the GADDS software on each detector image, resulting in diffraction patterns. The diffraction patterns for each sample were then merged and the background of subtracted within each resulting pattern. The martensitic phase transformation temperatures and Curie temperatures were determined from differential scanning calorimetry (DSC, Perkin Elmer Pyris 6) in the temperature range -10 °C to 140 °C (starting and ending points of plots were cut off at 25 °C and 125 °C). The reverse and forward martensitic transformation temperatures were determined during heating and cooling cycles (5°C min⁻¹), respectively. Saturation magnetization at room temperature was measured using vibrating sample magnetometry (Lakeshore model 7407), up to a field of 1.5 T. Thermo-magnetic plots were obtained using a Lakeshore model 74034 oven installed at the VSM between 25 °C and 140 °C.

3. Results and discussion

3.1. Characterization of manufactured foams

3.1.1. Porosity and density measurements using μ CT

Figure 2a and 2b illustrate μ CT micrographs of the sintered samples under vacuum and argon atmospheres, respectively. It was found that the relative density of both sintered samples was ~55%. The two- and three-dimensional micrographs indicate that pores were internally connected after sintering and surface connected porosity was obtained as well. The sintering was conducted at 1020 °C which was quite lower than the melting point for $\text{Ni}_{50}\text{Mn}_{30}\text{Ga}_{20}$ (reported in [34] which is 1088 °C), therefore, solid state sintering was dominant leading to surface and grain boundary diffusion that resulted in neck formation. Solid state sintering and liquid phase sintering of the Ni-based alloy were compared in [32] and indicated how sintering temperature affects densification.

3.1.2. Microstructural observations and elemental analyses

Figure 3 shows SEM micrographs of the sintered samples. It is seen in Figure 3a that a porous layer formed on the surface of Ni-Mn-Ga powder sintered in vacuum. EDS analysis conducted on selected areas on Figure 3b revealed that this layer was mainly composed of Ni and Ti elements, suggesting Ni_3Ti formation during the sintering process (area 1) while powder composition was similar to the used Ni-Mn-Ga powder (area 2) (results are summarized in Table 1). As mentioned in the experimental section, encapsulation included a Ti sponge to prevent oxidation of the Ni-Mn-Ga powder during sintering. Mn is a thermodynamically active element and reacts easily with oxygen, and Ti was intended to prevent or delay this oxidation reaction by forming TiO_2 . However, during vacuum sintering, Ti evaporated and condensed onto the surface of the powder (see Supplementary Figure 1). Figure 4 illustrates an SEM micrograph with corresponding EDS mapping analysis conducted on the inner surface of the quartz used for vacuum encapsulation. It was seen that a Ti-rich oxide layer formed on the inner surface of the

tube, confirming evaporation of Ti during sintering in vacuum. However, in the sample sintered in an argon atmosphere, no deposited Ti-rich layer was detected either on the Ni-Mn-Ga sintered powder (Figure 3c) or the inner surface of the quartz tube. Higher magnification in Figure 3d indicated that necking among neighboring powders occurred during the sintering process. EDS analysis conducted on the surface of powders (area 3) and/or broken powder surfaces (area 4) confirmed that the composition was approximately the same as the as-received Ni-Mn-Ga powder and no Ti-rich layer formed on the surface of powder during sintering in argon atmosphere (Table 1). It was seen in Figure 3d (selected area with higher magnification is illustrated in Suppl. Figure 2) that most of the martensitic plates are parallel to each other and grew diagonally viewed from the surface. SEM observation confirmed that the martensitic phase was present at room temperature.

Figure 5 illustrates cross sectional SEM micrographs with corresponding EDS line scan results taken from sintered samples. SEM micrographs of the sample sintered in vacuum (Figure 5a) showed a diffusive and outer porous layer was formed on the surface of sintered powders. EDS line scan results (Figure 5b) showed a compositional gradient of three regions including (1) where chemical composition was close to the used powder, with Mn lost; (2) a diffusive layer containing Ni with dissolved Mn and Ga; and (3) a deposited layer made of Ni and Ti. A cross sectional SEM micrograph taken from the sample sintered in argon atmosphere is shown in Figure 5c. No deposited layer formed on the powders' edges. Higher SEM magnification (Figure 5d) revealed a twinning structure in the powder. To confirm there was no composition change in the sintered sample in argon atmosphere relative to the used powder, the result of EDS line analysis is presented in Figure 5d.

To more closely examine the deposited Ti-rich layer which formed during vacuum sintering, EDS mapping was done on a particle cross section, as shown in Figure 6. It was seen that the outer layer was enriched in Ti and Ni, with a lower concentration of Mn and Ga. The overlay EDS map clearly shows that the outer formed layer is a Ni-Ti rich film.

3.1.3. Phase analysis using XRD

Figure 7 shows the room temperature XRD patterns for both the ball-milled Ni-Mn-Ga powder and sintered samples in vacuum and argon atmospheres. The Ni-Mn-Ga powder was indexed to be martensite phase. The observed peak broadening might be due to induced stress during ball-milling of the powder[28,40]. A detailed XRD pattern indicated broad $\{220\}_{10M}$ peaks ranging from 42° to 46° , $\{310\}_{10M}$ peaks around 49.3° , $\{400\}_{10M}$ peaks ranging from 53° to 55° and broad $\{422\}_{10M}$ peaks ranging from 79° to 85° . Based on the XRD results, it was concluded that the main phase in the used Ni-Mn-Ga powder was 10M martensite with calculated pseudo-tetragonal lattice parameters $a=b=5.935 \text{ \AA}$ and $c= 5.506 \text{ \AA}$ with a c/a ratio of 0.945 at room temperature, which is in agreement with the values reported by Richard *et al.*[10].

Indexed XRD diffraction peaks for the vacuum sintered sample (patterns b, b₁) revealed that the present phases were different from the powder. Various phases were detected in the X-ray diffraction pattern such as austenite (γ -Ni, higher nickel content compared to Ni-Mn-Ga powder) as the matrix, and Ni-Ti rich phases including NiTi and Ni₃Ti. In the vacuum sintered sample, austenite and Ni₃Ti were the two main phases, where the source of Ti was the sponge used during encapsulation under vacuum atmosphere. According to the indexed X-ray diffraction peaks for the argon sintered sample (patterns 'c, c₁'), the crystal structure can be indexed with the lattice parameters $a=b=5.947 \text{ \AA}$ and $c= 5.600 \text{ \AA}$ with the c/a ratio of 0.945. Sokolovskiy *et al.*[41] reported a ternary phase diagram for Ni-Mn-Ga alloys, indicating how the lattice

parameter varies depending on the composition and the calculated values in this study matched with the reported numbers. It is worth noting that the calculated crystal structures (a and c values), and consequently, the c/a ratio confirmed that the dominant phase was five-layer tetragonal martensite with $c/a < 1$ [8,42,43]. Lanksa *et al.* [8] reported that the c/a ratio for five-layer tetragonal martensite or 10M is between 0.93 and 0.95. Compared to the used powder and previous results, narrower and discrete peaks were detected in the sample sintered in argon atmosphere. Additional peaks were due to monoclinic distortion as detected in the XRD pattern of the argon sintered sample and can be found in the detailed indexed peaks shown in Figure 7. Therefore, the martensite predominantly existed in the Ni–Mn–Ga argon sintered sample and the content of the austenite was much smaller, according to comparison of the relative intensity of diffraction peaks.

3.1.4. Phase transformation studies and magnetic properties

To evaluate phase transformation temperatures, DSC was conducted on Ni–Mn–Ga ball-milled powder, and sintered samples in vacuum and argon atmospheres for heating and cooling cycles as illustrated in Figure 8. In general, the heating cycle displays an endothermic peak, which reveals the transformation of a low temperature martensite to a high temperature austenitic phase occurring at an onset A_S . The cooling cycle showed an exothermic peak representing forward martensitic transformation (austenite to martensite) with an onset at M_S . The A_F and M_F represented the austenitic and martensitic finish temperatures, respectively. The characteristic transformation temperatures attained from the DSC curves in Figure 8 are given in Table 2. For the ball-milled powder (Figure 8a), it was seen that broad peaks of phase transformation appeared on the DSC curve including austenitic transformation peak (A_P) in the range of 20 °C to 75 °C, Curie temperature (T_C) in the range of 100 °C to 115 °C and martensitic transformation temperature

peak (M_P) in the range of 14 °C to 59°C. The detected T_C was in the range of 100 °C to 105 °C. It was reported that peak broadening might be attributed to the atomic disordering caused by ball-milling[40]. The DSC curve of the vacuum sintered sample is shown in Figure 8b indicating no phase discernable transformation temperature. It is worth mentioning that the experiment was carried out in the temperature ranging from -10 °C to 140 °C. It was thought that phase transformation temperature might be below -10 °C due to the composition variation compared to the used powder, in light of elemental and phase analysis results (see Figure 6 and Figure 7).

Figure 8c displays the DSC curve of the sintered sample in argon atmosphere which exhibited a one-step austenitic transformation upon heating with A_S of 42 °C and A_F of 46.5 °C. The step at ~102 °C corresponded to the T_C indicating transition from ferromagnetic austenite to paramagnetic austenite. Similarly, the small step at 100 °C during cooling corresponded to the T_C from paramagnetic to ferromagnetic austenite. The M_P was at 34 °C with the M_S at 36 °C and M_F at 31.5 °C. The span of reverse martensite transformation (A_S-A_F) as well as its forward (M_F-M_S) was 4.5 °C. The thermal hysteresis (A_F-M_S) of the sintered sample in argon atmosphere was ~10 °C. The obtained DSC results for the argon sintered sample were similar to [7] in which Ni-Mn-Ga alloy with a similar composition displayed martensite phase transformation just above room temperature (about 35 °C).

To further study the magnetic behavior, the thermal variation of magnetization for the heating and cooling cycles were collected at a magnetizing field of 50 mT for the ball-milled powder and sintered samples as shown in Figure 9. It was seen that the ball-milled powder showed Curie temperature at ~112 °C (Figure 9a). Additionally, austenite start and finish (A_S and A_F , respectively) were determined to be 31 °C and 82 °C, respectively, and martensite start and finish (M_S and M_F , respectively) were determined to be 63 °C and < 25 °C, respectively. It was clearly seen that the martensite and austenite phase transformation of the sintered sample in vacuum atmosphere

disappeared. The elemental and phase analysis results confirmed composition variation in the sintered sample compared to the used powder, affecting magnetic behavior of the manufactured foam. However, the sintered sample in argon atmosphere displayed a clear phase transformation temperature. On heating, the austenite phase transformation appeared at 41 °C and was fully transformed at 45 °C (corresponding to A_S and A_F , respectively). Besides, the martensite phase transformation appeared at 36 °C and was fully transferred at 32 °C (corresponding to M_S and M_F , respectively). The Curie temperature was determined to be 107 °C. It can be seen that for the specimens sintered in argon atmosphere, the Curie temperature is slightly lower than that of ball milled powder. The suppression of the Curie temperature in the argon sintered sample is attributed to the atomic ordering in structure while atomic disordering induced by ball milling may lead to an increase of T_C . All phase transformation temperatures and Curie temperatures are summarized in Table 3. According to Richard *et al.* [10,45], the Ni-Mn-Ga alloys that are in the pseudo-tetragonal (10M) phase at room temperature showed a much sharper transition (5-10 °C) than those which are in pseudo-orthorhombic (14M) phase (20-30 °C). In other words, the terms “sharper” or “broader” refers to the temperature difference between the start and finish of the transition (during heating and cooling cycles). As seen in Figure 9, the magnetization of the sample sintered in argon as a function of temperature, curve c, displayed a small difference in $A_F - A_S$ or $M_S - M_F$ of about 4 °C. Additionally, the thermal hysteresis ($A_F - M_S$) was measured as ~9 °C. These results were in agreements with DSC curve results.

Figure 10 illustrates the magnetization hysteresis loops of the ball-milled Ni-Mn-Ga powder and sintered samples measured at room temperature (25 °C). The hysteresis loops confirm that the used powder and sample sintered in argon atmosphere exhibited ferromagnetic behaviors at room temperature. The measured values of saturation magnetization (M_s), coercivity (H_c) and remanent magnetization (M_r) of the powder and sintered samples are given in Table 4. The measured coercivity of the powder and samples sintered in vacuum and argon atmospheres were

359 mT, 58 mT and 78 mT respectively, meaning that the reverse field needed to drive the magnetization to zero after being saturated is higher for ball-milled powder than for sintered samples. It was seen that the ball-milled powder exhibited a typical ferromagnetic behavior with saturation magnetization of $26.4 \text{ Am}^2/\text{kg}$ when external magnetic field reached 1.5 T, which was ~50% less than the reported value by Tian *et al.* [28]. It has been known that ball-milling affects Mn-Mn ferromagnetic exchange leading to reduction in saturation magnetization [28,46]. The measured saturation magnetization for sintered samples were found to be $15.3 \text{ Am}^2/\text{kg}$ and $68.4 \text{ Am}^2/\text{kg}$ for samples sintered in vacuum and argon atmospheres, respectively. The main reason for saturation magnetization reduction in the vacuum sintered sample may be the composition changes. Interestingly, the saturation magnetization of the sample sintered in argon atmosphere increased to $68.4 \text{ Am}^2/\text{kg}$, which might be related to reorganization of crystal structure and the relief of internal stresses of the ball-milled powder during the sintering process [46–48]. Heczko *et al.* [26] reported that the Ni-Mn-Ga alloy with five-layered tetragonal structure had saturation magnetization about $64 \text{ Am}^2/\text{kg}$. The difference between the value obtained in this work compared to [26] might be attributed to the size of powder and manufacturing method leading to the foam structure.

3.2. Sintering, phase formation and properties of BJP Ni-Mn-Ga foam

Binder jetting is an additive manufacturing method in which powder is deposited layer-by-layer and selectively joined in each layer with binder. Since the powder does not melt during printing, the as-printed or “green” part must be sintered to increase density of the final product. The magnetic shape memory effect requires that martensitic plates in the microstructure form during the sintering process. Therefore, temperature and holding time play important roles in sintering. The porous bulk specimen with density less than 40% was binder jet printed and then solid-state

sintered to produce a foam. Since Mn is an easily oxidized element, the sintering process was conducted in an argon atmosphere in the presence of Ti sponge. Based on the isothermal section diagram of Ni-Mn-Ga ternary system, the foam was produced by solid-state sintering of the BJP specimen at just above 1000 °C[42]. Thus, the applied sintering temperature and time (1020 °C for 4 h) resulted in surface melting in powders, neck formation and the formation of a uniform foam with open pores. A schematic of sintering to produce a Ni-Mn-Ga BJP foam sample with 3 layers is illustrated in Figure 11.

The crystal structure of martensite is an important factor affecting the magnetic anisotropy as well as mechanical properties of Ni-Mn-Ga ferromagnetic shape memory alloys[49]. The lattice parameters of the martensitic crystal structure (a and c) determine the highest MFIS value determined by “ $1-c/a$ ”. Lanskaet *al.*[8] and Sozinovet *al.*[49] have reported the theoretical maximum value of MFIS in five-layered martensitic phase in the Ni–Mn–Ga system which is ~6%. Moreover, the relation between c/a and T_M , in which T_M is ascribed as $(M_S + M_F)/2$, was proposed by Lanskaet *al.*[8]. The calculated c/a indicated this ratio was 0.945 for the argon sintered sample and the martensitic phase transformation was found to be ~35 °C based on the DSC and thermal variation of magnetization which were in agreement with previous publications [8,9,44,49]. It has been known that martensitic phase transformation temperature, saturation magnetization and magnetic phase transformation temperature are highly composition dependent, thus, certain important properties of Ni-Mn-Ga have been mapped with their composition[50]. Moreover, the calculated average number of valence electrons per atom (e/a) was 7.690 for the sintered alloy in argon atmosphere with composition of 49.6 ± 0.4 at.% of Ni, 30.8 ± 0.2 at.% of Mn and 19.6 ± 0.4 at.% of Ga. It was proposed that the martensitic phases are found in Ni-Mn-Ga alloys with martensite phase transformation temperature range from 28 °C to 80 °C in the

electron concentration (e/a) range from 7.61 to 7.71. The ΔH of the BJP sample sintered in argon atmosphere was calculated for the reverse and forward phase transformations from the DSC curve. It was found that the forward transformation enthalpy ($\Delta H_{M \rightarrow A}$) and the reverse transformation enthalpy ($\Delta H_{A \rightarrow M}$) were 5.06 J/g and -5.75 J/g, respectively.

4. Conclusion

In the present work, binder jet printing as a new additive manufacturing method was used to produce foams made from angular Ni-Mn-Ga alloy powder. It was demonstrated that sintering at 1020°C for 4 h is effective in restoring the ferromagnetism of the ball milled Ni-Mn-Ga alloy. The microstructure, phase transformation temperatures and magnetic properties of the binder jet printed sintered Ni-Mn-Ga alloy were investigated. The XRD pattern indicated that the five-layered martensite (10M) phase was the main phase in the printed and argon atmosphere sintered foam structure with a homogeneous composition of 49.6±0.4 of Ni, 30.8±0.2 of Mn and 19.6±0.4 of Ga(at.-%). Additionally, the magnetization and DSC measurements showed that the martensitic phase of the Ni-Mn-Ga alloys sintered in argon atmosphere exhibited typical 10M magnetic shape-memory alloys ferromagnetic behavior with saturation magnetization of ~68.4 Am²/kg, a narrow phase transformation of around 38 °C and Curie temperature of around 107 °C. XRD and DSC also showed that the relief of the internal stresses of the ball-milled powder during the sintering process was needed to produce the similar martensite structure and behavior of bulk Ni-Mn-Ga alloys.

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References

- [1] S. Dey, S. Singh, R.K. Roy, M. Ghosh, A. Mitra, A.K. Panda, Influence of Mn incorporation for Ni on the magnetocaloric properties of rapidly solidified off-stoichiometric NiMnGa ribbons, *J. Magn. Magn. Mater.* 397 (2016) 342–346.
- [2] E. Faran, D. Shilo, Ferromagnetic Shape Memory Alloys—Challenges, Applications, and Experimental Characterization, *Exp. Tech.* 40 (2016) 1005–1031.
- [3] Y. Boonyongmaneerat, M. Chmielus, D. Dunand, P. Müllner, Increasing Magnetoplasticity in Polycrystalline Ni-Mn-Ga by Reducing Internal Constraints through Porosity, *Phys. Rev. Lett.* 99 (2007) 247201.
- [4] K. Ullakko, L. Wendell, A. Smith, P. Müllner, G. Hampikian, A magnetic shape memory micropump: contact-free, and compatible with PCR and human DNA profiling, *Smart Mater. Struct.* 21 (2012) 115020.
- [5] A.R. Smith, A. Saren, J. Järvinen, K. Ullakko, Characterization of a high-resolution solid-state micropump that can be integrated into microfluidic systems, *Microfluid. Nanofluidics.* 18 (2015) 1255–1263.
- [6] M. Chmielus, K. Rolfs, R. Wimpory, W. Reimers, P. Müllner, R. Schneider, Effects of surface roughness and training on the twinning stress of Ni–Mn–Ga single crystals, *Acta Mater.* 58 (2010) 3952–3962.
- [7] K. Rolfs, M. Chmielus, R.C. Wimpory, A. Mecklenburg, P. Müllner, R. Schneider, Double twinning in Ni-Mn-Ga-Co, *Acta Mater.* 58 (2010) 2646–2651.
- [8] N. Lanska, O. Soderberg, A. Sozinov, Y. Ge, K. Ullakko, V.K. Lindroos, Composition and temperature dependence of the crystal structure of Ni–Mn–Ga alloys, *J. Appl. Phys.* 95 (2004) 8074–8078.
- [9] K. Ullakko, J.K. Huang, C. Kantner, R.C. O’Handley, V. V. Kokorin, Large magnetic-field-induced strains in Ni₂MnGa single crystals, *Appl. Phys. Lett.* 69 (1996) 1966.
- [10] M. Richard, J. Feuchtwanger, D. Schlagel, T. Lograsso, S.M. Allen, R.C. O’Handley, Crystal structure and transformation behavior of Ni–Mn–Ga martensites, *Scri. Mater.* 54 (2006) 1797–1801.
- [11] A.K. Panda, S. Singh, R.K. Roy, M. Ghosh, A. Mitra, Effect of Mn incorporation for Ni on the properties of melt spun off-stoichiometric compositions of NiMnGa alloys, *J. Magn. Magn. Mater.* 323 (2011) 1161–1169.
- [12] O. Söderberg, D. Brown, I. Aaltio, J. Oksanen, J. Syrén, H. Pulkkinen, S.-P. Hannula, Microstructure and properties of Ni–Mn–Ga alloys produced by rapid solidification and pulsed electric current sintering, *J. Alloys Compd.* 509 (2011) 5981–5987.
- [13] J. Wang, C. Jiang, R. Techapiesanchaoenkij, D. Bono, S.M. Allen, R.C. O’Handley, Microstructure and magnetic properties of melt spinning Ni-Mn-Ga, *Intermetallics.* 32 (2013) 151–155.
- [14] X.H. Tian, J.H. Sui, X. Zhang, X. Feng, W. Cai, Martensitic transformation, mechanical property and magnetic-field-induced strain of Ni-Mn-Ga alloy fabricated by spark plasma sintering, *J. Alloys Compd.* 509 (2011) 4081–4083.
- [15] X.H. Tian, J.H. Sui, X. Zhang, X.H. Zheng, W. Cai, Grain size effect on martensitic transformation, mechanical and magnetic properties of Ni-Mn-Ga alloy fabricated by spark plasma sintering, *J. Alloys Compd.* 514 (2012) 210–213.
- [16] B. Tian, F. Chen, Y. Tong, L. Li, Y. Zheng, Magnetic field induced strain and damping behavior of Ni-Mn-Ga particles/epoxy resin composite, *J. Alloys Compd.* 604 (2014) 137–141.

- [17] B. Tian, Y.X. Tong, F. Chen, L. Li, Y.F. Zheng, Microstructure, phase transformation and mechanical property of Ni-Mn-Ga particles/Mg composites, *Mater. Sci. Eng. A*. 615 (2014) 273–277.
- [18] B. Tian, Z.G. Cheng, Y.X. Tong, L. Li, Y.F. Zheng, Q.Z. Li, Effect of enhanced interfacial reaction on the microstructure, phase transformation and mechanical property of Ni–Mn–Ga particles/Mg composites, *Mater. Des.* 82 (2015) 77–83.
- [19] F. Nilsén, I. Aaltio, Y. Ge, O. Söderberg, I. Glavastkyy, M. Lahelin, R. Maki, S.P. Hannula, Properties of the pulsed electric current sintered Ni-Mn-Ga-Co-WC composites, *J. Alloys Compd.* 656 (2016) 408–415.
- [20] S. Vinodh Kumar, R.K. Singh, S. Seenithurai, S. Bysakh, M. Manivel Raja, M. Mahendran, Phase structure and magnetic properties of the annealed Mn-rich Ni-Mn-Ga ferromagnetic shape memory thin films, *Mater. Res. Bull.* 61 (2015) 95–100.
- [21] A. Sharma, S. Mohan, S. Suwas, The effect of the deposition rate on the crystallographic texture, microstructure evolution and magnetic properties in sputter deposited Ni-Mn-Ga thin films, *Thin Solid Films*. 616 (2016) 530–542.
- [22] I.R. Aseguinolaza, V. Golub, O.Y. Salyuk, B. Muntifering, W.B. Knowlton, P. Müllner, J.M. Barandiaran, V.A. Chernenko, Self-patterning of epitaxial Ni-Mn-Ga/MgO(001) thin films, *Acta Mater.* 111 (2016) 194–201.
- [23] M. Chmielus, X.X. Zhang, C. Witherspoon, D.C. Dunand, P. Müllner, Giant magnetic-field-induced strains in polycrystalline Ni-Mn-Ga foams, *Nat. Mater.* 8 (2009) 863–866.
- [24] M. Chmielus, C. Witherspoon, R.C. Wimpory, A. Paulke, A. Hilger, X. Zhang, D.C. Dunand, P. Müllner, Magnetic-field-induced recovery strain in polycrystalline Ni-Mn-Ga foam, *J. Appl. Phys.* 108 (2010) 1–7.
- [25] P. Müllner, X.X. Zhang, Y. Boonyongmaneerat, C. Witherspoon, M. Chmielus, D.C. Dunand, Recent Developments in Ni-Mn-Ga Foam Research, *Mater. Sci. Forum.* 635 (2010) 119–124.
- [26] O. Heczko, N. Lanska, O. Soderberg, K. Ullakko, Temperature variation of structure and magnetic properties of Ni-Mn-Ga magnetic shape memory alloys, *J. Magn. Magn. Mater.* 242–245 (2002) 1446–1449.
- [27] O. Heczko, K. Jurek, K. Ullakko, Magnetic properties and domain structure of magnetic shape memory Ni-Mn-Ga alloy, *J. Magn. Magn. Mater.* 226 (2001) 996.
- [28] B. Tian, F. Chen, Y. Liu, Y.F. Zheng, Effect of ball milling and post-annealing on magnetic properties of Ni_{49.8}Mn_{28.5}Ga_{21.7} alloy powders, *Intermetallics*. 16 (2008) 1279–1284.
- [29] A. Mostafaei, E. Stevens, E. Hughes, S. Biery, C. Hilla, M. Chmielus, Powder bed binder jet printed alloy 625: densification, microstructure and mechanical properties, *Mater. Des.* 108 (2016) 126–135.
- [30] A. Mostafaei, Y. Behnamian, Y.L. Krimer, E.L. Stevens, J.L. Luo, M. Chmielus, Effect of solutionizing and aging on the microstructure and mechanical properties of powder bed binder jet printed nickel-based superalloy 625, *Mater. Des.* 111 (2016) 482–491.
- [31] A. Mostafaei, Y. Behnamian, Y.L. Krimer, E.L. Stevens, J.L. Luo, M. Chmielus, Brief data overview of differently heat treated binder jet printed samples made from argon atomized alloy 625 powder, *Data Br.* 9 (2016) 556–562.
- [32] A. Mostafaei, J. Toman, E.L. Stevens, E.T. Hughes, Y.L. Krimer, M. Chmielus, Microstructural evolution and mechanical properties of differently heat-treated binder jet printed samples from gas- and water-atomized alloy 625 powders, *Acta Mater.* 124 (2017)

- 280–289.
- [33] A. Mostafaei, E.T. Hughes, C. Hilla, E.L. Stevens, M. Chmielus, Data on the densification during sintering of binder jet printed samples made from water- and gas-atomized alloy 625 powders, *Data Br.* 10 (2017) 116–221.
 - [34] R.W. Overholser, M. Wuttig, D.A. Neumann, Chemical ordering in Ni-Mn-Ga Heusler alloys, *Scr. Mater.* 40 (1999) 1095–1102.
 - [35] C. Mahalakshmi, S.V. Kumar, M. Muthuraman, S. Seenithurai, M. Mahendran, Effect of Mn substitution on Structural and Magnetic Properties of Ferromagnetic Shape Memory alloys, *Mech. Adv. Mater. Struct.* 23 (2015) 631–635.
 - [36] T. Maki, S. Shimooka, S. Fujiwara, I. Tamura, Formation Temperature Thin Plate Martensite and Growth Behavior of in Fe-Ni-C Alloys, *Trans. Japan Institute Met.* 16 (1975) 35–41.
 - [37] T.N. Durlu, Dislocations in fully twinned thin plate martensite of an Fe-Ni-C alloy, 15 (1996) 11–13.
 - [38] R.L. Patterson, C.M. Wayman, The crystallography and growth of partially-twinned martensite plates in Fe-Ni alloys, *Acta Metall.* 14 (1966) 347–369.
 - [39] P. La Roca, L. Isola, P. Vermaut, J. Malarria, Relationship between martensitic plate size and austenitic grain size in martensitic transformations, *Appl. Phys. Lett.* 106 (2015).
 - [40] B. Tian, F. Chen, Y.X. Tong, L. Li, Y.F. Zheng, Phase Transformation and Magnetic Property of Ni-Mn-Ga Powders Prepared by Dry Ball Milling, *J. Mater. Eng. Perform.* 21 (2012) 2530–2534.
 - [41] V. Sokolovskiy, A. Grünebohm, V. Buchelnikov, P. Entel, Ab Initio and Monte Carlo Approaches For the Magnetocaloric Effect in Co- and In-Doped Ni-Mn-Ga Heusler Alloys, *Entropy.* 16 (2014) 4992–5019.
 - [42] S. Yang, C. Wang, X. Liu, Phase equilibria and composition dependence of martensitic transformation in Ni-Mn-Ga ternary system, *Intermetallics.* 25 (2012) 101–108.
 - [43] S.K. Wu, S.T. Yang, Effect of composition on transformation temperatures of Ni-Mn-Ga shape memory alloys, *Mater. Lett.* 57 (2003) 4291–4296.
 - [44] K. Ullakko, Y. Ezer, A. Sozinov, G. Kimmel, P. Yakovenko, V.K. Lindroos, Magnetic-field-induced strains in polycrystalline Ni-Mn-Ga at room temperature, *Scr. Mater.* 44 (2001) 475–480.
 - [45] M.L. Richard, J. Feuchtwanger, S.M. Allen, R.C. O’handley, P. Lázpita, J.M. Barandiaran, Martensite transformation in Ni-Mn-Ga ferromagnetic shape-memory alloys, *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* 38 (2007) 777–780.
 - [46] F. Nilsén, I. Aaltio, Y. Ge, T. Lindroos, S.P. Hannula, Characterization of Gas Atomized Ni-Mn-Ga Powders, *Mater. Today Proc.* 2 (2015) S879–S882.
 - [47] B. Tian, R. Ji, Y.X. Tong, L. Li, Y.F. Zheng, Microstructure, phase transformation and mechanical property of Nb-doped Ni-Mn-Ga alloys, *Intermetallics.* 64 (2015) 37–43.
 - [48] B. Tian, F. Chen, Y.X. Tong, L. Li, Y.F. Zheng, Y. Liu, Q.Z. Li, Phase transition of Ni-Mn-Ga alloy powders prepared by vibration ball milling, *J. Alloys Compd.* 509 (2011) 4563–4568.
 - [49] A. Sozinov, A.A. Likhachev, N. Lanska, K. Ullakko, Giant magnetic-field-induced strain in NiMnGa seven-layered martensitic phase, *Appl. Phys. Lett.* 80 (2002) 1746–1748.
 - [50] X. Jin, M. Marioni, D. Bono, S.M. Allen, R.C. O’Handley, T.Y. Hsu, Empirical mapping of Ni-Mn-Ga properties with composition and valence electron concentration, *J. Appl. Phys.* 91 (2002) 8222–8224.

Tables:

Table 1. Chemical composition in at.-% of the selected areas on SEM micrographs in Figure 3.

	Selected area for EDS analysis			
	1	2	3	4
Ti	13.1	0.9	--	--
Mn	5.4	23.3	30.9	30.6
Ni	72.6	55.2	49.2	49.3
Ga	8.9	20.6	19.9	20.1

Table 2. DSC characteristic temperatures for the ball-milled Ni-Mn-Ga powder, and sintered samples in vacuum and argon atmospheres.

	Heating cycle			Cooling Cycle			Curie Temperature, T_c (°C)
	A_P (°C)	A_S (°C)	A_F (°C)	M_P (°C)	M_S (°C)	M_F (°C)	
Ball-milled Ni-Mn-Ga powders	20-75	n/a ¹	n/a	14-59	n/a	n/a	100-105
Sintered sample in vacuum atmosphere	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Sintered sample in argon atmosphere	44	42	46.5	34	36	31.5	102

¹ n/a: not available, meaning that the transformation temperatures were not detected during DSC test in the range of -10 °C to 140 °C.

Table 3. Variation in magnetization as a function of temperature for the ball-milled Ni-Mn-Ga powder, and sintered samples in vacuum and argon atmospheres.

	Heating cycle		Cooling Cycle		Curie Temperature, T_c (°C)
	A_S (°C)	A_F (°C)	M_S (°C)	M_F (°C)	
Ball-milled Ni-Mn-Ga powders	31	82	63	< 25	112
Sintered sample in vacuum atmosphere	n/a ¹	n/a	n/a	n/a	n/a
Sintered sample in argon atmosphere	41	45	36	32	107

¹ n/a: not available, meaning that the transformation temperatures were not detected during DSC test in the range of 25 °C to 140 °C.

Table 4. Calculated magnetic properties of the ball-milled Ni-Mn-Ga powder, and sintered samples in vacuum and argon atmospheres from Figure 10.

Samples	Remnant magnetization (Am ² /kg)	Coercivity (mT)	Magnetization (A m ² /kg)
Ball-milled Ni-Mn-Ga powders	2.9	359	26.4
Sintered sample in vacuum atmosphere	1.4	58	15.3
Sintered sample in argon atmosphere	3.5	78	68.4

Figures caption:

Figure 1. SEM micrograph of the ball-milled Ni-Mn-Ga powder.

Figure 2. μ CT micrographs taken from sintered samples in (a) vacuum and (b) argon atmospheres. 3D Reconstruction for visualization of densification and internal porosity of Ni-Mn-Ga foam: (top) grayscale image where porosity is dark and (bottom) colorized cross sections where the color bar represents density.

Figure 3. SEM micrographs taken from samples sintered in (a) vacuum and (c) argon atmospheres. (b) shows a magnified view of the Ni_3Ti layer formed on the surface of the sample sintered under vacuum atmosphere, while (d) shows no such layer is present. Numbers correspond to EDS areas, for which data is given in Table 1.

Figure 4. SEM micrograph with corresponding elemental analysis maps of Ti, O, Mn and their overlay, taken from the film formed on the inner surface of the vacuum-sintering quartz tube.

Figure 5. SEM cross section and EDS analysis conducted on the samples sintered in (a,b) vacuum and (c-e) argon atmospheres.

Figure 6. SEM micrographs with elemental map of O, Ti, Ga, Mn, Ni and overlay taken from the sintered sample in vacuum. , showing that the Ni-Mn-Ga alloy was surrounded by a Ni-Ti rich layer.

Figure 7. XRD patterns of the (a) powder, and sintered samples in (b) vacuum and (c) argon atmospheres.

Figure 8. DSC curves of (a) ball-milled Ni-Mn-Ga powder, and sintered samples (b) vacuum and (c) argon atmospheres for representing reverse and forward transformations during heating and cooling cycles, respectively.

Figure 9. Representative magnetization versus temperature measurements performed at 50 mT. (a) ball-milled Ni-Mn-Ga powder, and sintered samples in (b) vacuum and (c) argon atmospheres.

Figure 10. Magnetic hysteresis loops measured at 25 °C for ball-milled Ni-Mn-Ga powder, and sintered samples in vacuum and argon atmospheres. Inset is a magnified view of the origin.

Figure 11. Schematic illustrating the binder jet printed sample with three layers and then sintered in argon atmosphere at 1020 °C for 4 h.

Bender jet printed part
density ~40%

Sintering in Ar atmosphere
at 1020 °C for 4 h

1st layer

2nd layer

3rd layer

Ni-Mn-Ga foam
density ~55%

Martensitic plates

Surface melting resulting in
necking among powders

Magnetization [a.u.]

Binder jet printed part
density $\sim 40\%$

Sintering in Ar atmosphere
at $1020\text{ }^{\circ}\text{C}$ for 4 h

- 1st layer
- 2nd layer
- 3rd layer

Ni-Mn-Ga foam
density $\sim 55\%$

Martensitic plates

Surface melting resulting in
necking among powders